



HAL
open science

ND70 Series Basaltic Glass Reference Materials for Volatile Element (H₂O , CO₂, S, Cl, F) Measurement and the C Ionisation Efficiency Suppression Effect of Water in Silicate Glasses in SIMS

Yves Moussallam, William Henry Towbin, Terry Plank, H el ene Bureau, Hicham Khodja, Yunbin Guan, Chi Ma, Michael B Baker, Edward M Stolper, Fabian U Naab, et al.

► To cite this version:

Yves Moussallam, William Henry Towbin, Terry Plank, H el ene Bureau, Hicham Khodja, et al.. ND70 Series Basaltic Glass Reference Materials for Volatile Element (H₂O , CO₂, S, Cl, F) Measurement and the C Ionisation Efficiency Suppression Effect of Water in Silicate Glasses in SIMS. *Geostandards and Geoanalytical Research*, inPress, 10.1111/ggr.12572 . hal-04662147

HAL Id: hal-04662147

<https://hal.science/hal-04662147v1>

Submitted on 25 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destin ee au d ep ot et  a la diffusion de documents scientifiques de niveau recherche, publi es ou non,  emanant des  tablissements d'enseignement et de recherche fran ais ou  trangers, des laboratoires publics ou priv es.

1 ND70 series basaltic glass reference materials for volatile
2 element (H₂O, CO₂, S, Cl, F) analysis and the C ionization
3 efficiency suppression effect of water in silicate glasses in
4 SIMS analysis.

5 **Yves Moussallam¹, William Henry Towbin², Terry Plank¹, H el ene Bureau³, Hicham**
6 **Khodja⁴, Yunbin Guan⁵, Chi Ma⁵, Michael B. Baker⁵, Edward M. Stolper⁵, Fabian U.**
7 **Naab⁶, Brian D. Monteleone⁷, Glenn G. Gaetani⁷, Kenji Shimizu⁸, Takayuki Ushikubo⁸,**
8 **Hyun Joo Lee¹, Shuo Ding¹, Sarah Shi¹, Estelle F. Rose-Koga⁹.**

9

10 ¹ *Lamont-Doherty Earth Observatory, Columbia University, New York, USA*

11 ² *Gemological Institute of America, 50 W. 47th Street, New York, NY 10036, United States of America*

12 ³ *IMPMC, Sorbonne Universit e, CNRS UMR 7590, MNHN, IRD UR 206, 4 place Jussieu, 75252*
13 *Paris Cedex 05, France*

14 ⁴ *LEEL, NIMBE, CEA, CNRS, Universit e Paris–Saclay, CEA Saclay, 91191 Gif sur Yvette Cedex,*
15 *France*

16 ⁵ *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena,*
17 *California 91125, USA*

18 ⁶ *Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor,*
19 *Michigan 48109, USA*

20 ⁷ *Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA*
21 *02543, USA.*

22 ⁸ *Kochi Institute for Core Sample Research, X-star, Japan Agency for Marine-Earth Science and*
23 *Technology, Monobe-otsu 200, Nankoku, Kochi 783-8502, Japan*

24 ⁹ *ISTO, UMR 7327, CNRS-UO-BRGM, 1A rue de la F erollerie, 45071 Orl eans cedex 2, France*

25

26 Corresponding author: Yves Moussallam; yves.moussallam@ldeo.columbia.edu

27

28 Keywords: standards; volatiles; silicate melts; SIMS; ERDA; NRA; FTIR; EMPA

29

30 **ABSTRACT**

31 We present a new set of reference materials, the ND70-series, for in situ analysis of volatile
32 elements (H₂O, CO₂, S, Cl, F) in silicate glass of basaltic composition. Samples have been
33 synthesised in piston cylinders at pressures of 1 to 1.5 GPa at volatile-undersaturated
34 conditions. They span mass fractions from 0 to 6 wt.% H₂O, from 0 to 1.6 wt.% CO₂ and
35 from 0 to 1 wt.% S, Cl and F. The samples have been characterised by Elastic Recoil
36 Detection Analysis (ERDA) for H₂O, by Nuclear Reaction Analysis (NRA) for CO₂, by
37 Elemental Analyser (EA) for CO₂, by Fourier Transform Infrared Spectroscopy (FTIR) for
38 H₂O and CO₂, by Secondary Ion Mass Spectrometry (SIMS) for H₂O, CO₂, S, Cl and F, and
39 by Electron Microprobe (EMP) for CO₂, S, Cl, and major elements. Comparison between
40 expected and measured volatile amounts across techniques and institutions is excellent. It was
41 found however that SIMS analyses of CO₂ mass fractions using either Cs⁺ or O⁻ primary
42 beams are strongly affected by the glass H₂O content. Reference materials have been made
43 available to users at Ion probe facilities in the US, Europe and Japan. Remaining reference
44 materials are preserved at the Smithsonian National Museum of Natural History where they
45 are freely available on loan to any researcher.

46

47 I. INTRODUCTION

48 Volatile elements (C-O-H-S-Cl-F) play a major role in planetary processes including
49 habitability (e.g., Ehlmann et al., 2016; Foley & Smye, 2018; Dehant et al., 2019), plate
50 tectonics (e.g., Albarède, 2009; Stern, 2018; Nicoli & Ferrero, 2021), mantle melting (e.g.,
51 Wyllie, 1971; Eggler, 1976; Dasgupta & Hirschmann, 2006) and volcanic eruptions (e.g.,
52 Elskens et al., 1968; Allard, 2010; Edmonds & Woods, 2018). Understanding the planetary-
53 scale cycling of volatiles has hence long been a subject of interest to geoscientists. Critical to
54 that effort is the ability to reliably measure volatiles in geological materials. For
55 volcanologists, igneous petrologists and mantle geochemists, the ability to measure volatile
56 elements in melts (i.e., glasses) and mineral-hosted melt inclusions is of particular interest
57 (e.g., Dixon et al., 1988; Hauri et al., 2002; Métrich & Wallace, 2008). Secondary Ion Mass
58 Spectrometry (SIMS) is a technique that allows for the measurements of all major volatile
59 species in silicate glasses (e.g., Shimizu et al., 2017). One persistent issue with SIMS
60 analyses however is that the ionization efficiency varies by element, primary beam, and
61 major element matrix. To be fully quantitative, the technique requires well characterized
62 reference materials with bulk compositions similar to that of the sample. To date, ion
63 microprobe facilities in Nancy, Paris, Lausanne, Edinburgh, Washington, Woods Hole,
64 Pasadena, Tempe and Kochi, amongst other, have all either acquired or synthesised their own
65 sets of reference material for volatile elements in basaltic glasses. Although sharing natural
66 standards is quite common (e.g., Shimizu et al., 2017), efforts to synthesize large amounts of
67 glasses and to cross-calibrate instruments prior to using the synthetic glasses as standards
68 have been quite limited, particularly on an international scale. This has resulted in significant
69 challenges when attempting to directly compare analytical results generated by different
70 facilities. Furthermore, not all of these facilities possess reference materials that span the
71 entire range of volatile mass fractions found in geological samples. As a consequence, some
72 measurements rely on extrapolation from calibration curves. In this context, we introduce and
73 thoroughly characterize a new series of synthetic basaltic glasses. These glasses are intended
74 to serve as international reference materials for the analysis of H₂O, CO₂, S, Cl, and F mass
75 fractions in natural glasses with a basaltic composition, particularly in the context of SIMS
76 and other micro-beam techniques.

77 II. EXPERIMENTAL METHOD

78 We used as starting material a natural Back-Arc-Basin-Basalt, ND-70, dredged at Lat:15° 52' S,
79 Lon:174°51' W from a depth of 2500 m b.s.l. (Keller et al., 2008) at the Mangatolu Triple

80 Junction in the northern Lau back-arc region (initial composition: 49.2 wt.% SiO₂, 0.8 wt.% TiO₂,
81 16.1wt.% Al₂O₃, 7.9 wt.% FeO_{tot}, 8.2 wt.% MgO, 12.8 wt.% CaO, 1.9 wt.% Na₂O, 0.15 wt.%
82 K₂O, 0.1 wt.% P₂O₅, 889 ppm S, 219 ppm Cl, 1.02 wt.% H₂O, 76 ppm CO₂, and 148 ppm F;
83 Keller et al., 2008; Caulfield et al., 2012; Lloyd et al., 2013; note that ppm throughout the
84 manuscript refers to μg·g⁻¹). Five grams of material were crushed, placed in a platinum crucible
85 and fused at 0.1MPa, in air, at 1350 °C for two hours, quenched in water (without submersing the
86 crucible), crushed and mixed again and fused a second time at 1350 °C, 0.1MPa, in air, for an
87 additional two hours and quenched again in water (without submersing the crucible). This
88 volatile-free glass (ND70-degassed) constitutes the first sample in our standard suite (i.e., the
89 blank), and was then used as the starting powder for subsequent piston cylinder experiments.

90

91 High-pressure experiments were prepared by adding powdered ND70-degassed glass with the
92 desired amounts of H₂O, CO₂, S, Cl and F in Au₈₀Pd₂₀ capsules which were then welded shut.
93 H₂O was loaded as deionized water (using a micro-pipette), CO₂ was loaded as powdered calcite
94 (CaCO₃), S was loaded as anhydrite (CaSO₄), Cl was loaded as halite (NaCl) and F was loaded as
95 Sellaite (MgF₂). **Table 1** gives the intended composition of each experiment based on the added
96 weight of each component (given in **Table S1** and totalling 150 to 200mg per experiment). High-
97 pressure experiments were all performed in a piston cylinder apparatus at the Lamont-Doherty
98 Earth Observatory (LDEO). We used a 1/2-inch assembly composed of a CaF₂ pressure cell, a
99 graphite furnace, and MgO sleeves and spacers surrounding the (Ø_{ext} = 5.0 mm, Ø_{int} = 4.8 mm,
100 length = 8.0 mm) Au₈₀Pd₂₀ capsule. The temperature was monitored with a D-type (W₉₇Re₃-
101 W₇₅Re₂₅) thermocouple, separated from the capsule by a 0.8 mm alumina disc. No attempt at
102 controlling oxygen fugacity was made, although given that our starting powder (ND70-degassed)
103 was fused in air, we assume highly oxidised conditions. Run conditions for each experiment are
104 reported in **Table 2**. Piston cylinder experiments were conducted at pressures of 1 and 1.5 GPa,
105 temperatures of 1225 and 1325°C and equilibrated for 2 h. Experiments were quenched by
106 turning off the electric power and took approximately 5 s to cool below 400 °C. An additional
107 experiment, INSOL_MX1_BA4, was run using a powdered mixture of natural basalt (60%) and
108 dacite (30%) (from Kilauea and Tutupaca volcanoes, respectively, Moussallam et al.,
109 unpublished) with dolomite (10%) following the same piston cylinder methodology as described
110 above and equilibrated at 1GPa and 1275°C for 2h. No additional water, S, Cl nor F was added.
111 Initial CO₂ was far above saturation. Finally another experiment VILLA_P2 was run using a
112 powdered mixture of natural basaltic andesite from Villarrica volcano (same starting material as
113 described in Moussallam et al., 2023) to which deionized water, elemental sulfur and oxalic acid
114 dihydrate were added such that the initial mass fractions of CO₂ and S would be above saturation

115 level (based on previous experiments on similar compositions) at the conditions of the
116 experiment. The charge was run in an internally heated pressure vessel at the American Museum
117 of Natural History and equilibrated at 300 MPa, 1150°C for 2h at the intrinsic fO_2 of the vessel
118 (~NNO+2; Webster et al., 2011). Both INSOL_MX1_BA4 and VILLA_P2 are not part of the
119 reference material suite that we present here as they were not synthesised in sufficient quantities
120 but were used for calibration purposes during some of the SIMS sessions discussed below. All
121 samples were entirely glassy except ND70-4-01 which partially crystallised on one side of the
122 capsule (the partially crystallized portion was mechanically removed).

123

124 III. ANALYTICAL TECHNIQUES

125 Experiments were analysed by Elastic Recoil Detection Analysis (ERDA) for H₂O, by
126 Nuclear Reaction Analysis (NRA) for CO₂, by Elemental Analyser (EA) for CO₂, by Fourier
127 Transform Infrared Spectroscopy (FTIR) for H₂O and CO₂, by Secondary Ion Mass
128 Spectrometry (SIMS) for H₂O, CO₂, S, Cl and F, and by Electron Microprobe (EMP) for
129 CO₂, S, Cl and major elements.

130

131 a) Nuclear Microprobe (ERDA and NRA)

132 H₂O and CO₂ absolute mass fractions were evaluated using two Ion Beam Analysis
133 techniques, namely Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction
134 Analysis (NRA). Measurements were performed at the Laboratoire d'Etude des Eléments
135 Légers (LEEL) joint CEA-CNRS laboratory in Saclay (Khodja et al., 2001) where these
136 techniques are regularly employed to quantify light elements in various materials, including
137 geological samples (Clesi et al., 2018; Malavergne et al., 2019). H₂O was analysed as H by
138 ERDA following the approaches described in Bureau et al. (2009). We used a ⁴He⁺ ion beam
139 at 2.7 MeV energy that interacts with the samples at grazing incidence. A 12 µm Mylar
140 absorber was mounted between the sample and the forward (30°) particle detector to stop all
141 scattered ⁴He⁺ and let recoil H⁺ ions reach the detector. The CO₂ was analysed as C by NRA,
142 making use of the sensitive ¹²C(d,p)¹³C nuclear reaction at 170° detection angle using a
143 deuteron (²H⁺) microbeam at 1.4 MeV. Although no absorber was used, detected protons, in
144 the 2750–3150 keV energy range, are far above backscattered deuterons. Quantification was
145 performed by precisely measuring detector solid angles using reference materials and by
146 adjusting experimental spectra with the SIMNRA software (Mayer, 1999). The parasitic

147 contribution from the $^{28}\text{Si}(\text{d,p})^{29}\text{Si}$ was systematically subtracted using a Suprasil reference
148 spectrum ($\text{H}_2\text{O} < 1$ ppm; e.g., Shimizu et al., 2019).

149

150 **b) Elemental Analyser**

151 We used a Costech elemental analyzer (ECS4010) at the Lamont–Doherty Earth Observatory
152 to measure CO_2 (as C) in the two most CO_2 -rich experiments (with > 1 wt% CO_2). Hand-
153 picked glass samples were precisely weighed on a microbalance with a precision of ± 0.001
154 mg, and then wrapped in 3.2×4 mm tin foil envelopes. 18.253 mg were used for sample
155 ND70-5-02 and 12.636 mg were used for sample ND70-6-02. These encapsulated samples
156 were subjected to combustion (at ~ 1700 °C) over a chromium (III) oxide catalyst with excess
157 oxygen (25 mL/min). The carrier gas was helium, flowing at a rate of 100 mL/min. To ensure
158 complete oxidation of sample carbon into CO_2 and the elimination of remaining halogens or
159 sulfur, silvered cobaltous/cobaltic oxide, positioned lower in the quartz combustion tube, was
160 used. The analyser was calibrated directly prior to sample analysis using mixtures of oxalic
161 acid and SiO_2 with 1, 2, 5, 20, and 70 wt% of CO_2 . This calibration ($R^2 = 0.9999$; Fig. S1)
162 was then used to determine the CO_2 content of the samples. Error on C was estimated at $\pm 2\%$
163 ($\pm 7.3\%$ on CO_2) based on reproducibility of external standards (calcite and dolomite) similar
164 to other studies using an elemental analyser for silicate glasses (e.g., Moussallam et al., 2015,
165 2016).

166

167 **c) Fourier Transform Infrared Spectroscopy (FTIR)**

168 H_2O and CO_2 mass fractions in doubly polished experimental glasses were measured using a
169 N_2 purged Thermo Scientific Nicolet iN10 mx Fourier Transform Infrared Spectrometer
170 (FTIR) at LDEO. Measurements were collected with aperture sizes varying between $100 \times$
171 100 μm and 200×200 μm . Thickness of the doubly polished wafers were measured using a
172 digital micrometer (Mitutoyo Digimatic Indicator) and calculated using the “interference
173 fringe” method (Tamic et al., 2001) that requires determining the wavelength of interference
174 fringes of reflectance spectra collected from the sample. The latter method enables
175 determining the thickness at the same spot where the transmission spectra is collected.
176 Several spots were measured on each glass to ensure no heterogeneity. Baseline fitting,
177 density calculations, absorption coefficients and ultimately H_2O and CO_2 concentration were
178 determined using PyIRoGlass (Shi et al., 2023; <https://github.com/sarahshi/PyIRoGlass>),
179 except for INSOL_MX1_BA4 where we used the spectra obtained from a de-volatized (i.e.,
180 fused twice at 0.1MPa in air for 2h) version of the same composition to define the baseline.

181

d) Secondary Ion Mass Spectrometry at CNRS-Nancy

182 A first indium mount containing all the experimental glasses was cleaned with DI and
183 Millipore filtered water, dried and then coated with a ~20 nm Au layer. Volatile (H₂O, CO₂,
184 Cl, F, S) contents in experimental glasses were determined using a Cameca IMS 1280 ion
185 microprobe at CRPG-CNRS-Nancy, France. We used a 20 kV (10 kV for the ion acceleration
186 at the source and 10 kV for ion extraction at the sample surface) Cs⁺ primary beam with a
187 current of 1 nA. A -10 kV electron flood gun was applied at the sample surface to charge
188 compensate the positive Cs⁺ ion surface implantation. During analysis (with e-gun on), the
189 sample potential is held at -5 kV and the electron gun is operated at -5 kV, so that electrons
190 arrive at the sample surface with near-zero energy. A 180 s pre-sputter with a 30 × 30 μm
191 square raster was applied, then analyses were collected on the 15 to 20 μm spot in the center
192 of the rastered area using a mechanical aperture placed at the secondary ion image plane.
193 Analyses were performed in multi-collector mode; CO₂, H₂O, F, Cl and S were measured
194 using an electron multiplier, while Si and O were measured on a faraday cup. We collected
195 signals for ¹²C (8 s), ¹⁷O (3 s), ¹⁶O¹H (6 s), ¹⁸O (3 s), ¹⁹F (4 s), ²⁷Al (3 s), ³⁰Si (3 s), ³²S (4 s)
196 and ³⁵Cl (6 s; counting times in parentheses), with 2 s waiting time after each switch of the
197 magnet. This cycle was repeated 10 times during one analysis for a total analysis duration of
198 12 minutes. The mass resolution of ~7000 (with the contrast aperture at 400 μm, the energy
199 aperture at 40 eV, the entrance slit at 52 μm and the exit slit at 173 μm) meant that complete
200 discrimination of the following mass interferences was achieved: ³⁴S¹H on ³⁵Cl; ¹⁷O on
201 ¹⁶O¹H; ²⁹Si¹H on ³⁰Si; ³¹P¹H on ³²S.

202 Together with our experimental glasses, we measured natural and experimental basaltic
203 glasses KL2G (Jochum et al. 2006) KE12 (Mosbah et al. 1991), VG2 (Jarosewich et al.
204 1980), experimental glasses N72, M34, M35, M40, M43 and M48 (Shishkina et al. 2010),
205 and the Macquarie glasses 40428 and 47963 (Kamenetsky et al. 2000) under the same
206 analytical conditions at the beginning and end of the session. The Calibration lines are shown
207 in **Fig. S2 to S6**. All existing standard values are reported in **Table S2**.

208

e) Secondary Ion Mass Spectrometry at Woods Hole Oceanographic Institution

209
210 A second indium mount containing a different set of chips of the experimental glasses, was
211 cleaned with DI and Millipore filtered water, dried and then coated with a ~20 nm Au layer.
212 Volatile concentration analyses were conducted on a Cameca IMS1280 at the Northeast
213 National Ion Microprobe Facility (NENIMF) at the Woods Hole Oceanographic Institution.
214

215 The standards were measured in separate sessions using a $^{133}\text{Cs}^+$ primary beam, then a $^{16}\text{O}^-$
216 primary beam. The calibration lines are shown in [Fig. S2 to S7](#).

217

218 *Cs SIMS measurements:*

219 A 500pA to 1nA $^{133}\text{Cs}^+$ primary ion beam, accelerated 10kV, was focused to a 10–15 μm
220 diameter, then rastered to produce a $\sim 25 \times 25 \mu\text{m}$ crater. Secondary ions ($^{12}\text{C}^-$, $^{16}\text{OH}^-$, $^{18}\text{O}^-$,
221 $^{19}\text{F}^-$, $^{30}\text{Si}^-$, $^{31}\text{P}^-$, $^{32}\text{S}^-$ and $^{35}\text{Cl}^-$) were extracted with a 10kV voltage potential. The extracted
222 and magnified secondary ions were centered through a $600 \times 600 \mu\text{m}$ mechanical field
223 aperture, which blocked transmission of secondary ions from outside of the central $\sim 7.5 \times 7.5$
224 μm^2 of the crater. The secondary field aperture is necessary to minimize the transmission of
225 background and surficial volatile ions residing in the sample chamber, the surrounding
226 sample surface, and within the outer edges of the sputtered crater. A normal-incidence
227 electron gun set at -10kV was used to compensate for positive charge buildup within the
228 sample crater. The energy bandwidth for the secondary ions was $\sim 60 \text{ eV}$. A mass resolving
229 power > 5500 was used to separate interfering masses, such as $^{17}\text{O}^-$ from $^{16}\text{OH}^-$. Each
230 measurement consisted of 180 seconds of presputtering, automatic secondary beam centering,
231 and automatic mass calibration, followed by five cycles of counting of each ion intensity on
232 an ETP electron multiplier in magnet peak jumping mode. Count times in seconds for each
233 mass were as follows: $^{12}\text{C}^- = 10$, $^{16}\text{OH}^- = 5$, $^{18}\text{O}^- = 3$, $^{19}\text{F}^- = 5$, $^{30}\text{Si}^- = 3$, $^{31}\text{P}^- = 5$, $^{32}\text{S}^- = 5$,
234 $^{35}\text{Cl}^- = 5$. Background intensities were measured on Suprasil 3002 glass for C, OH, F, P, and
235 S, and on Herasil glass for Cl.

236

237 *O⁻ SIMS measurements:*

238 A 10nA $^{16}\text{O}^-$ primary ion beam, accelerated 13kV, was focused to a $\sim 25 \mu\text{m}$ diameter, then
239 rastered to produce a ~ 30 to $35 \mu\text{m}$ diameter crater. Secondary ions ($^{12}\text{C}^+$, $^{16}\text{O}^+$, $^{16}\text{OH}^+$, $^{19}\text{F}^+$,
240 $^{30}\text{Si}^+$, $^{31}\text{P}^+$, $^{32}\text{S}^+$ and $^{35}\text{Cl}^+$) were extracted with a 10kV voltage potential. A $1250 \times 1250 \mu\text{m}$
241 mechanical field aperture was set to blocked transmission of secondary ions from outside of
242 the central $\sim 15 \times 15 \mu\text{m}$ the measurement crater. The energy bandwidth for the secondary
243 ions was $\sim 50 \text{ eV}$. A mass resolving power > 5500 was used to separate interfering masses,
244 such as $^{17}\text{O}^+$ from $^{16}\text{OH}^+$. Each measurement consisted of 120 seconds of presputtering,
245 automatic secondary beam centering, and automatic mass calibration, followed by five cycles
246 of counting of each ion intensity on an ETP electron multiplier in magnet peak jumping
247 mode. Count times in seconds for each mass were as follows: $^{12}\text{C}^+ = 5$, $^{16}\text{O}^+ = 3$, $^{16}\text{OH}^+ = 5$,

248 $^{19}\text{F}^+ = 5$, $^{30}\text{Si}^- = 2$, $^{31}\text{P}^+ = 5$, $^{32}\text{S}^+ = 5$, $^{35}\text{Cl}^+ = 5$. Background intensities were measured on
249 Suprasil 3002 glass for C, OH, F, P, and S, and on Herasil glass for Cl.

250

251 **f) Secondary Ion Mass Spectrometry at Caltech**

252 Volatile concentration analyses were conducted on a Cameca ims-7f GEO instrument at the
253 Caltech Microanalysis Center on the second indium mount. The standards were first
254 measured with a Cs^+ beam, and later with an $^{16}\text{O}^-$ beam. The calibration lines are shown in
255 Fig. S2 to S7.

256

257 ***Cs⁺ SIMS measurements:***

258 A 10 kV Cs^+ primary ion beam of ~3–4 nA (~15 μm in diameter) was used to sputter the
259 samples and produce secondary ions. The beam was rastered to produce craters ~25 \times 25 μm
260 in dimension, and a 100 μm field aperture was used to enable only the ions from the central 8
261 μm of the craters to be transmitted for detection. Possible edge effects were further eliminated
262 with electronic gating (36% in area). Secondary ions ($^{12}\text{C}^-$, $^{16}\text{OH}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$, $^{30}\text{Si}^-$, $^{31}\text{P}^-$, $^{32}\text{S}^-$
263 and $^{35}\text{Cl}^-$) of -9 keV were collected with an electron multiplier (EM) in the peak-jumping
264 mode. Each measurement consisted of 120 s pre-sputtering, followed by automated
265 secondary beam alignment, peak centering, and 20 cycles of data collection. The counting
266 time of each mass was 1 s per cycle. The energy bandwidth for the secondary ions was set at
267 ~45 eV. Sample charging compensation was provided by a normal-incidence electron gun
268 NEG at -9 kV. A mass resolving power (MRP) of ~5000 was used to remove any
269 significant interferences to the masses of interest (e.g., $^{17}\text{O}^-$ from the $^{16}\text{OH}^-$ peak). Data were
270 corrected for EM background and deadtime. The instrumental volatile backgrounds were
271 checked with the Suprasil 3002 glass.

272

273 ***O⁻ SIMS measurements:***

274 For this SIMS setup, a focused $^{16}\text{O}^-$ primary beam of -13 kV and ~8 nA was used to sputter
275 areas of 25 \times 25 μm for analysis. Positive secondary ions of $^1\text{H}^+$, $^{12}\text{C}^+$, and $^{28}\text{Si}^+$ of +8.5 kV
276 were collected in the peak-jumping mode with an EM (for $^1\text{H}^+$, $^{12}\text{C}^+$) or a Faraday cup (FC,
277 for $^{28}\text{Si}^+$). Each measurement consisted of 20 cycles of counting of $^1\text{H}^+$ (1s), $^{12}\text{C}^+$ (3s), and
278 $^{28}\text{Si}^+$ (1s). Because there were no significant interferences to the masses of interest, the mass
279 spectrometer was operated at low mass resolution conditions (MRP ~1800). Minimal sample
280 charging was corrected with automatic scan and adjustment of the sample high voltage during

281 measurement. The other analytical parameters and operation were similar to those used for
282 the Cs⁺ session. The C and H backgrounds were checked with Suprasil for this O⁻ session,
283 which yielded $^1\text{H}^+/^{28}\text{Si}^+ = 3.7\text{E}-5$ and $^{12}\text{C}^+/^{28}\text{Si}^+ = 2.1\text{E}-7$. Such backgrounds were
284 insignificant to the measured CO₂ and H₂O concentrations in this set of standards.
285 Nevertheless, the reported results were corrected for this background.

286

287 **g) Secondary Ion Mass Spectrometry at JAMSTEC-Kochi**

288 All the experimental glasses were polished and embedded in a third, indium-filled aluminium
289 disc together with an internal standard basaltic glass of EPR-G3. After cleaning by acetone
290 and de-ionized water, the sample mount was dried in a vacuum oven for a day and then
291 coated with ~30 nm Au. Volatile (H₂O, CO₂, Cl, F, S) contents in the experimental glasses
292 were determined using a Cameca IMS 1280 ion microprobe at Kochi Institute, JAMSTEC,
293 Japan, following the method of Shimizu et al. (2017). We used a 10 to 15 μm diameter
294 Cs⁺ primary beam with a current of ~0.5 nA and an electron gun to compensate for charge
295 build-up at the sample surface. The field aperture size was set at 1 × 1 mm corresponding to 5
296 × 5 μm of the field of view of the secondary ion image in order to collect signals from the
297 centre of the analysis spot to avoid surface contamination near the beam edge. Mass resolving
298 power of ~6000 was applied for separating interference signals. Analyses were performed by
299 a magnetic peak switching method. Secondary ion signals of ¹²C (3s counting time), ¹⁶OH
300 (1s), ¹⁹F (1s), ³⁰Si (1s), ³¹P (1s), ³²S (1s) and ³⁵Cl (1s) were detected by an axial electron
301 multiplier (there was a 2s waiting time after each switch of the magnet). Each analysis
302 consisted of 20s for pre-sputtering, 120s for auto-centering of secondary ions to the field and
303 contrast apertures and 10 cycles of measurements. The total measurement duration for each
304 analysis was ~7 mins. To evaluate the volatile contents of the experimental glasses, we used
305 in-house synthetic and natural silicate standard glasses described in Shimizu et al. (2017).
306 The volatile contents of these in-house standards were determined by FTIR (H₂O and CO₂
307 contents) and pyrohydrolysis-ion chromatography (F, Cl and S contents) (Shimizu et al.,
308 2015). Calibration lines are show in **Fig. S2 to S7**.

309

310 **h) Electron Microprobe at Caltech**

311 Carbon contents of the glass samples ND70-3-01, ND70-4-02, ND70-5-02, and ND70-6-02
312 as well as the following secondary standards: five gem-quality scapolites (from Prof. George
313 Rossman), a natural spurrite (from the Caltech mineral collection; CIT-11435; Joesten, 1974),
314 and a eutectic glass composition in the CaO-Al₂O₃-SiO₂ (CAS) system were analyzed at

315 Caltech using a JEOL JXA-iHP200F field-emission electron microprobe in WDS mode,
316 interfaced with the Probe for EPMA software from Probe Software, Inc. The secondary
317 standards were carefully polished down to a $\frac{1}{4}$ μm finish and ultrasonicated in ethanol; the
318 scapolites were mounted in indium while the spurrite and CAS glass were mounted in epoxy
319 (the ND-series glasses were prepared at Lamont). Just prior to the start of the analytical
320 session, the ND-series glasses, secondary standards, and primary standards were plasma
321 cleaned using an Evactron system to remove hydrocarbon contamination on their surfaces
322 and then coated with an ~ 1 -nm layer of Ir (Armstrong & Crispin, 2013) using a Cressington
323 208HR sputter coater (all samples were coated at the same time). Analytical conditions were
324 10 kV and 15 kV accelerating voltages, a 50 nA beam current, and a 10 μm defocused beam.
325 The LDE2 crystal was used for carbon analysis and counting times were 60 s on peak and 30
326 s on each background. The on-peak O interference with the C peak, revealed by WDS scans
327 of the glass samples, was corrected using the Probe for EPMA program. Cohenite (Fe_3C ;
328 $\text{CK}\alpha$) from the iron meteorite Canyon Diablo and Elba hematite ($\text{OK}\alpha$; for the C on-peak
329 interference correction) were used as primary standards. Each ND-series glass and secondary
330 standard was analyzed five times. Quantitative carbon analyses were processed with the
331 CITZAF matrix correction procedure (Armstrong, 1995) using the major and minor element
332 composition of each phase.

333

334 For the secondary standards, the CO_2 contents of the five gem-quality scapolites were
335 determined using NRA at the Michigan Ion Beam Laboratory at the University of Michigan
336 using a deuteron beam energy of 1.35 MeV and procedures described in Hammerli et al.
337 (2021). The measured CO_2 contents ranged from 0.70 to 3.57 wt.%. The CAS eutectic glass
338 was fused at 1-atm in air and is assumed to have a CO_2 content of zero (the extremely low
339 solubility of CO_2 in basalts and more silica-rich compositions at $p\text{CO}_2 = 1$ bar, and the very
340 low mole fraction of CO_2 in air support this assumption e.g., Blank, 1993; Stolper &
341 Holloway, 1988). The CO_2 content of the spurrite was calculated from stoichiometry, i.e., the
342 wt.% CO_2 was adjusted until the cation sum of C and B (on the basis of 11 oxygens) was
343 equal to 1 (the boron content was determined by SIMS using the Cameca IMS 7f-GEO at
344 Caltech; see Krzhizhanovskaya et al., 2023 for a discussion of B- and S-bearing spurrite).
345 The calculated CO_2 content (9.36 wt.%), plus the B_2O_3 content determined by SIMS, plus the
346 remaining oxide concentrations determined by EMPA resulted in an oxide sum of 100.06

347 wt.%. We used this stoichiometric approach because the abundant small inclusions on the
348 surface of the polished spurrite sample precluded determining its C content by NRA.

349

350 Supplemental Fig. S8 compares the measured EMP CO₂ contents of the secondary standards
351 with their accepted values and shows that the probe analyses are systematically low and
352 offset from the solid 1:1 line. The dashed line, an unweighted least-squares fit to the seven
353 secondary standards, has an R²-value of 0.998. The fact that the best-fit line doesn't go
354 through the origin most likely reflects an over-correction of the oxygen interference with the
355 carbon peak. We assumed that the EMP carbon analyses for the ND-series glasses were
356 similarly offset from their "true" values, and we used the dashed-best-fit line to adjust their
357 CO₂ contents, i.e., to project them onto the y-axis in Fig. S8. It is these projected ND-series
358 CO₂ concentrations that are plotted in Fig. 2 and listed in Table 4.

359

360 i) Electron Microprobe at AMNH

361 The S, Cl and major element compositions were measured with a Cameca SX5-Tactis at the
362 American Museum of Natural History on a new set of polished glasses mounted in resin. We
363 used an accelerating voltage of 15 kV, a defocused beam of 10 μm, a beam current of 4 nA
364 for Na (with 10s count time), 10 nA for Mg, Al, Si, Ca (20s count time), P, K, Ti, Mn, Fe
365 (30s count time), and 40 nA for S and Cl (70s and 40s count times respectively). Na was
366 analysed first to minimize Na loss during analysis. The instrument was calibrated on natural
367 and synthetic mineral standards and glasses: albite (Na), olivine (Mg), potassium-feldspar
368 (Al, Si and K), berlinite (P), anorthite (Ca), rutile (Ti), rhodonite (Mn), fayalite (Fe), barium
369 sulfate (S) and scapolite (Cl). Errors (two standard deviation) are ±0.43 for SiO₂, ±0.18 for
370 Na₂O, ±0.02 for K₂O, ±0.17 for Al₂O₃, ±0.36 for CaO, ±0.24 for FeO, ±0.11 for MgO, ±0.04
371 for TiO₂, ±0.05 for MnO, ±0.04 for P₂O₅, ±0.01 for S and ±0.03 for Cl.

372

373 IV. RESULTS

374 Here we compare results of the different analytical methods against the mass fractions
375 calculated from the quantities loaded into the experimental capsules. Loaded mass fractions
376 are used as a starting point for comparisons with no assumption that they might represent
377 "correct" values. Results from EMPA analyses are given in Table 3, results from ERDA,
378 NRA, FTIR and EA are given in Table 4 and results from SIMS are given in Table 5. Raw
379 SIMS results are given in Tables S3 to S7. SIMS calibration lines are shown in Fig. S2 to S7.

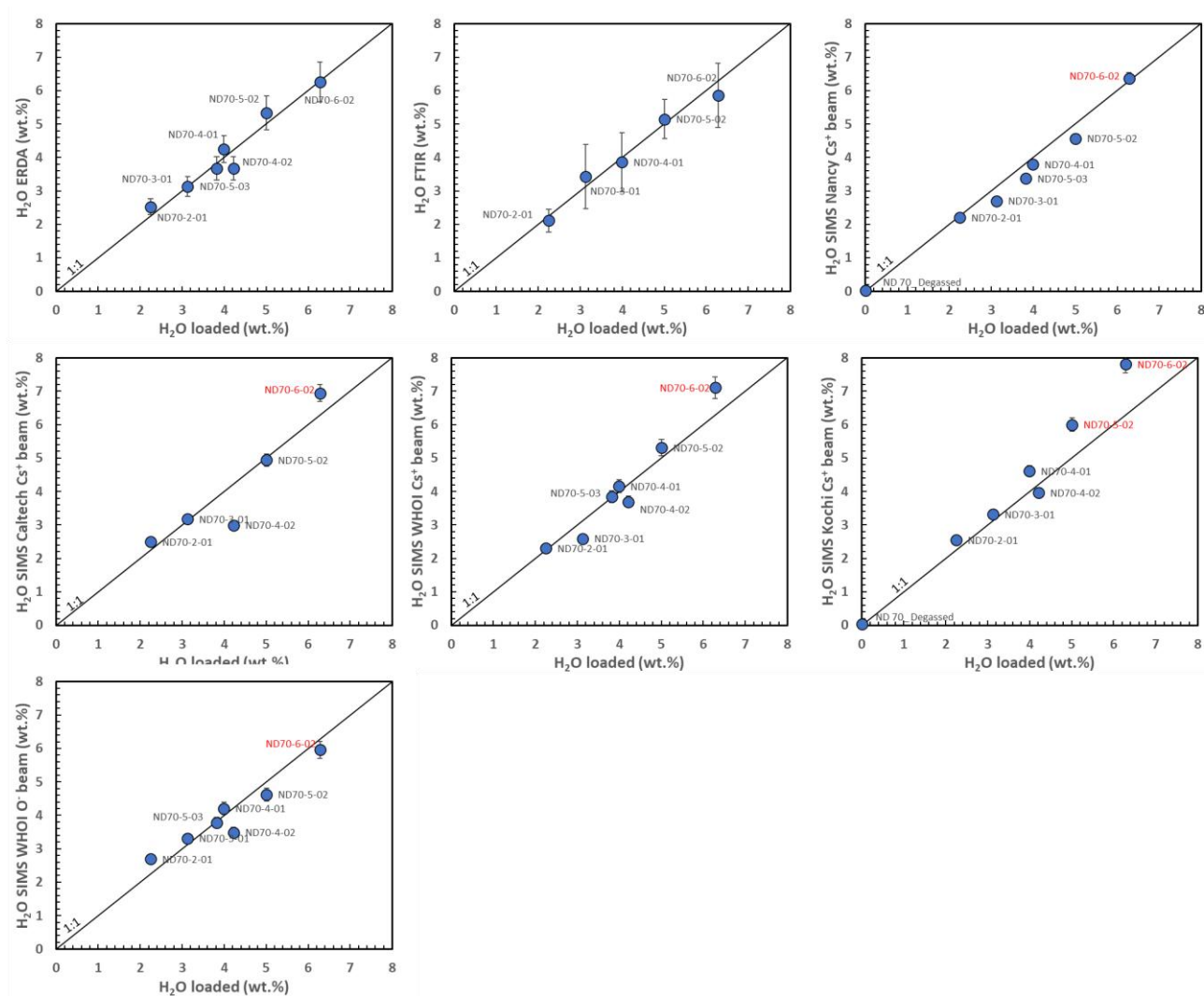
380 FTIR spectra and deconvolutions are shown in Fig. S9. Raw FTIR spectra are given in
381 Moussallam (2024a). Raw NRA spectra are given in Moussallam (2024b).

382

383 **a) H₂O**

384 Water in the new reference glasses was analysed by ERDA, FTIR and at the ion microprobe
385 facilities at CRPG-CNRS-Nancy, WHOI, Caltech and JAMSTEC-Kochi. Figure 1 compares
386 the water contents measured by all of these techniques with the expected (i.e., loaded) values.
387 The agreement is in most cases excellent (better than 8%). Significant deviation from the
388 one-to-one line is found for one Caltech Cs⁺ beam SIMS analysis of sample ND70-4-02
389 although the discrepancy between loaded and measure H₂O content in ND70-4-02 disappears
390 if the measured ¹⁶O¹H/¹⁸O ratio is used instead of the ¹⁶O¹H/³⁰Si ratio. Significant deviation
391 from the one-to-one lines is also found for the Kochi Cs⁺ beam SIMS analyses of sample
392 ND70-5-02 and ND70-6-02. Note that these two samples have concentrations that require
393 very significant extrapolation of the calibration line (Fig. S2). Caltech O⁻ beam SIMS
394 analyses are not shown as most unknown glasses had values outside the calibration range for
395 that session.

396



397

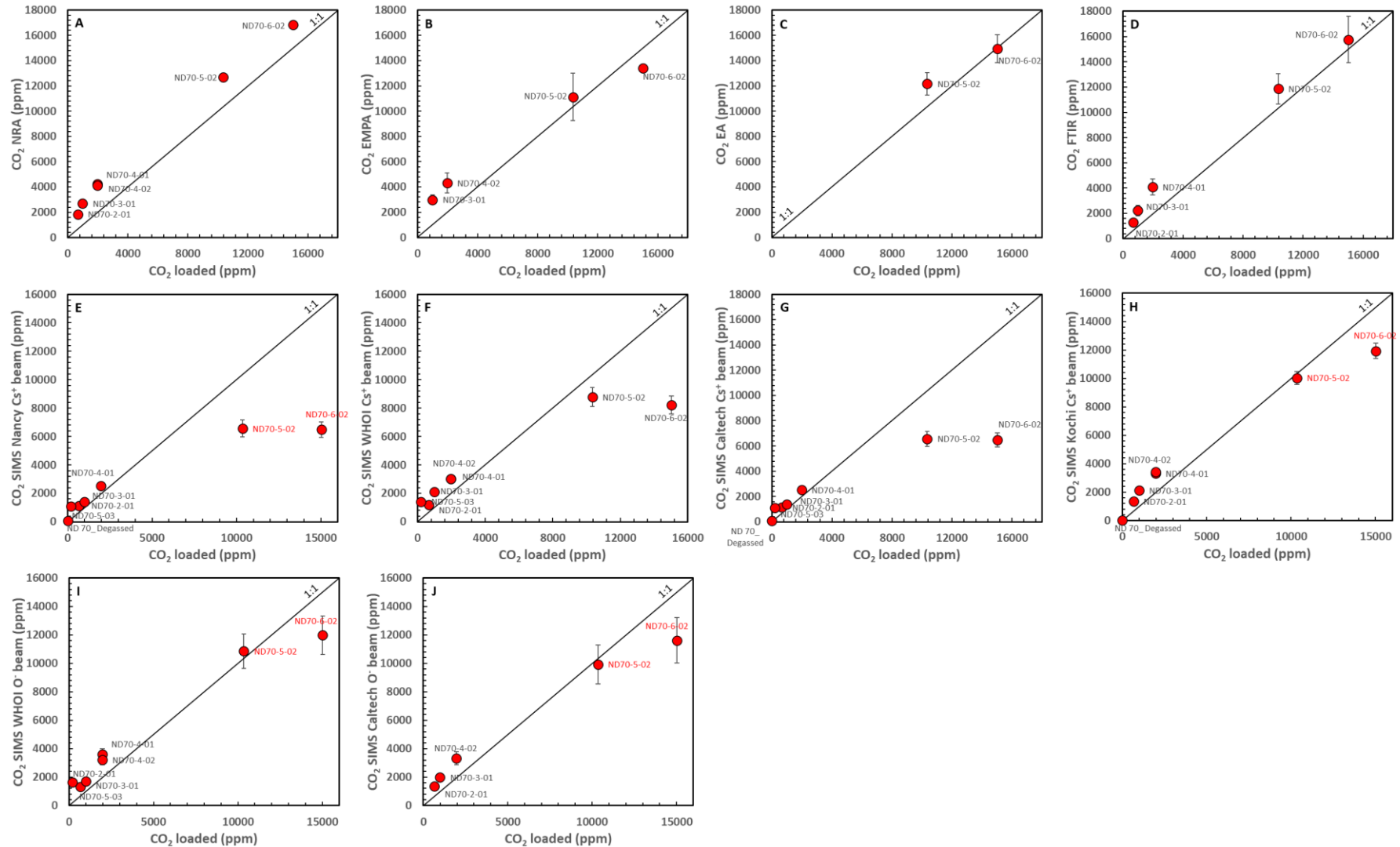
398 **Figure 1:** Comparison between the expected (i.e., loaded) and measured water content in the new reference materials. Samples labelled in red

399 were measured outside their respective calibration ranges (Fig. S2).

400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423

b) Carbon dioxide

CO₂ in the new reference glasses was analysed by NRA, EA, FTIR, EMPA and at the ion microprobe facilities at CRPG-CNRS-Nancy, WHOI, Caltech and JAMSTEC-Kochi. Figure 2 compares the CO₂ contents measured by all these techniques with the expected (i.e., loaded) values. Sample ND70_Degassed was measured by SIMS at CRPG-CNRS-Nancy and JAMSTEC-Kochi. We found that the sample provides a good “blank” for CO₂ with ¹²C/³⁰Si signals comparable to those obtained on pure quartz and San Carlos olivine (Table S8). Figure 2 shows that samples ND70-2-01, ND70-3-01, ND70-4-01, ND70-4-02 and ND70-5-03 have measured CO₂ contents significantly higher than expected based on the loaded amounts of CO₂ (although not all five samples were analysed using all of the techniques or ion probes). For sample ND70-5-02, measured CO₂ contents from NRA and EA analyses were significantly higher than the loaded (i.e., expected) CO₂ concentration. In contrast, EMP analyses, O⁻ beam SIMS analyses from Caltech and WHOI and Cs⁺ beam SIMS analyses from JAMSTEC-Kochi were close to the expected concentration, while Cs⁺ beam SIMS analyses at CRPG-CNRS-Nancy, WHOI and Caltech yielded significantly lower concentrations. The measured CO₂ content of sample ND70-6-02 by NRA is higher than the amount loaded, close to the expected amount when using EA and FTIR, but significantly lower than the amount loaded when considering EMPA and all SIMS analyses (regardless of primary species). The mismatch between loaded and measured CO₂ contents in most experiments may reflect C contamination either during sample preparation or during the experiment. C diffusion through platinum capsules has been documented by Brooker et al., (1998) at temperatures around 1650°C, significantly higher than the temperatures used here and no “blackening” of our glasses was observed.



424

425 **Figure 2:** Comparison between the expected (i.e., loaded) and measured CO₂ content in the new reference materials. Samples labelled in red
 426 were measured outside their respective calibration ranges (Fig. S3 and S7).

427 **c) Sulfur**

428 S in the new reference glasses was analysed by EMP at AMNH and at the ion microprobe
429 facilities at CRPG-CNRS-Nancy, WHOI, Caltech and JAMSTEC-Kochi. **Figure 3** compares
430 the loaded S contents with the mass fractions measured by EMP and the four ion probes. The
431 agreement is excellent for samples ND70_Degassed, ND70-2-01, ND70-3-01, ND70-5-03
432 and, except for the Kochi analyses, ND70-5-02. Samples ND70-4-01 and ND70-4-02 show
433 somewhat lower than expected values in the Caltech and WHOI SIMS analyses. Compared to
434 the loaded concentration, the measured S content in sample ND70-6-02 was significantly
435 lower in the EMP and Caltech and WHOI SIMS analyses and higher in the Nancy and Kochi
436 SIMS analyses. Note that the SIMS S measurements for both ND70-5-02 and ND70-6-02 are
437 based on very significant extrapolation from calibration ranges (**Fig. S4**).

438

439 **d) Chlorine**

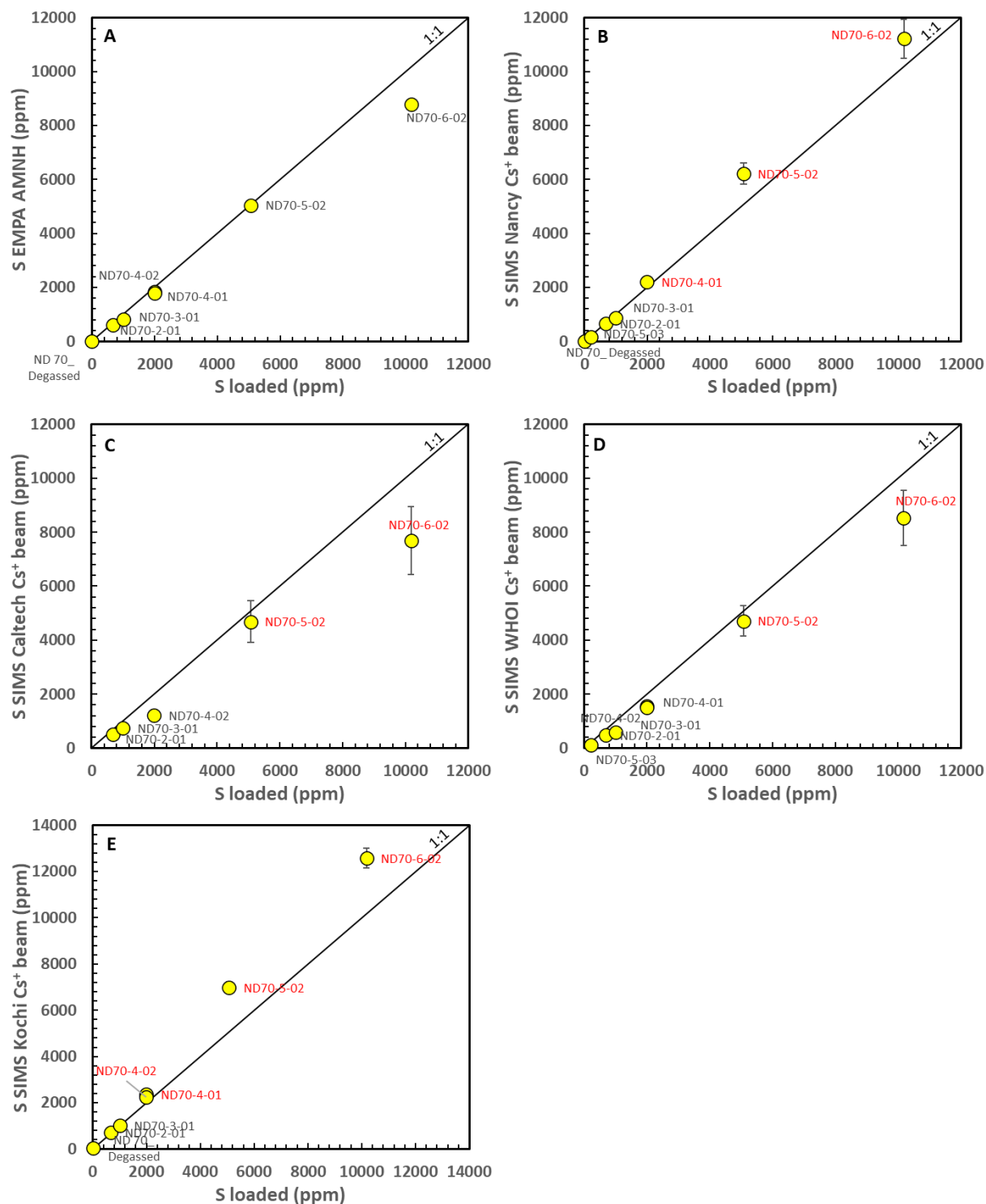
440 Chlorine in the new reference glasses was analysed by EMP at AMNH and at the ion
441 microprobe facilities at CRPG-CNRS-Nancy, WHOI, Caltech and JAMSTEC-Kochi (the
442 Caltech analyses are not shown as most of the unknown glasses had values outside the
443 calibration range for that session). **Figure 4** compares the Cl contents measured by these
444 techniques with the expected (i.e., loaded) values. Samples ND70_Degassed, ND70-2-01,
445 ND70-3-01, ND70-4-01, ND70-4-02 and ND70-5-03 all show good to excellent agreements.
446 The measured Cl contents in samples ND70-5-02 and ND70-6-02 are significantly higher
447 than loaded amounts in all three sets of SIMS analyses and in the EMP analyses. Note that
448 the SIMS Cl measurements for both ND70-5-02 and ND70-6-02 are based on very significant
449 extrapolation from calibration ranges (**Fig. S5**).

450

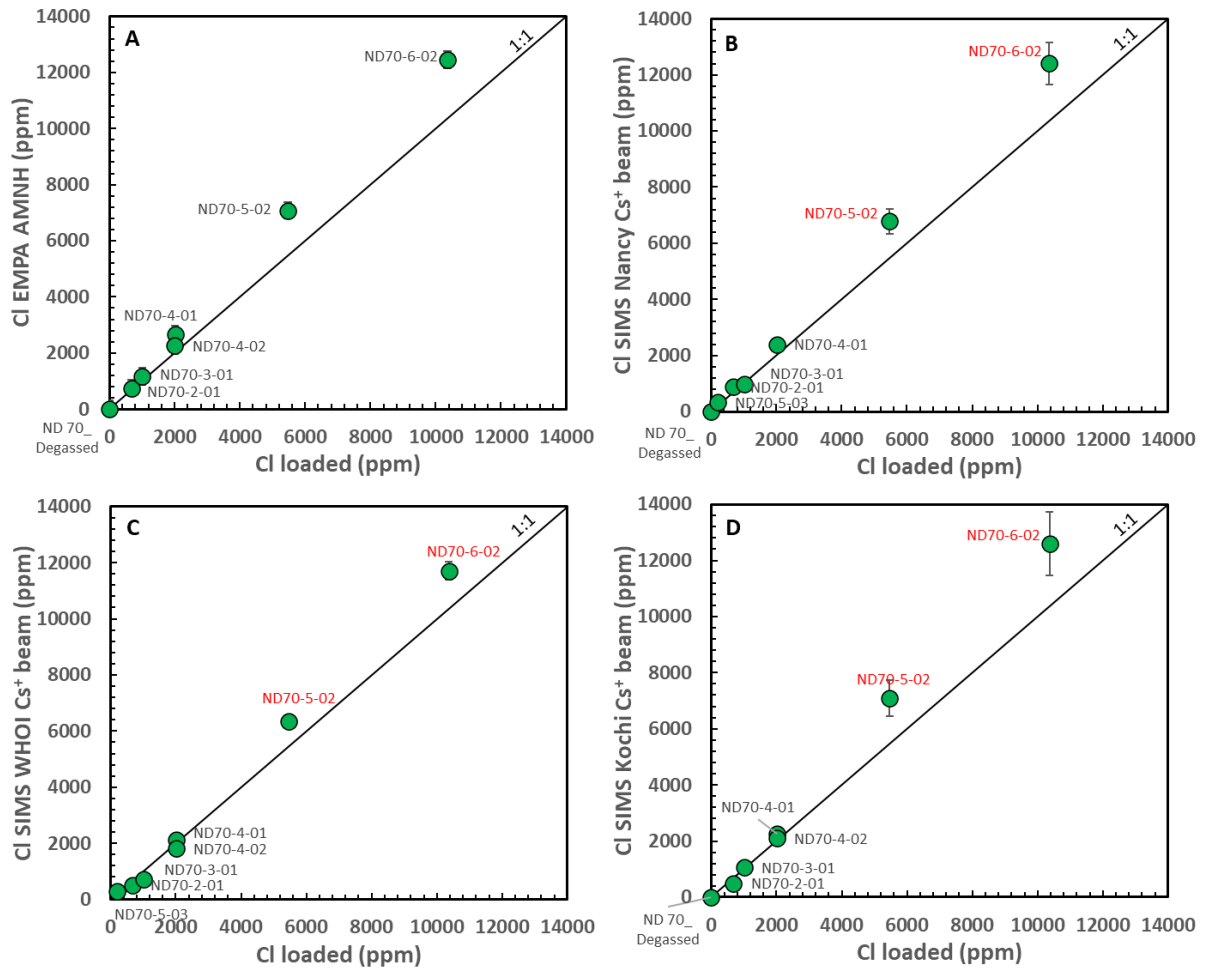
451 **e) Fluorine**

452 Fluorine in the new reference glasses was analysed at the ion microprobe facilities at CRPG-
453 CNRS-Nancy, WHOI, JAMSTEC-Kochi and Caltech but Caltech analyses are not shown as
454 most of the unknown glasses had F mass fractions outside the calibration range for that
455 session. **Figure 5** compares the F contents measured by the Nancy, WHOI and Kochi ion
456 probes with the expected (i.e., loaded) values. Samples ND70_Degassed, ND70-2-01, ND70-
457 3-01, ND70-4-01, ND70-4-02 and ND70-5-03 all show good to excellent agreements
458 between the measured and expected mass fractions. For samples ND70-5-02 and ND70-6-02
459 where measurements are based on very significant extrapolation from calibration ranges (**Fig.**

460 **S6)** the agreement is excellent for the Nancy and WHOI SIMS analyses but the Kochi
 461 analyses for these glasses are significantly higher.



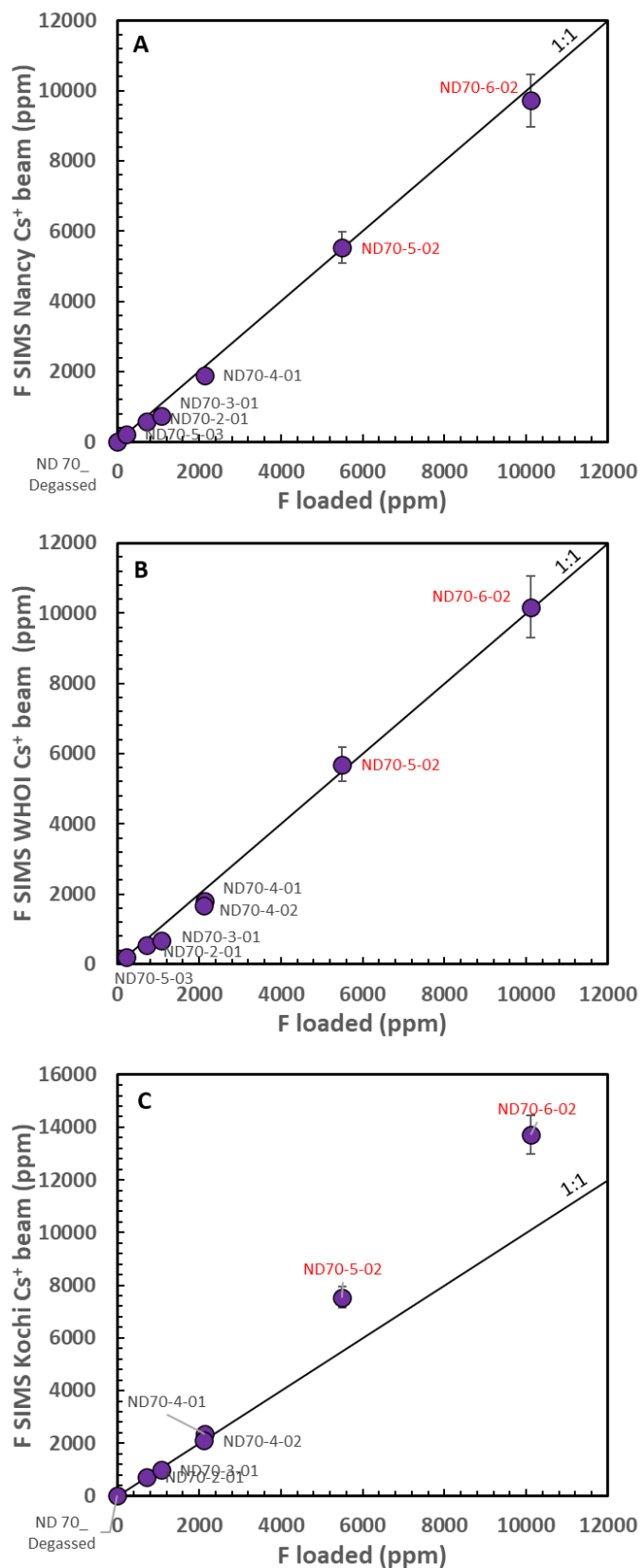
462
 463 **Figure 3:** Comparison between the expected (i.e., loaded) and measured S content in the new
 464 reference materials. Samples labelled in red were measured outside their respective
 465 calibration ranges (Fig. S4).



466

467 **Figure 4:** Comparison between the expected (i.e., loaded) and measured Cl content in the
 468 new reference materials. Samples labelled in red were measured outside their respective
 469 calibration ranges (Fig. S5).

470



471

472 **Figure 5:** Comparison between the expected (i.e., loaded) and measured F content in the new
 473 reference materials. Samples labelled in red were measured outside their respective
 474 calibration ranges (Fig. S6).

475

476

477 **f) Reference material homogeneity**

478 Based on volatile solubility experiments described in the literature (e.g., Stolper & Holloway,
479 1988; Blank & Brooker, 1994; Lesne et al., 2011; Iacono-Marziano et al., 2012; Moussallam,
480 et al., 2015; Allison et al., 2019) our experimental durations and temperatures should have
481 been sufficient to achieve homogeneity in term of both major and volatile element
482 distributions in the experimental glasses (recall that the starting material was a twice-fused
483 glass). Evidence of homogeneity is further provided by the good inter-instrument comparison
484 (see following section). Excepted for the WHOI and Caltech SIMS analyses which were
485 performed on the same mount (i.e., the same pieces of glass), all other techniques were
486 performed on distinct sets of glasses.

487 V. DISCUSSION

488

489 a) Inter-instrument comparison

490 **Figure 6** compares the mean absolute deviation (i.e., $\frac{\sum \text{normalized}(|\Delta|)}{n}$, in %) between all the
 491 techniques used to measure H₂O, CO₂, S, Cl and F contents in the ND70 suite, and **Fig. 7**
 492 graphically compares all the measurements. For H₂O, results from ERDA, FTIR and five
 493 SIMS sessions all agree with average mean absolute deviations around 10% between
 494 methods. The JAMSTEC-Kochi SIMS results show larger deviations (15% on average) but
 495 this is entirely due to samples ND70-5-02 and ND70-6-02 being outside the calibration range
 496 for that SIMS session. For CO₂, NRA, EA, FTIR and EMPA analyses agree on average
 497 within $\pm 9\%$. Cs⁺ primary beam SIMS analyses at Caltech, WHOI and Nancy agree
 498 reasonably well with each other (on average within $\pm 18\%$) but agree poorly with the other
 499 techniques due to the low values measured in samples ND70-5-02 and ND70-6-02, which
 500 were outside the calibration range for the Nancy SIMS session and dominate the mean
 501 absolute deviation calculation (more on this in the following section). Cs⁺ primary beam
 502 SIMS analyses at Kochi however agrees with O⁻ primary beam SIMS analyses at Caltech and
 503 WHOI (on average within $\pm 5\%$) and agrees poorly with the other Cs⁺ primary beam SIMS
 504 analyses (on average within $\pm 33\%$). O⁻ primary beam SIMS analyses at Caltech and WHOI
 505 agree with each other within $\pm 6\%$ and are in reasonable agreement with the results from
 506 NRA, EA and FTIR, on average within $\pm 19\%$, but differ from the EMPA mass fractions by,
 507 on average, $\pm 27\%$. Note that only two samples were analysed by EA, partially explaining
 508 why this technique shows the lowest average mean absolute deviation.

509 For S, the averages of the EMP analyses and the four sets of Cs⁺ primary beam SIMS
 510 analyses (Caltech, WHOI, Kochi and Nancy) all agree within approximately $\pm 30\%$ with
 511 much of this error being dominated by the large differences between the Kochi and WHOI
 512 analyses. For Cl, the means of the EMP analyses and the three sets of Cs⁺ primary beam
 513 SIMS analyses (WHOI, Nancy and Kochi) all agree, on average, within $\pm 17\%$; the agreement
 514 is similar when the means are compared to the loaded amounts of Cl despite samples ND70-
 515 5-02 and ND70-6-02 being outside the calibration range for the SIMS analyses. The EMP,
 516 Nancy and Kochi SIMS analyses all agree on average within $\pm 11\%$. In contrast, the
 517 agreement between the WHOI analyses and the other techniques is poorer (due to strong
 518 deviations on samples ND70-5-02 and ND70-6-02). For F, all three SIMS sessions (WHOI,
 519 Nancy, Kochi) agree with the loaded values, within $\sim 14\%$, on average despite samples

520 ND70-5-02 and ND70-6-02 being outside the calibration range for all SIMS sessions. The
 521 WHOI and Nancy SIMS sessions agree best, on average, within $\pm 10\%$, while the Kochi
 522 session agreement is poorer (due to strong deviations on samples ND70-5-02 and ND70-6-
 523 02).

H ₂ O	ERDA	FTIR	SIMS Cs+ Caltech	SIMS Cs+ WHOI	SIMS O- WHOI	SIMS Cs+ Nancy	SIMS Cs+ Kochi	Average*
Loaded	6	6	11	8	9	7	14	9
ERDA		9	8	7	6	10	10	8
FTIR			12	13	10	10	19	11
SIMS Cs+ Caltech				12	10	11	15	11
SIMS Cs+ WHOI					12	9	13	11
SIMS O- WHOI						11	15	10
SIMS Cs+ Nancy							20	11
SIMS Cs+ Kochi								15

CO ₂	NRA	EA	FTIR	SIMS Cs+ Caltech	SIMS O- Caltech	SIMS Cs+ WHOI	SIMS O- WHOI	SIMS Cs+ Nancy	SIMS Cs+ Kochi	EMPA	Average*
Loaded	101	9	69	48	59	140	155	115	64	85	85
NRA		8	13	42	25	32	24	47	23	12	33
EA			4	42	20	36	15	51	19	9	21
FTIR				28	15	22	14	38	14	19	23
SIMS Cs+ Caltech					33	17	35	14	37	74	37
SIMS O- Caltech						13	6	31	3	27	23
SIMS Cs+ WHOI							20	21	16	44	36
SIMS O- WHOI								30	8	31	34
SIMS Cs+ Nancy									48	97	49
SIMS Cs+ Kochi										23	25
EMPA											42

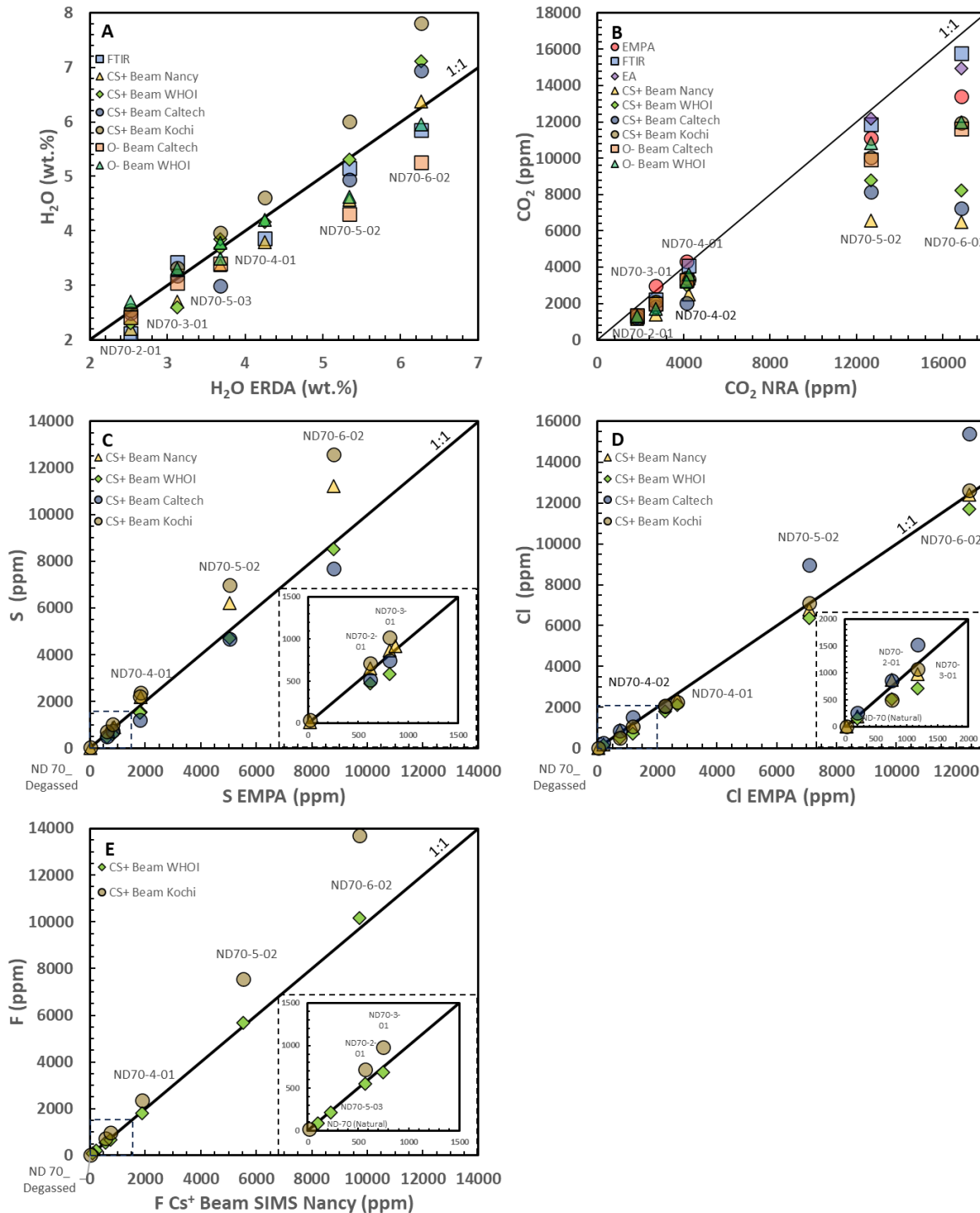
S	EMPA AMNH	SIMS Cs+ Caltech	SIMS Cs+ WHOI	SIMS Cs+ Nancy	SIMS Cs+ Kochi	Average*
Loaded	10	24	25	12	17	18
EMPA AMNH		16	15	15	29	17
SIMS Cs+ Caltech			13	30	54	27
SIMS Cs+ WHOI				38	140	46
SIMS Cs+ Nancy					12	21
SIMS Cs+ Kochi						50

Cl	Loaded	EMPA AMNH	SIMS Cs+ WHOI	SIMS Cs+ Nancy	SIMS Cs+ Kochi	Average*
Loaded		20	21	19	17	19
EMPA AMNH			21	10	11	16
SIMS Cs+ WHOI				24	16	21
SIMS Cs+ Nancy					13	16
SIMS Cs+ Kochi						14

F	Loaded	SIMS Cs+ WHOI	SIMS Cs+ Nancy	SIMS Cs+ Kochi	Average*
Loaded		15	12	15	14
SIMS Cs+ WHOI			5	33	18
SIMS Cs+ Nancy				30	16
SIMS Cs+ Kochi					26

*Average of mean absolute deviation across methods (in %)

525 **Figure 6:** Matrices showing the mean absolute deviation (in %) between all techniques used
 526 to measure H_2O , CO_2 , S , Cl and F contents in the new reference materials. Background
 527 boxes colours are scaled with the mean absolute deviation from green to red. For each box,
 528 the mean absolute deviation is calculated by summing all absolute differences between the
 529 volatile contents determined by the row and column techniques normalized by the row
 530 technique and dividing by the number of analyses.



531 **Figure 7:** Comparison of measured H_2O , CO_2 , S , Cl and F volatile content in ND70-series
 532 glasses by several techniques. With the exception of the last panel, the X-axis of each plot is
 533 the technique we have highest confidence in. All F analyses (panel E) were done by SIMS. Y-
 534 axis gives the value measured by all other techniques.
 535
 536

537 **b) Effect of water on SIMS CO₂ measurements**

538 All four Cs⁺ primary beam SIMS sessions (Kochi, Caltech, WHOI and Nancy), yielded CO₂
539 contents for ND70-6-02, that were low relative to the loaded abundance of CO₂. The loaded
540 CO₂ abundance in sample ND70-6-02 was 1.5 wt.% (verified by FTIR, EA and NRA), yet
541 the Cs⁺ primary beam SIMS analyses at all four ion probes measured ¹²C/³⁰Si ratios much
542 lower than expected for such a mass fraction (see Fig. S3). In three out of four cases, the
543 measured ¹²C/³⁰Si ratios were even lower than those measured in sample ND70-5-02 which
544 contained 1 wt.% CO₂. We attribute this anomaly to the high water mass fraction in the
545 ND70-6-02 glass (> 6 wt%), limiting the ionization efficiency of ¹²C, a phenomenon
546 previously reported in an AGU abstract by Hervig et al. (2009) and similar to the decreasing
547 yield of H⁻ ions observed with increasing water mass fraction (e.g., Hauri et al., 2002; Befus
548 et al., 2020) although in this case the species are different.

549

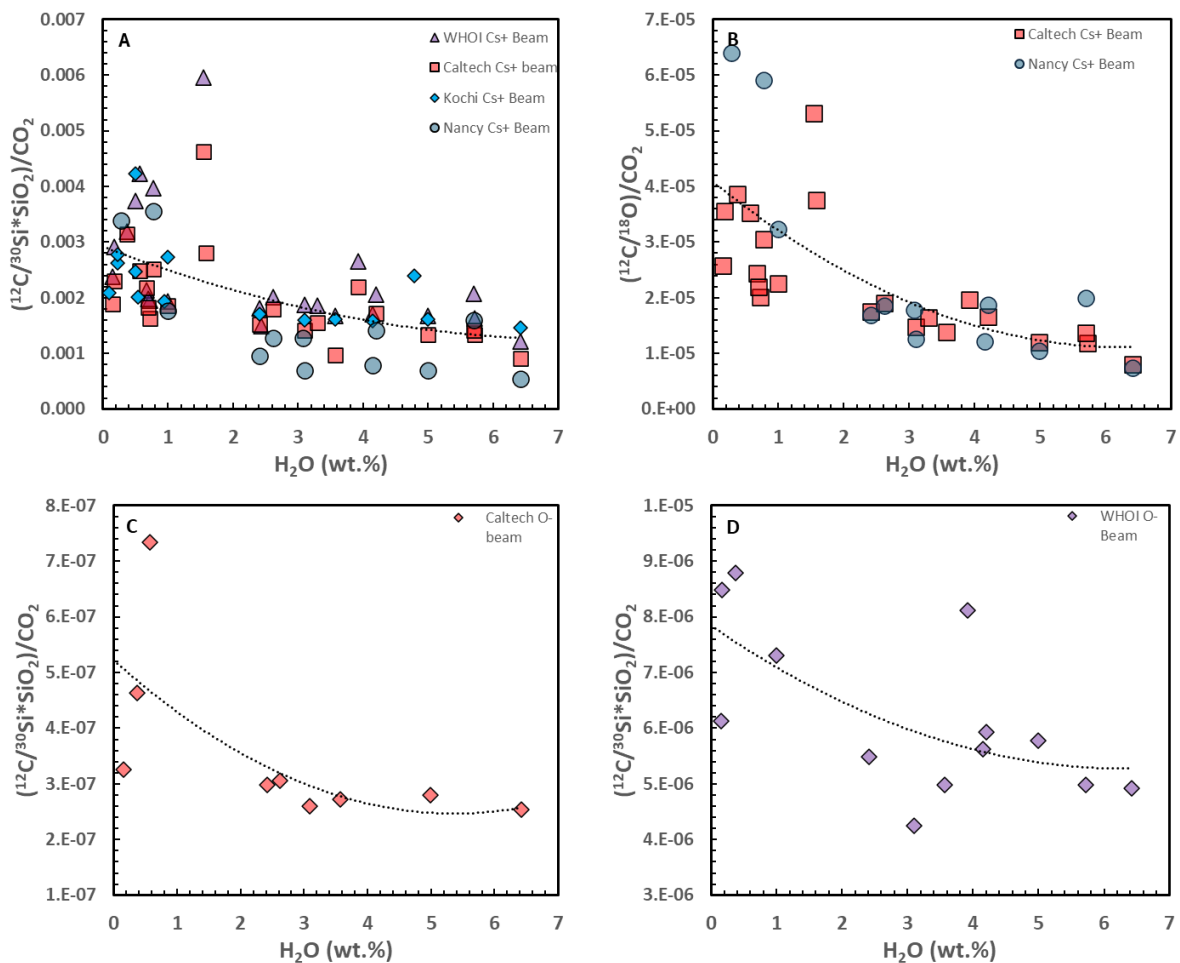
550

551 **Figure 8** shows the ionization efficiency ratios, (¹²C/³⁰Si)×SiO₂/CO₂ and (¹²C/¹⁸O)/CO₂, as a
552 function of the water content in all the glasses analysed during all SIMS sessions (note, we
553 have not plotted glasses with CO₂ content near 0). If water had no effect on the ¹²C ion probe
554 signal, both ratios should remain constant as a function of water content. What we observe,
555 however, is that these ratios vary greatly. At low water contents (<2 wt.%), the ratios are
556 quite variable; in the Caltech and WHOI SIMS sessions, there is a hint of a possible positive
557 correlation between C ionization efficiency and the glass water content, peaking at ~1.5 wt.%
558 H₂O. At higher water contents (>2 wt.%), the C ionization efficiency seems to become more
559 stable, at least in the explored range (2.5 to 6 wt.% H₂O), although there is still a hint of an
560 inverse correlation between water content and C ionization efficiency (**Fig. 8A and B**). The
561 fact that the C ionization efficiency is so variable between SIMS sessions suggests that the
562 magnitude of the effect may be related to beam conditions.

563

564 Although Hervig et al. (2009) reported that using an O⁻ primary beam significantly mitigates
565 the influence of H₂O on the carbon ion yield, we found that O⁻ primary beam analyses also
566 suffered from the same effect (**Fig. 8 C and D**; note that the magnitude of the effect, although
567 based on a smaller number of analyses, may potentially be less), The consequences of this C
568 ionization efficiency reduction for SIMS carbon analyses are potentially dire. For example, if
569 one were to analyse carbon in a natural basaltic glass containing 4 wt.% water using a Cs⁺
570 primary beam and glass standards with less than 2 wt.% water, the unknown CO₂ mass

571 fractions could be underestimated by two to three-fold. The corollary is also true, using
 572 standards with high water contents to measure CO₂ mass fractions in samples with low water
 573 contents will result in large overestimations. It is likely that these effects permeate the
 574 literature of published glass and melt inclusion CO₂ concentration data. Thus, to accurately
 575 measure CO₂ by SIMS, one needs to select reference materials with water mass fractions
 576 matching that of the unknown sample or to characterise the signal dependency on water
 577 concentration as in **Fig. 8**.
 578



579

580 **Figure 8:** Effect of water on the $((^{12}\text{C}/^{30}\text{Si})\times\text{SiO}_2)/\text{CO}_2$ and $(^{12}\text{C}/^{18}\text{O})/\text{CO}_2$ ratios measured by
 581 SIMS (i.e., the calibration line). The results of four SIMS sessions using a Cs⁺ primary beam
 582 and two SIMS sessions using a O⁻ primary beam are reported. In all cases the glass water
 583 content seems to greatly reduce the ionization efficiency of ¹²C. Data used to generate the
 584 figure are reported in **Table S9**. Dotted lines are 2nd order polynomial best fit to all data.
 585

586

587 **c) Recommended values for ND70 glasses**

588 The compositions of the new reference materials we see as the most accurate, and which we
589 encourage researchers to use in future studies are reported in **Table 6**. For H₂O, since all
590 techniques agree within 13% (**Fig. 6**), we used the unweighted arithmetic mean values from
591 ERDA, FTIR, the three Cs⁺ primary beam SIMS sessions at Caltech, WHOI and Nancy, the
592 O⁻ primary beam session at WHOI and the Cs⁺ primary beam SIMS session at Kochi
593 (excluding samples ND70-5-02 and ND70-6-02 which were outside calibration range for the
594 Kochi session). We report the uncertainty as the standard deviation from these means. For
595 CO₂, given the strong effect of water on suppressing C ionization efficiency (see previous
596 section), we used the unweighted arithmetic mean of the NRA, EA and FTIR analyses and,
597 for the low C (<5000 ppm) samples, we also included the EMP analyses. We report the
598 uncertainty as the standard deviation from these means. For ND70_Natural we report the
599 unweighted arithmetic mean of all SIMS and FTIR sessions along with the associated
600 standard deviation. For S, since all techniques agreed reasonably well, we used the
601 unweighted arithmetic mean values from EMPA and the four Cs⁺ primary beam SIMS
602 sessions (Caltech, WHOI, Kochi and Nancy) and report the uncertainty as the standard
603 deviation from these means. For Cl, we used the unweighted arithmetic mean values from
604 EMPA and three Cs⁺ primary beam SIMS sessions at WHOI, Nancy and Kochi (but
605 excluding samples ND70-5-02 and ND70-6-02 from the WHOI session which deviated
606 significantly from all other estimates) and report the uncertainty as the standard deviation
607 from these means. For F, we used the mean values from three Cs⁺ primary beam SIMS
608 sessions at WHOI, Nancy and Kochi (excluding samples ND70-5-02 and ND70-6-02 from
609 the Kochi session which deviated significantly from all other estimates) and report the
610 uncertainty as the standard deviation from these means.

611

612 **d) ND70 glasses, use and availability.**

613 The ND70 reference materials are now readily accessible to users at various Ion Microprobe
614 facilities, including those in France (CNRS-CRGP-Nancy and INSU-CNRS-IMPMC-Paris),
615 the United Kingdom (NERC-Edinburgh), Switzerland (SNF-Lausanne), the United States
616 (WHOI and Caltech), and Japan (JAMSTEC-Kochi). Furthermore, these resources are
617 available for researchers to borrow from the Smithsonian National Museum of Natural
618 History. Catalogue numbers for these materials are given in Table 6. We encourage
619 researchers to use at least a subset of these glasses (depending on the range of interest) to
620 improve the inter-comparability of future studies presenting microbeam analyses of H₂O,

621 CO₂, S, Cl and F in basaltic glasses. In particular, we expect the high volatile glasses to fill a
622 gap in the standards currently available at most ion microprobe facilities.

623

624 VI. CONCLUSION

625

626 We present a new set of reference materials designed for *in situ* analysis of volatile elements
627 (H₂O, CO₂, S, Cl, F) in basaltic silicate glass. The starting material was fused in air and 150
628 to 200mg splits with variable amounts of volatiles were subsequently run in the piston
629 cylinder. The resulting reference glasses (the ND-70 series) span a wide range of mass
630 fractions from 0 to 6 wt.% H₂O, 0 to 1.6 wt.% CO₂, and 0 to 1 wt.% S, Cl and F. The samples
631 were characterized by Elastic Recoil Detection Analysis, Nuclear Reaction Analysis,
632 Elemental Analyser, Fourier Transform Infrared Spectroscopy, Secondary Ion Mass
633 Spectrometry, and Electron Microprobe.

634

635 Most analytical techniques provided good agreement with the expected volatile mass
636 fractions in each of the glasses; agreement between techniques and between different ion
637 probes is also generally good. CO₂ measurements are the exception and deviated significantly
638 from expected values across analytical methods; however, inter-method reproducibility was
639 good except for SIMS measurements. We found that this discrepancy in the SIMS results was
640 likely due to the samples' high-water contents, which have a substantial impact on the
641 ionization efficiency of ¹²C during SIMS analyses. This underscores the importance of
642 carefully selecting reference materials with water mass fractions matching those of unknown
643 samples or characterizing the signal dependency on water content to ensure accurate CO₂
644 measurements by SIMS.

645

646 The reference materials we have presented in this study offer a community resource for the
647 analysis of volatile elements in basaltic silicate glass, particularly when using SIMS and other
648 micro-beam techniques. These materials are available to users at the Ion Microprobe facilities
649 in France (CNRS-CRGP-Nancy and INSU-CNRS-IMPIC-Paris), the United Kingdom
650 (NERC-Edinburgh), Switzerland (SNF-Lausanne), the United States (WHOI and Caltech)
651 and Japan (JAMSTEC-Kochi). They are also freely available to researchers on a loan basis
652 from the Smithsonian National Museum of Natural History (Catalogue numbers given in

653 Table 6). We encourage researchers to utilize them to improve the accuracy and inter-
654 laboratory comparability of their measurements.

655 **DATA AVAILABILITY STATEMENT**

656 Raw FTIR spectra are archived as Moussallam (2024a). Raw NRA spectra are archived as
657 Moussallam (2024b).

658 **ACKNOWLEDGEMENTS**

659 We thank Nordine Bouden and Johan Villeneuve for their invaluable support during the ion
660 probe analyses at CNRS-CRPG-Nancy. We are very grateful to Richard Hervig and an
661 anonymous reviewer for their comments which greatly improved the manuscript and to
662 Thomas Meisel for editorial handling.

663 **AUTHOR CONTRIBUTIONS**

664 Initial study design: W.H.T., Y.M., T.P.

665 Experiments: W.H.T., Y.M., S.D.

666 ERDA: H.B., H.K.

667 NRA: H.B., H.K.

668 EA: H.L.

669 FTIR: S.D., H.L., S.S.

670 SIMS (Nancy): Y.M., E.R.K.

671 SIMS (WHOI): B.M., G.G.,

672 SIMS (Caltech): T.P., Y.G.

673 SIMS (Kochi): K.S., T.U.

674 EMPA (Caltech): E.M.S., M.B., C.M.

675 EMPA (AMNH): Y.M., S.D., W.H.T.

676 Visualisation and data compilation: Y.M.

677 Writing and interpretation: All authors, first draft Y.M.

678

679

680 **REFERENCES**

681 Albarède, F. (2009). Volatile accretion history of the terrestrial planets and dynamic
682 implications. *Nature*, 461(7268), 1227–1233. <https://doi.org/10.1038/nature08477>

- 683 Allard, P. (2010). A CO₂-rich gas trigger of explosive paroxysms at Stromboli basaltic
684 volcano, Italy. *Journal of Volcanology and Geothermal Research*, 189(3–4), 363–374.
685 <https://doi.org/10.1016/j.jvolgeores.2009.11.018>
- 686 Allison, C. M., Roggensack, K., & Clarke, A. B. (2019). H₂O–CO₂ solubility in alkali-rich
687 mafic magmas: new experiments at mid-crustal pressures. *Contributions to*
688 *Mineralogy and Petrology*, 174(7), 58. <https://doi.org/10.1007/s00410-019-1592-4>
- 689 Armstrong, J. (1995). CITZAF: a package of correction programs for the quantitative
690 electron microbeam X-ray-analysis of thick polished materials, thin films, and
691 particles. *Microbeam Analysis*, 4, 177.
- 692 Armstrong, J., & Crispin, K. (2013). Ultra-thin Iridium as a Replacement Coating for Carbon
693 in High Resolution Quantitative Analyses of Insulating Specimens. *Microscopy and*
694 *Microanalysis*, 19(S2), 1070–1071. <https://doi.org/10.1017/S1431927613007344>
- 695 Befus, K. S., Walowski, K. J., Hervig, R. L., & Cullen, J. T. (2020). Hydrogen Isotope
696 Composition of a Large Silicic Magma Reservoir Preserved in Quartz-Hosted Glass
697 Inclusions of the Bishop Tuff Plinian Eruption. *Geochemistry, Geophysics,*
698 *Geosystems*, 21(12), e2020GC009358. <https://doi.org/10.1029/2020GC009358>
- 699 Blank, Jennifer G., & Brooker, R. A. (1994). Experimental studies of carbon dioxide in
700 silicate melts; solubility, speciation, and stable carbon isotope behavior. *Reviews in*
701 *Mineralogy and Geochemistry*, 30(1), 157–186.
- 702 Blank, Jennifer Glee. (1993). *An experimental investigation of the behavior of carbon dioxide*
703 *in rhyolitic melt* (phd). California Institute of Technology.
704 <https://doi.org/10.7907/tq3x-2059>
- 705 Brooker, R., Holloway, J. R., & Hervig, R. (1998). Reduction in piston-cylinder experiments;
706 the detection of carbon infiltration into platinum capsules. *American Mineralogist*,
707 83(9–10), 985–994. <https://doi.org/10.2138/am-1998-9-1006>
- 708 Bureau, H., Raepsaet, C., Khodja, H., Carraro, A., & Aubaud, C. (2009). Determination of
709 hydrogen content in geological samples using elastic recoil detection analysis
710 (ERDA). *Geochimica et Cosmochimica Acta*, 73(11), 3311–3322.
711 <https://doi.org/10.1016/j.gca.2009.03.009>
- 712 Caulfield, J., Turner, S., Arculus, R., Dale, C., Jenner, F., Pearce, J., et al. (2012). Mantle
713 flow, volatiles, slab-surface temperatures and melting dynamics in the north Tonga
714 arc–Lau back-arc basin. *Journal of Geophysical Research: Solid Earth*, 117(B11).
715 <https://doi.org/10.1029/2012JB009526>

- 716 Clesi, V., Bouhifd, M. A., Bolfan-Casanova, N., Manthilake, G., Schiavi, F., Raepsaet, C., et
717 al. (2018). Low hydrogen contents in the cores of terrestrial planets. *Science*
718 *Advances*, 4(3), e1701876. <https://doi.org/10.1126/sciadv.1701876>
- 719 Dasgupta, R., & Hirschmann, M. M. (2006). Melting in the Earth's deep upper mantle caused
720 by carbon dioxide. *Nature*, 440(7084), 659–662. <https://doi.org/10.1038/nature04612>
- 721 Dehant, V., Debaille, V., Dobos, V., Gaillard, F., Gillmann, C., Goderis, S., et al. (2019).
722 Geoscience for Understanding Habitability in the Solar System and Beyond. *Space*
723 *Science Reviews*, 215(6), 42. <https://doi.org/10.1007/s11214-019-0608-8>
- 724 Dixon, J. E., Stolper, E., & Delaney, J. R. (1988). Infrared spectroscopic measurements of
725 CO₂ and H₂O in Juan de Fuca Ridge basaltic glasses. *Earth and Planetary Science*
726 *Letters*, 90(1), 87–104. [https://doi.org/10.1016/0012-821X\(88\)90114-8](https://doi.org/10.1016/0012-821X(88)90114-8)
- 727 Edmonds, M., & Woods, A. W. (2018). Exsolved volatiles in magma reservoirs. *Journal of*
728 *Volcanology and Geothermal Research*, 368, 13–30.
729 <https://doi.org/10.1016/j.jvolgeores.2018.10.018>
- 730 Eggler, D. H. (1976). Does CO₂ cause partial melting in the low-velocity layer of the mantle?
731 *Geology*, 4(2), 69–72. [https://doi.org/10.1130/0091-](https://doi.org/10.1130/0091-7613(1976)4<69:DCCPMI>2.0.CO;2)
732 [7613\(1976\)4<69:DCCPMI>2.0.CO;2](https://doi.org/10.1130/0091-7613(1976)4<69:DCCPMI>2.0.CO;2)
- 733 Ehlmann, B. L., Anderson, F. S., Andrews-Hanna, J., Catling, D. C., Christensen, P. R.,
734 Cohen, B. A., et al. (2016). The sustainability of habitability on terrestrial planets:
735 Insights, questions, and needed measurements from Mars for understanding the
736 evolution of Earth-like worlds. *Journal of Geophysical Research: Planets*, 121(10),
737 1927–1961. <https://doi.org/10.1002/2016JE005134>
- 738 Elskens, I., Tazieff, H., & Tonani, F. (1968). Investigations Nouvelles sur les Gaz
739 Volcaniques. *Bulletin Volcanologique*, 32(3), 521–574.
740 <https://doi.org/10.1007/BF02599800>
- 741 Foley, B. J., & Smye, A. J. (2018). Carbon Cycling and Habitability of Earth-Sized Stagnant
742 Lid Planets. *Astrobiology*, 18(7), 873–896. <https://doi.org/10.1089/ast.2017.1695>
- 743 Hammerli, J., Hermann, J., Tollan, P., & Naab, F. (2021). Measuring in situ CO₂ and H₂O in
744 apatite via ATR-FTIR. *Contributions to Mineralogy and Petrology*, 176(12), 105.
745 <https://doi.org/10.1007/s00410-021-01858-6>
- 746 Hauri, E., Wang, J., Dixon, J. E., King, P. L., Mandeville, C., & Newman, S. (2002). SIMS
747 analysis of volatiles in silicate glasses: 1. Calibration, matrix effects and comparisons
748 with FTIR. *Chemical Geology*, 183(1–4), 99–114. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2541(01)00375-8)
749 [2541\(01\)00375-8](https://doi.org/10.1016/S0009-2541(01)00375-8)

- 750 Hervig, R. L., Moore, G. M., & Roggensack, K. (2009). Calibrating Carbon Measurements in
751 Basaltic Glass Using SIMS and FTIR: The Effect of Variable H₂O Contents, 2009,
752 V51E-1755. Presented at the AGU Fall Meeting Abstracts.
- 753 Iacono-Marziano, G., Morizet, Y., Le Trong, E., & Gaillard, F. (2012). New experimental
754 data and semi-empirical parameterization of H₂O–CO₂ solubility in mafic melts.
755 *Geochimica et Cosmochimica Acta*, 97, 1–23.
756 <https://doi.org/10.1016/j.gca.2012.08.035>
- 757 Jarosewich, E., Nelen, J. a., & Norberg, J. A. (1980). Reference Samples for Electron
758 Microprobe Analysis*. *Geostandards Newsletter*, 4(1), 43–47.
759 <https://doi.org/10.1111/j.1751-908X.1980.tb00273.x>
- 760 Jochum, K. P., Stoll, B., Herwig, K., Willbold, M., Hofmann, A. W., Amini, M., et al.
761 (2006). MPI-DING reference glasses for in situ microanalysis: New reference values
762 for element concentrations and isotope ratios. *Geochemistry, Geophysics, Geosystems*,
763 7(2). <https://doi.org/10.1029/2005GC001060>
- 764 Joesten, R. L. (1974). *Metasomatism and magmatic assimilation at a gabbro-limestone*
765 *contact, Christmas Mountains, Big Bend region, Texas* (phd). California Institute of
766 Technology. Retrieved from [https://resolver.caltech.edu/CaltechTHESIS:02272014-](https://resolver.caltech.edu/CaltechTHESIS:02272014-085454874)
767 [085454874](https://resolver.caltech.edu/CaltechTHESIS:02272014-085454874)
- 768 Kamenetsky, V. S., Everard, J. L., Crawford, A. J., Varne, R., Eggins, S. M., & Lanyon, R.
769 (2000). Enriched End-member of Primitive MORB Melts: Petrology and
770 Geochemistry of Glasses from Macquarie Island (SW Pacific). *Journal of Petrology*,
771 41(3), 411–430. <https://doi.org/10.1093/petrology/41.3.411>
- 772 Keller, N. S., Arculus, R. J., Hermann, J., & Richards, S. (2008). Submarine back-arc lava
773 with arc signature: Fonualei Spreading Center, northeast Lau Basin, Tonga. *Journal of*
774 *Geophysical Research: Solid Earth*, 113(B8). <https://doi.org/10.1029/2007JB005451>
- 775 Khodja, H., Berthoumieux, E., Daudin, L., & Gallien, J.-P. (2001). The Pierre Süe Laboratory
776 nuclear microprobe as a multi-disciplinary analysis tool. *Nuclear Instruments and*
777 *Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*,
778 181(1), 83–86. [https://doi.org/10.1016/S0168-583X\(01\)00564-X](https://doi.org/10.1016/S0168-583X(01)00564-X)
- 779 Krzhizhanovskaya, M. G., Chukanov, N. V., Mazur, A. S., Pautov, L. A., Varlamov, D. A., &
780 Bocharov, V. N. (2023). Crystal chemistry and thermal behavior of B-, S- and Na-
781 bearing spurrite. *Physics and Chemistry of Minerals*, 50(4), 33.
782 <https://doi.org/10.1007/s00269-023-01257-2>

- 783 Lesne, P., Scaillet, B., Pichavant, M., & Beny, J.-M. (2011). The carbon dioxide solubility in
784 alkali basalts: an experimental study. *Contributions to Mineralogy and Petrology*,
785 *162*(1), 153–168. <https://doi.org/10.1007/s00410-010-0585-0>
- 786 Lloyd, A. S., Plank, T., Ruprecht, P., Hauri, E. H., & Rose, W. (2013). Volatile loss from
787 melt inclusions in pyroclasts of differing sizes. *Contributions to Mineralogy and*
788 *Petrology*, *165*(1), 129–153. <https://doi.org/10.1007/s00410-012-0800-2>
- 789 Malavergne, V., Bureau, H., Raepsaet, C., Gaillard, F., Poncet, M., Surblé, S., et al. (2019).
790 Experimental constraints on the fate of H and C during planetary core-mantle
791 differentiation. Implications for the Earth. *Icarus*, *321*, 473–485.
792 <https://doi.org/10.1016/j.icarus.2018.11.027>
- 793 Mayer, M. (1999). SIMNRA, a simulation program for the analysis of NRA, RBS and
794 ERDA. *AIP Conference Proceedings*, *475*(1), 541–544.
795 <https://doi.org/10.1063/1.59188>
- 796 Métrich, N., & Wallace, P. J. (2008). Volatile Abundances in Basaltic Magmas and Their
797 Degassing Paths Tracked by Melt Inclusions. *Reviews in Mineralogy and*
798 *Geochemistry*, *69*(1), 363–402. <https://doi.org/10.2138/rmg.2008.69.10>
- 799 Mosbah, M., Métrich, N., & Massiot, P. (1991). PIGME fluorine determination using a
800 nuclear microprobe with application to glass inclusions. *Nuclear Instruments and*
801 *Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*,
802 *58*(2), 227–231. [https://doi.org/10.1016/0168-583X\(91\)95592-2](https://doi.org/10.1016/0168-583X(91)95592-2)
- 803 Moussallam, Y. (2024a). ND70 paper_Raw FTIR spectra [Data set]. figshare.
804 <https://doi.org/10.6084/m9.figshare.25292692.v1>
- 805 Moussallam, Y. (2024b). ND70 paper_Raw NRA Spectra [Data set]. figshare.
806 <https://doi.org/10.6084/m9.figshare.25292674.v1>
- 807 Moussallam, Y., Morizet, Y., Massuyeau, M., Laumonier, M., & Gaillard, F. (2015). CO₂
808 solubility in kimberlite melts. *Chemical Geology*, *418*, 198–205.
809 <https://doi.org/10.1016/j.chemgeo.2014.11.017>
- 810 Moussallam, Y., Oppenheimer, C., Scaillet, B., Buisman, I., Kimball, C., Dunbar, N., et al.
811 (2015). Megacrystals track magma convection between reservoir and surface. *Earth*
812 *and Planetary Science Letters*, *413*, 1–12. <https://doi.org/10.1016/j.epsl.2014.12.022>
- 813 Moussallam, Y., Morizet, Y., & Gaillard, F. (2016). H₂O–CO₂ solubility in low SiO₂-melts
814 and the unique mode of kimberlite degassing and emplacement. *Earth and Planetary*
815 *Science Letters*, *447*, 151–160. <https://doi.org/10.1016/j.epsl.2016.04.037>

- 816 Moussallam, Y., Lee, H. J., Ding, S., DeLessio, M., Everard, J. L., Spittle, E., et al. (2023).
817 Temperature of the Villarrica Lava Lake from 1963 to 2015 Constrained by Phase-
818 Equilibrium and a New Glass Geothermometer for Basaltic Andesites. *Journal of*
819 *Petrology*, 64(2). <https://doi.org/10.1093/petrology/egad003>
- 820 Nicoli, G., & Ferrero, S. (2021). Nanorocks, volatiles and plate tectonics. *Geoscience*
821 *Frontiers*, 12(5), 101188. <https://doi.org/10.1016/j.gsf.2021.101188>
- 822 Shi, S. C., Towbin, W. H., Plank, T., Barth, A., Rasmussen, D., Moussallam, Y., et al.
823 (2023). PyIRoGlass: An Open-Source, Bayesian MCMC Algorithm for Fitting
824 Baselines to FTIR Spectra of Basaltic-Andesitic Glasses. Retrieved from
825 <https://eartharxiv.org/repository/view/6193/>
- 826 Shimizu, Kei, Saal, A. E., Hauri, E. H., Perfit, M. R., & Hékinian, R. (2019). Evaluating the
827 roles of melt-rock interaction and partial degassing on the CO₂/Ba ratios of MORB:
828 Implications for the CO₂ budget in the Earth's depleted upper mantle. *Geochimica et*
829 *Cosmochimica Acta*, 260, 29–48. <https://doi.org/10.1016/j.gca.2019.06.013>
- 830 Shimizu, Kenji, Suzuki, K., Saitoh, M., Konno, U., Kawagucci, S., & Ueno, Y. (2015).
831 Simultaneous determinations of fluorine, chlorine, and sulfur in rock samples by ion
832 chromatography combined with pyrohydrolysis. *Geochemical Journal*, 49(1), 113–
833 124. <https://doi.org/10.2343/geochemj.2.0338>
- 834 Shimizu, Kenji, Ushikubo, T., Hamada, M., Itoh, S., Higashi, Y., Takahashi, E., & Ito, M.
835 (2017). H₂O, CO₂, F, S, Cl, and P₂O₅ analyses of silicate glasses using SIMS: Report
836 of volatile standard glasses. *Geochemical Journal*, 51(4), 299–313.
837 <https://doi.org/10.2343/geochemj.2.0470>
- 838 Shishkina, T. A., Botcharnikov, R. E., Holtz, F., Almeev, R. R., & Portnyagin, M. V. (2010).
839 Solubility of H₂O- and CO₂-bearing fluids in tholeiitic basalts at pressures up to
840 500 MPa. *Chemical Geology*, 277(1–2), 115–125.
841 <https://doi.org/10.1016/j.chemgeo.2010.07.014>
- 842 Stern, R. J. (2018). The evolution of plate tectonics. *Philosophical Transactions of the Royal*
843 *Society A: Mathematical, Physical and Engineering Sciences*, 376(2132), 20170406.
844 <https://doi.org/10.1098/rsta.2017.0406>
- 845 Stolper, E., & Holloway, J. R. (1988). Experimental determination of the solubility of carbon
846 dioxide in molten basalt at low pressure. *Earth and Planetary Science Letters*, 87(4),
847 397–408. [https://doi.org/10.1016/0012-821X\(88\)90004-0](https://doi.org/10.1016/0012-821X(88)90004-0)

- 848 Tamic, N., Behrens, H., & Holtz, F. (2001). The solubility of H₂O and CO₂ in rhyolitic melts
849 in equilibrium with a mixed CO₂-H₂O fluid phase. *Chemical Geology*, 174(1–3),
850 333–347. [https://doi.org/10.1016/S0009-2541\(00\)00324-7](https://doi.org/10.1016/S0009-2541(00)00324-7)
- 851 Webster, J. D., Goldoff, B., & Shimizu, N. (2011). C–O–H–S fluids and granitic magma:
852 how S partitions and modifies CO₂ concentrations of fluid-saturated felsic melt at
853 200 MPa. *Contributions to Mineralogy and Petrology*, 162(4), 849–865.
854 <https://doi.org/10.1007/s00410-011-0628-1>
- 855 Wyllie, P. J. (1971). Role of water in magma generation and initiation of diapiric uprise in the
856 mantle. *Journal of Geophysical Research (1896-1977)*, 76(5), 1328–1338.
857 <https://doi.org/10.1029/JB076i005p01328>
858

859 **TABLES**

860

861 **Table 1.** Expected chemical composition (in wt.% unless otherwise indicated) of all
862 experiments based on loaded amounts of starting material.

Sample Name	Si O ₂	Ti O ₂	Al ₂ O ₃	Fe O _{to} t	M nO	M gO	Ca O	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	CO ₂ (ppm)	S (ppm)	Cl (ppm)	F (ppm)	Total
ND 70_ Degassed	50.18	0.85	16.54	8.18	0.17	8.44	13.18	2.21	0.17	0.09	0.00	0	0	0	0	100
ND70-2-01	48.74	0.82	16.06	7.95	0.17	8.28	13.01	2.20	0.17	0.08	0.25	665	672	679	717	100
ND70-3-01	48.15	0.81	15.87	7.85	0.16	8.21	12.95	2.21	0.16	0.08	0.13	989	100	1011	106	100
ND70-4-01	47.26	0.80	15.58	7.71	0.16	8.18	13.01	2.26	0.16	0.08	0.99	1970	199	2013	212	100
ND70-4-02	47.15	0.80	15.54	7.69	0.16	8.16	12.98	2.25	0.16	0.08	0.22	1965	198	2008	212	100
ND70-5-02	47.27	0.71	13.88	6.87	0.14	7.67	13.27	2.33	0.14	0.07	0.01	10349	507	5468	549	100
ND70-5-03	48.17	0.81	15.88	7.85	0.16	8.13	12.71	2.14	0.16	0.08	0.82	197	200	202	213	100
ND70-6-02	44.29	0.67	13.01	6.43	0.13	7.71	14.06	2.64	0.13	0.07	0.28	15023	101	1036	101	100

863

864 **Table 2.** Experimental conditions.

Experiment # Pressure (MPa) Temperature (°C) Duration (h)

ND 70_ Degassed	0.1	1350	4
ND70-2-01	1000	1325	2
ND70-3-01	1000	1325	2
ND70-4-01	1000	1225	2
ND70-4-02	1000	1325	2
ND70-5-02	1500	1325	2
ND70-5-03	1500	1325	2
ND70-6-02	1500	1325	2

865

866

867 **Table 3.** Measured major and volatile composition by electron microprobe (in wt.% unless
 868 otherwise indicated) of experimental glasses and other glasses analysed during the same
 869 analytical sessions. n denotes the number of analyses from which averages are reported.
 870 Errors (two standard deviation) are ± 0.43 for SiO₂, ± 0.18 for Na₂O, ± 0.02 for K₂O, ± 0.17 for
 871 Al₂O₃, ± 0.36 for CaO, ± 0.24 for FeO, ± 0.11 for MgO, ± 0.04 for TiO₂, ± 0.05 for MnO, ± 0.04
 872 for P₂O₅, ± 0.01 for S and ± 0.03 for Cl.

Experiment #	EMPA (AMNH)											
	n	SiO ₂	TiO ₂	Al ₂ O ₃	FeO _{tot}	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S (ppm)
ND 70_ Degassed	5	49.68	0.80	16.12	8.27	0.14	8.71	13.01	2.22	0.16	0.09	15
ND70-2-01	10	47.81	0.76	15.58	8.00	0.15	8.51	12.66	2.17	0.17	0.08	621
ND70-3-01	10	47.18	0.77	15.21	8.04	0.15	8.61	12.76	2.09	0.16	0.08	814
ND70-4-01	10	47.37	0.75	15.13	7.60	0.16	8.23	12.30	2.19	0.16	0.07	1831
ND70-4-02	10	44.27	0.73	14.54	7.59	0.14	8.23	12.60	2.21	0.16	0.09	1796
ND70-5-02	10	46.12	0.65	13.21	6.83	0.12	7.89	13.15	2.34	0.15	0.07	5045
ND70-6-02	12	44.01	0.64	12.62	6.19	0.11	8.22	13.16	2.12	0.18	0.08	8786
Other glasses analysed												
ND-70 (Natural)	3	49.92	0.81	16.11	8.17	0.15	8.27	12.95	2.10	0.16	0.09	871
VILLA_P2	12	50.60	1.29	15.42	9.15	0.16	5.41	8.55	3.10	0.75	0.28	3529
INSOL_MX1_BA4	1	52.36	1.62	12.87	8.12	0.11	9.55	10.53	2.66	1.41	0.23	18

873

874

875

876 **Table 4.** ERDA, NRA, EA and FTIR measurements (in wt.% for H₂O and in ppm for all
 877 other species) of experimental glasses and other glasses analysed during the same analytical
 878 sessions. All errors are given as one standard deviation on repeat analyses or as one standard
 879 deviation from analytical error (whichever is the highest), n denotes the number of analyses
 880 from which averages are reported.

Experiment #	ERDA (CEA-CNRS-Saclay)			NRA (CEA-CNRS-Saclay)			EA (LDEO)			FTIR (LDEO)					EMPA (Caltech)		
	n	H ₂ O	±	n	CO ₂	±	n	CO ₂	±	n	H ₂ O	±	CO ₂	±	n	CO ₂ (ppm)	±
ND 70_ Degassed																	
ND70-2-01	2	2.53	0.24	1	1837	35				6	2.	0.	128	12			
ND70-3-01	2	3.13	0.30	1	2689	54				6	12	34	3	0	5	2997	36
ND70-4-01	1	4.25	0.40	1	4228	71				7	3.	0.	222	40			
ND70-4-02	2	3.68	0.35	1	4122	65				7	43	97	6	3			
ND70-5-02	2	5.34	0.51	1	12682	105	1	121	89	8	3.	0.	409	62			
ND70-5-03	1	3.68	0.35				1	60	1	8	86	89	5	1	5	4306	79
ND70-6-02	2	6.26	0.59	1	16847	120	1	149	10						5	11125	18
Other glasses analysed ND-70 (Natural)							1	40	95	6	5.	0.	118	12	5	13397	31
Suprasil	2	0.02	0.00							3	85	96	54	35			
BF73	2	0.73	0.07	1	2832	56				3	0.	0.					
BF76										3	66	15	59	23			
BF77										3	0.	0.	304		5	6579	35
M15										3	82	06	2	84			
M19										3	0.	0.	231		5	3560	26
M20	1	5.82	0.55	1	2417	51				3	75	06	9	68			
M34										3	0.	0.			5	2506	14
M35	1	4.31	0.41	1	1436	40				3	86	08	891	47			
M40																	
M43																	
M48																	
KL2																	
KE12																	
40428																	
47963																	
N72																	
ALV519-4-1																	
ALV1846-12																	
80-1-3																	
ALV1846-9										3	4.	0.	100		5	3119	34
										3	1.	0.	18	8			

				43	12				
NS-1				0.	0.	354	12		
				3	35	03	6	9	5
				3.	0.				4708
Villa_P2				6	92	7	835	74	
INSOL_MX1_B					0.	0.	820	37	
A4				3	15	01	7	7	
VG2									10
									60

881

882

883

884

885

886 **Table 5.** SIMS measurements (in wt.% for H₂O and in ppm for all other species) of
 887 experimental glasses and other glasses analysed during the same analytical sessions. Errors
 888 are calculated using two standard error (i.e., 95% confidence interval) on calibration lines for
 889 each session, n denotes the number of analyses from which averages are reported. Values in
 890 red were determined outside calibration range.

		SIMS (CNRS-Nancy, Cs+beam)									
Experiment #	n	H ₂		CO ₂	±	S	±	Cl	±	F	±
		O	±								
ND 70_ Degassed	2	3	0	66	6	17	1	4	0	13	1
		2.2	0.0	114							
ND70-2-01	3	1	6	1	101	649	42	876	110	572	40
		2.7	0.0	139							
ND70-3-01	2	0	7	7	124	862	56	983	124	745	52
		3.7	0.1	251		220		240		189	
ND70-4-01	2	9	0	9	224	7	142	1	302	6	133
		4.5	0.1	656		621		677		553	
ND70-5-02	2	7	2	6	583	1	400	7	852	8	388
		3.3	0.0	109							
ND70-5-03	2	7	9	8	98	175	11	326	41	228	16
		6.3	0.1	648		112		124	155	972	
ND70-6-02	2	7	7	2	576	14	722	05	9	5	681
Other glasses analysed											
ND-70 (Natural)	1	1.0	0.0	195	17	916	59	194	24	98	7
		4	3								
M34	3	5.5	0.1	458	41	11	1	36	4	79	6
		9	5								
M35	1	4.1	0.1	1100	98	11	1	33	4	75	5
		0	1								
M40	1	3.3	0.0	2118	188	12	1	33	4	73	5
		0	1								
M43	1	2.7	0.0	3071	273	5	0	29	4	68	5
		0	7								
M48	1	0.8	0.0	477	42	3	0	28	4	64	4
		0	2								
KL2	1	0.0	0.0	157	14	6	0	14	2	58	4
		0	1								
KE12	1	0.1	0.0	116	10	264	17	3419	430	4251	298
		0	6								
40428	9	0.8	0.0	256	23	889	57	349	44	413	29
		8	2								
47963	1	1.2	0.0	229	20	646	42	902	113	638	45
		0	3								
N72	5	0.0	0.0	186	17	4	0	28	4	77	5
		2	0								
VG2	1	0.3	0.0	396	35	1450	93	233	29	160	11
		0	4								
		SIMS (WHOI, Cs+beam)									
Experiment #	n	H ₂		CO ₂	±	S	±	Cl	±	F	±
		O	±								

ND70-2-01	3	2.3 1	0.1 0	120 4	92	476	57	518	14	550	47
ND70-3-01	2	2.5 9	0.1 2	210 6	160	582	70	708	20	683	58
ND70-4-01	3	4.1 6	0.1 9	303 7	231	155 3	187	212 5	59	180 8	155
ND70-4-02	3	3.6 9	0.1 7	302 6	231	150 5	181	181 1	50	166 5	142
ND70-5-02	3	5.3 1	0.2 4	877 0	668	471 4	567	635 7	177	569 4	487
ND70-5-03	3	3.8 5	0.1 7	141 2	108	128	15	300	8	217	19
ND70-6-02	3	7.1 1	0.3 2	821 6	626	852 5	102 6	117 13	326	101 77	870
Other glasses analysed											
ND-70 (Natural)	3	1.0 2	0.0 5	120	9	625	75	160	4	86	7
Suprasil	3	0.0 1	0.0 0	25	2	0	0	191 2	53	3	0
BF73	2	0.8 7	0.0 4	250 2	191	0	0	36	1	36	3
BF76	2	0.8 2	0.0 4	213 4	163	0	0	34	1	27	2
BF77	3	0.8 2	0.0 4	791	60	0	0	34	1	27	2
M15	3	1.6 4	0.0 7	152	12	1	0	21	1	53	5
M19	3	3.0 6	0.1 4	260 8	199	3	0	21	1	54	5
M20	3	5.7 6	0.2 6	1689	129	8	1	25	1	62	5
M34	3	5.5 2	0.2 5	332	25	6	1	24	1	60	5
M35	3	4.4 1	0.2 0	896	68	5	1	24	1	60	5
M43	3	2.7 6	0.1 3	2720	207	2	0	23	1	55	5
M48	3	0.7 6	0.0 3	298	23	0	0	19	1	50	4
KE12	3	0.2 0	0.0 1	5	0	204	25	3287	92	4220	361
ALV519-4-1	5	0.1 9	0.0 1	205	16	614	74	39	1	62	5
80-1-3	3	0.6 4	0.0 3	532	41	596	72	47	1	161	14
1846-9	4	1.7 8	0.0 8	9	1	236	28	206	6	269	23
NS-1	3	0.4 2	0.0 2	4295	327	31	4	24	1	60	5
Villa_P2	3	4.6 7	0.2 1	946	72	3638	438	106	3	144	12
INSOL_MX1_BA4	3	0.2 2	0.0 1	8314	634	8	1	81	2	271	23

Run101@2.asc	3	1.9 3	0.0 9	55	4	285	34	570	16	268	23
Run10@2.asc	3	4.3 5	0.2 0	23	2	20	2	401	11	4	0
ALV_1833-1	3	2.2 8	0.1 0	15	1	497	60	553	15	254	22
WOK28-3	3	0.5 2	0.0 2	292	22	650	78	45	1	95	8
SIMS (Caltech, Cs+beam)											
Experiment #	n	H ₂ O	±	CO ₂	±	S	±	Cl	±	F	±
ND70-2-01	2	2.4 9	0.0 9	118 3	117	513	84	859	156	124 7	99
ND70-3-01	8	3.1 8	0.1 2	185 1	184	745	122	152 7	277	182 8	145
ND70-4-02	3	2.9 9	0.1 1	203 9	202	121 9	199	206 1	374	265 8	210
ND70-5-02	2	4.9 4	0.1 8	815 1	808	468 7	766	895 5	162 6	121 18	959
ND70-6-02	2	6.9 5	0.2 6	723 4	718	768 7	125	154 7	279 8	203 58	161 1
Other glasses analysed											
ND-70 (Natural)	2	1.0 9	0.0 4	135	13	657	107	257	47	193	15
Suprasil	2	0.0 0	0.0 0	2	0	0	0	245 6	446	0	0
BF73	2	0.7 9	0.0 3	243 5	242	0	0	53	10	73	6
BF76	2	0.8 5	0.0 3	253 4	251	0	0	54	10	61	5
BF77	2	0.8 3	0.0 3	853	85	0	0	51	9	57	5
M15	2	1.6 8	0.0 6	138	14	1	0	32	6	115	9
M19	2	3.4 1	0.1 3	252 0	250	3	1	35	6	122	10
M20	2	5.3 6	0.2 0	1609	160	8	1	39	7	132	10
M34	1	5.4 0	0.2 0	265	26	6	1	34	6	124	10
M35	2	4.1 5	0.1 5	869	86	5	1	34	6	126	10
M43	1	2.8 0	0.1 0	2834	281	2	0	35	6	121	10
M48	1	0.8 4	0.0 3	221	22	0	0	31	6	113	9
ALV519-4-1	2	0.1 6	0.0 1	189	19	541	88	46	8	111	9
1846-12	2	1.3 8	0.0 5	126	12	617	101	347	63	282	22
80-1-3	2	0.5 5	0.0 2	365	36	566	93	60	11	317	25
1846-9	2	1.7	0.0	7	1	223	36	275	50	574	45

NS-1	3	1 0.4 2	6 0.0 2	4931	489	32	5	36	6	135	11
Villa_P2	2	4.5 2	0.1 7	909	90	3698	604	151	27	303	24
INSOL_MX1_BA4	2	0.1 8	0.0 1	7737	767	6	1	95	17	492	39
Run101@2.asc	2	1.7 4	0.0 6	49	5	252	41	781	142	548	43
Run10@2.asc	2	3.7 8	0.1 4	14	1	16	3	482	88	2	0
SIMS (JAMSTEC-Kochi) Cs+ primary beam											
Experiment #	n	H2		CO2	S	Cl	F				
		O	±	±	±	±	±	±	±	±	±
ND 70_ Degassed	2	0.0 3	0.0 0	8	0	39	1	12	1	16	1
ND70-2-01	3	2.5 5	0.0 9	133 9	61	709	24	495	44	722	39
ND70-3-01	3	3.3 2	0.1 1	212 1	96	101 7	34	106 8	96	982	53
ND70-4-01	3	4.6 2	0.1 6	332 0	151	236 5	80	227 6	204	235 5	126
ND70-4-02	3	3.9 6	0.1 4	342 1	155	223 8	76	210 1	188	210 9	113
ND70-5-02	3	6.0 0	0.2 1	100 34	455	698 2	236	709 5	636	754 3	404
ND70-6-02	3	7.8 1	0.2 7	119 34	542	125 67	426	126 06	113 0	137 03	735
Other glasses (and minerals) analyzed											
ND-70 (Natural)	2	1.0 6	0.0 4	200	9	883	30	176	16	105	6
Vol-std-G_EPR-G3	5	0.2 4	0.0 1	355	16	123 6	42	118	11	117	6
Vol-std-G_SC-ol	1	0.0 0	0.0 0	9	0	0	0	0	0	1	0
Vol-std-G_ELA-qz	4	0.0 1	0.0 0	12	1	0	0	0	0	1	0
Vol-std-G_IND-G1	1	0.5 1	0.0 2	206	9	104 3	35	78	7	172	9
Vol-std-G_Vol-3A	1	3.4 6	0.1 2	478 6	217	104 6	35	254 7	228	299 6	161
Vol-std-G_Vol-1B	1	0.9 4	0.0 3	454 6	206	673	23	743	67	847	45
Vol-std-G_Vol-05A	1	0.5 7	0.0 2	3384	154	521	18	272	24	418	22
Vol-std-G_Vol-005B	1	0.0 9	0.0 0	503	23	44	1	32	3	46	2
Vol-std-G_MRN-G1	1	2.1 2	0.0 7	6	0	72	2	2854	256	650	35
Vol-std-G_MA42	1	4.7 4	0.1 6	1492	68	29	1	111	10	72	4
Vol-std-G_FJ-G2	1	0.2	0.0	429	19	1328	45	90	8	117	6

		4	1								
Vol-std-G_IND-G2	1	0.5	0.0	482	22	1042	35	80	7	209	11
		4	2								
Vol-std-G_vol-0B	1	0.0	0.0	8	0	1	0	1	0	5	0
		2	0								
		SIMS (WHOI, O-beam)									
Experiment #	n	H ₂		CO ₂	±						
		O	±								
ND70-2-01	3	2.7	0.1	131	±						
		0	1	5	148						
ND70-3-01	5	3.3	0.1	172	±						
		1	4	1	193						
ND70-4-01	5	4.2	0.1	359	±						
		1	8	5	404						
ND70-4-02	3	3.4	0.1	321	±						
		9	5	9	362						
ND70-5-02	3	4.6	0.1	108	122						
		2	9	55	0						
ND70-5-03	3	3.7	0.1	165	±						
		9	6	5	186						
ND70-6-02	3	5.9	0.2	119	134						
		6	5	81	6						
Other glasses analyzed											
ND-70 (Natural)	3	1.1	0.0	163	±						
		2	5		18						
Suprasil	3	0.0	0.0	30	±						
		1	0		3						
M20	3	5.4	0.2	1851	±						
		9	3		208						
M35	3	4.1	0.1	927	±						
		0	7		104						
ALV519-4-1	3	0.2	0.0	215	±						
		0	1		24						
NS-1	3	0.4	0.0	4254	±						
		8	2		478						
Villa_P2	3	4.2	0.1	1040	±						
		6	8		117						
INSOL_MX1_BA4	3	0.2	0.0	7718	±						
		4	1		867						
		SIMS (Caltech, O-beam)									
Experiment #	n	H ₂		CO ₂	±						
		O	±								
ND70-2-01	2	2.4	0.1	134	±						
		2	5	3	184						
ND70-3-01	8	3.0	0.1	197	±						
		5	9	9	271						
ND70-4-02	3	3.4	0.2	330	±						
		0	1	9	454						
ND70-5-02	2	4.3	0.2	992	136						
		1	6	8	1						

ND70-6-02	2	5.2	0.3	116	159
		6	2	15	3
Other glasses analyzed					
ND-70 (Natural)					
Suprasil	1	0.0	0.0	0	0
		0	0		
M43	1	2.5	0.1	2806	385
		8	6		
80-1-3	2	0.6	0.0	626	86
		8	4		
NS-1	3	0.4	0.0	4223	579
		5	3		
INSOL_MX1_BA4	2	0.2	0.0	7729	106
		3	1		0

891

892

893

894 **Table 6.** Major element and volatile content of the new reference glasses. For H₂O we used
895 the mean values from ERDA, FTIR, the three Cs⁺ primary beam SIMS sessions at Caltech,
896 WHOI and Nancy, the O⁻ primary beam session at WHOI and the Cs⁺ primary beam SIMS
897 sessions at Kochi but excluding samples ND70-5-02 and ND70-6-02, outside calibration
898 range in that session. We report the uncertainty as the standard deviation from these means.
899 For CO₂ we used the mean of the NRA, EA and FTIR analyses and, for the low C (<5000
900 ppm) samples, we also included the EMP analyses. We report the uncertainty as the standard
901 deviation from these means. For ND70_Natural we report the mean of all SIMS and FTIR
902 sessions along with the associated standard deviation. For S, we used the mean values from
903 EMPA and the four Cs⁺ primary beam SIMS sessions (Caltech, WHOI, Kochi and Nancy)
904 and report the uncertainty as the standard deviation from these means. For Cl, we used the
905 mean values from EMPA and three Cs⁺ primary beam SIMS sessions at WHOI, Nancy and
906 Kochi (but excluding samples ND70-5-02 and ND70-6-02 from the WHOI session which
907 deviated significantly from all other estimates) and report the uncertainty as the standard
908 deviation from these means. For F, we used the mean values from three Cs⁺ primary beam
909 SIMS sessions at WHOI, Nancy and Kochi (but excluding samples ND70-5-02 and ND70-6-
910 02 from the Kochi session which deviated significantly from all other estimates) and report
911 the uncertainty as the standard deviation from these means. International Generic Sample
912 Number (IGSN) and catalogue numbers from the Smithsonian National Museum of Natural
913 History (NMNH) Rock & Ore Collections are provided.

914

Sample #	IGSN:	NM NH catalogue number	Majors (normalized)											Volatiles											
			Si	Ti	Al ₂ O ₃	Fe	Mn	Mg	Ca	N	P ₂ O ₅	S	Cl	F	H ₂ O	CO ₂	S	Cl	F						
ND 70_ Degassed	10.58052/1 EYM10001	118 554-1	50.9	0.08	0.16	8.2	0.34	8.0	0.7	8.13	2.1	0.23	0.0	0.0	0.1	bl	an	k	24	13	11	8	15	2	
ND-70 (Natural)		118 554-8	50.15	0.08	0.16	8.27	0.15	8.0	0.3	8.13	2.1	0.13	0.0	0.0	0.1	1.00	0.7	145	53	790	138	182	18	96	9
ND70-2-01	10.58052/1 EYM10002	118 554-2	49.8	0.07	0.16	8.34	0.16	8.0	0.8	8.13	2.2	0.26	0.0	0.0	0.1	2.41	0.1	1560	2	594	97	661	85	615	93
ND70-3-01	10.58052/1 EYM10003	118 554-3	49.6	0.08	0.16	8.46	0.15	8.0	0.4	8.13	2.2	0.20	0.0	0.0	0.1	3.09	0.3	2637	88	804	160	984	0	803	58
ND70-4-01	10.58052/1 EYM10004	118 554-4	50.4	0.08	0.16	8.09	0.17	8.0	0.7	8.13	2.0	0.33	0.0	0.0	0.1	4.15	0.3	4161	4	198	367	236	38	202	94

ND70-4-02	10.58052/1 EYM10005	118	48	0.	16			9.	13	2.	0.	0.	1	3.	0.		1	168	43	206	2	188	3
		554-	.8	8	.0	8.	0.	0	.9	0	.9	1	1	0	56	3	4214	3	9	5	0	3	7
ND70-5-02	10.58052/1 EYM10006	118	50	0.	14			8.	14	2.	0.	0.	1	4.	0.	1223	4	552	10	698	1	561	1
		554-	.9	7	.5	7.	0.	7	.5	58	1	0	0	99	3	7	1	8	23	4	8	6	1
ND70-6-02	10.58052/1 EYM10007	118	50	0.	14			9.	15	2.	0.	0.	1	6.	0.	1584	9	975	20	122	3	995	3
		554-	.3	7	.4	7.	0.	4	.0	43	2	2	0	42	5	7	5	6	47	93	9	1	9
		7	9	3	5			1	6	1	9	0		1		7	7	6	47	93	6	1	9

915

916

917 SUPPLEMENTARY to: “ND70-series basaltic glass
918 reference materials for volatile element (H₂O, CO₂, S, Cl, F)
919 analyses and the C ionization efficiency suppressing effect of
920 water in silicate glasses.”

921 **Yves Moussallam¹, William Henry Towbin², Terry Plank¹, H el ene Bureau³, Hicham**
922 **Khodja⁴, Yunbin Guan⁵, Chi Ma⁵, Michael B. Baker⁵, Edward M. Stolper⁵, Fabian U.**
923 **Naab⁶, Brian D. Monteleone⁷, Glenn G. Gaetani⁷, Kenji Shimizu⁸, Takayuki Ushikubo⁸,**
924 **Hyun Joo Lee¹, Shuo Ding¹, Sarah Shi¹, Estelle F. Rose-Koga⁹.**

925

926 ¹ *Lamont-Doherty Earth Observatory, Columbia University, New York, USA*

927 ² *Gemological Institute of America, 50 W. 47th Street, New York, NY 10036, United States of America*

928 ³ *IMPMC, Sorbonne Universit e, CNRS UMR 7590, MNHN, IRD UR 206, 4 place Jussieu, 75252*
929 *Paris Cedex 05, France*

930 ⁴ *LEEL, NIMBE, CEA, CNRS, Universit e Paris–Saclay, CEA Saclay, 91191 Gif sur Yvette Cedex,*
931 *France*

932 ⁵ *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena,*
933 *California 91125, USA*

934 ⁶ *Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor,*
935 *Michigan 48109, USA*

936 ⁷ *Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA*
937 *02543, USA.*

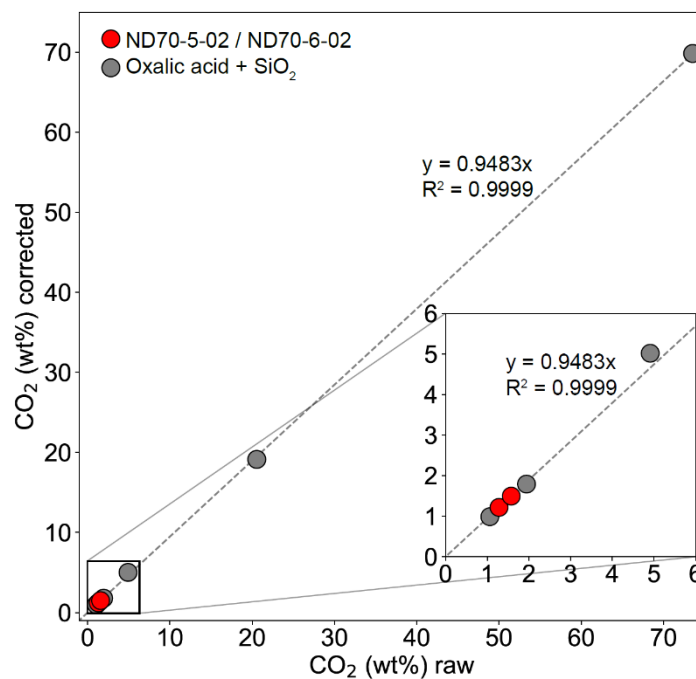
938 ⁸ *Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology,*
939 *Monobe-otsu 200, Nankoku, Kochi 783-8502, Japan*

940 ⁹ *ISTO, UMR 7327, CNRS-UO-BRGM, 1A rue de la F erollerie, 45071 Orl eans cedex 2, France*

941

942 Corresponding author: Yves Moussallam; yves.moussallam@ldeo.columbia.edu

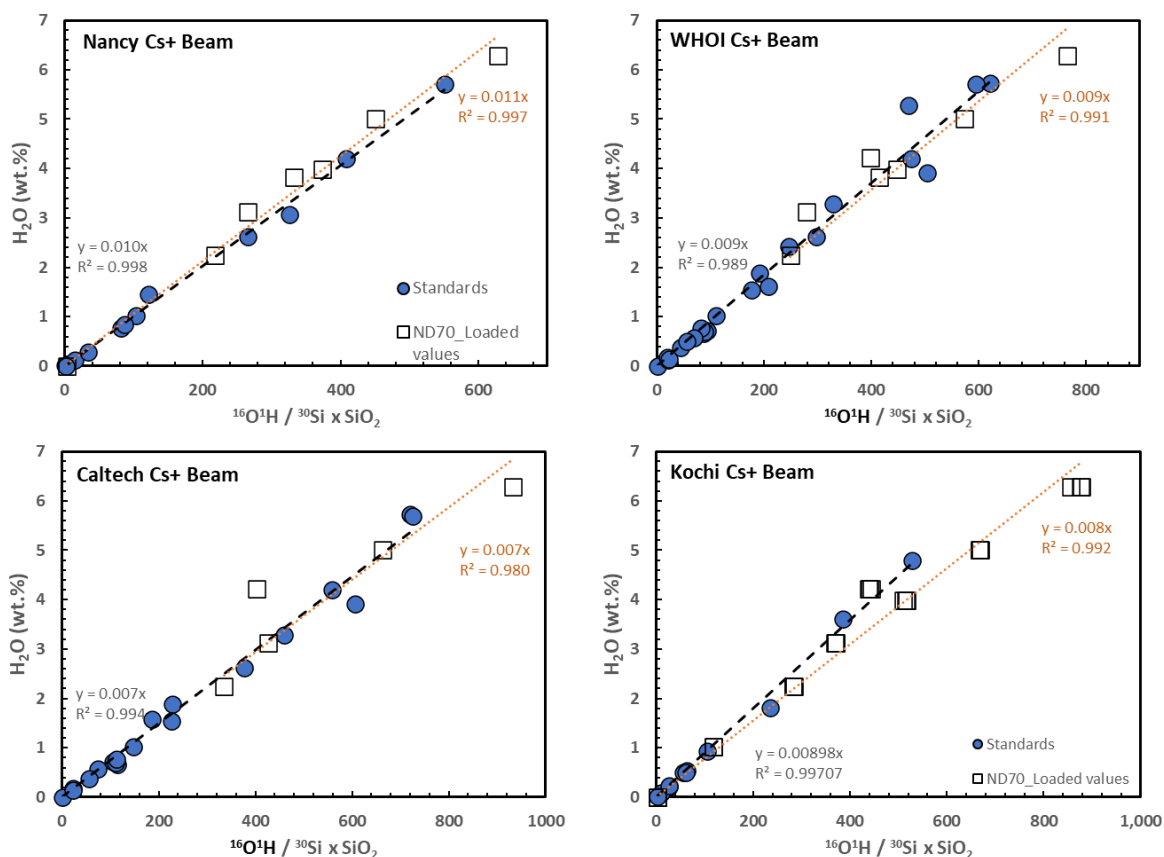
943 SUPPLEMENTARY FIGURES



944

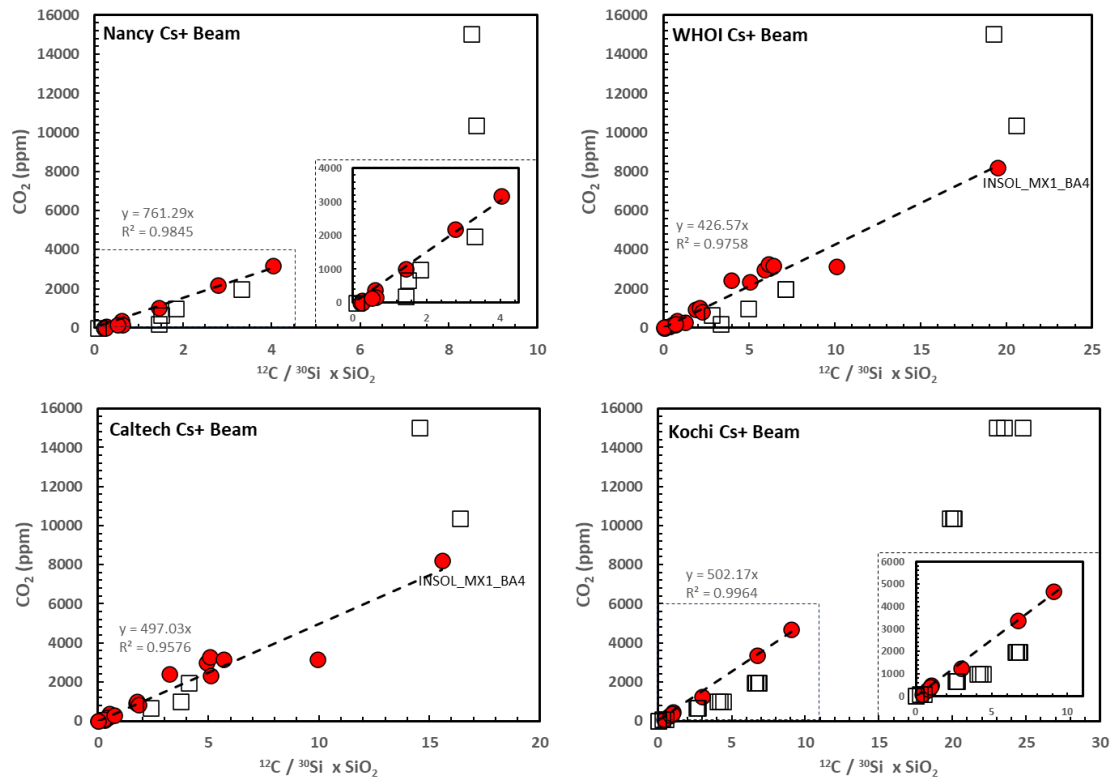
945 **Figure S1:** Elemental Analyser secondary calibration. CO₂ (wt%) raw indicates the raw EA
946 result calibrated by acetanilide. CO₂ (wt%) corrected is calibrated by a series of oxalic acid
947 and SiO₂ mixtures. Gray circles are oxalic acid and SiO₂ mixtures. Red circles are
948 ND70_5_02 and ND70_6_02. Dashed line is the calibration line based on oxalic acid and
949 SiO₂.

950



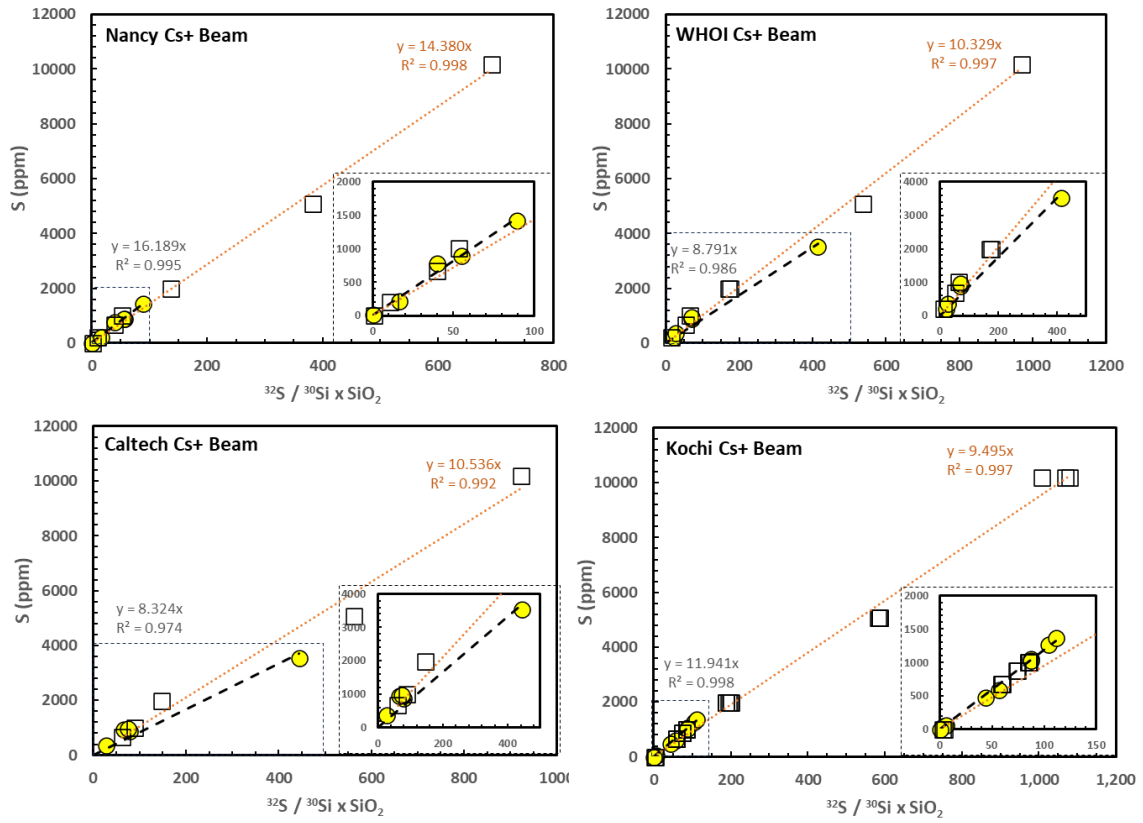
951

952 **Figure S2:** ¹⁶O¹H signal retrieved by SIMS using a Cs⁺ primary beam at Nancy, Kochi,
 953 WHOI and Caltech Ion Probe facilities. Filled circle symbols show glasses used as standards
 954 for volatile analyses (marked as “Other glasses analysed” in Table 5) in addition to
 955 INSOL_MX1_BA and VILLA_YM whose volatile contents were determined as part of this
 956 study. Square symbols represent the new ND70 reference series plotted on the y-axis
 957 according to their expected (i.e., loaded) values. Data in Tables S3 to S5. Black dashed lines
 958 are the calibration lines while red dotted lines are linear regressions through the ND series
 959 glasses.



960

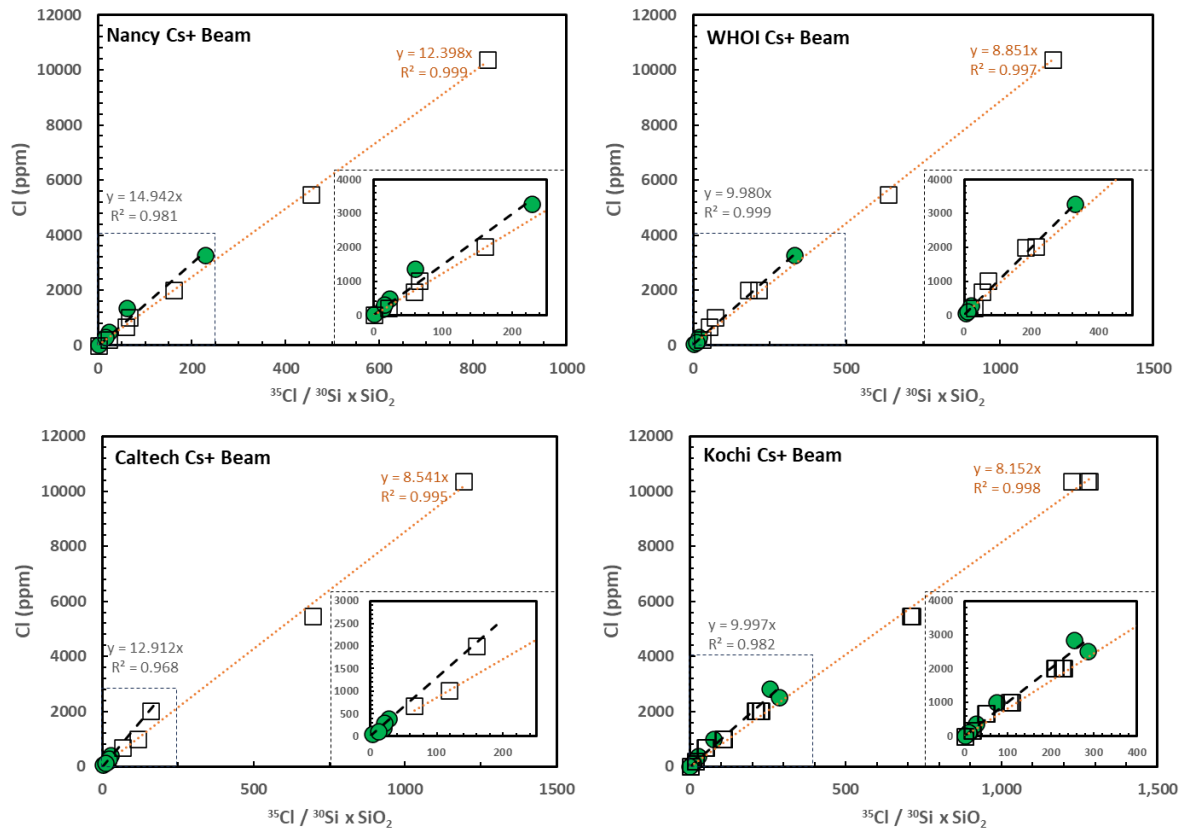
961 *Figure S3: Same as Fig. S2, for ^{12}C .*



962

963 *Figure S4: Same as Fig. S2, for ^{32}S .*

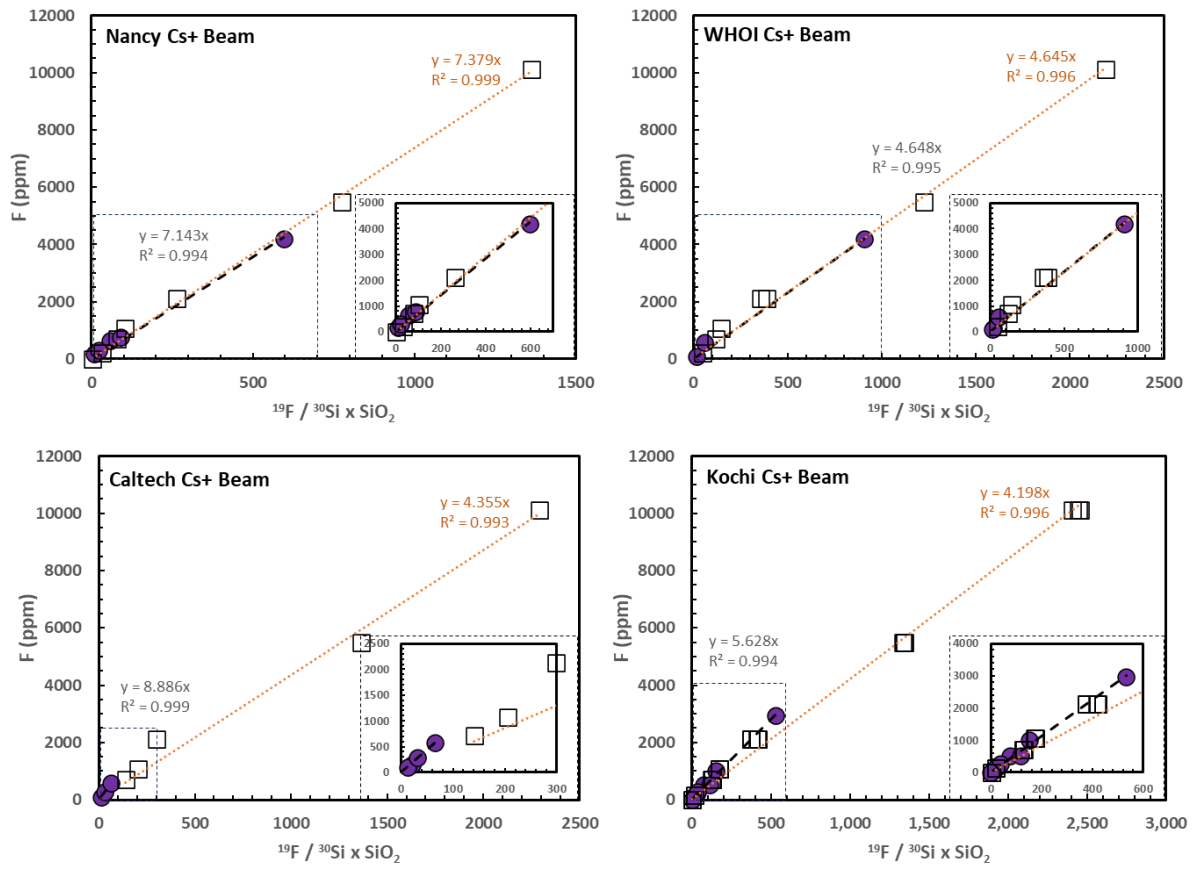
964



965

966 *Figure S5: Same as Fig. S2, for ^{35}Cl .*

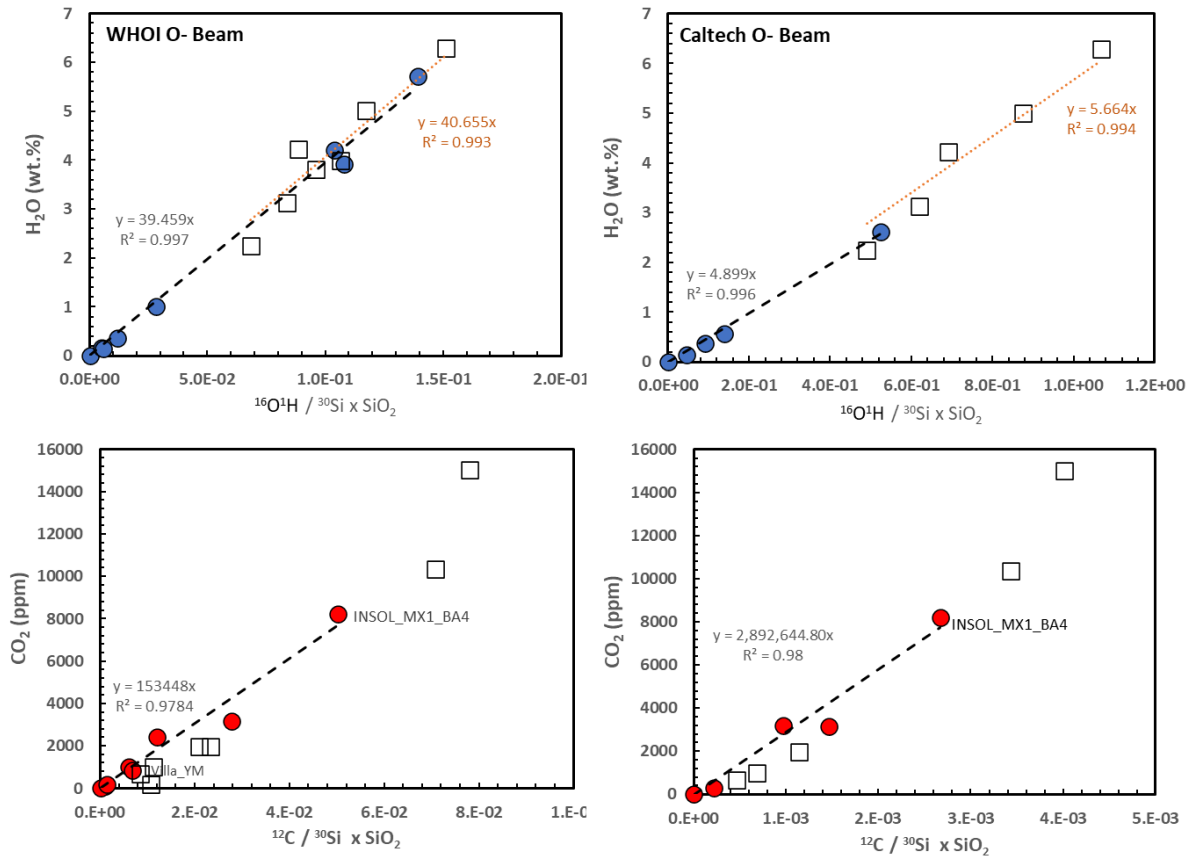
967



968

969 *Figure S6: Same as Fig. S2, for ^{19}F .*

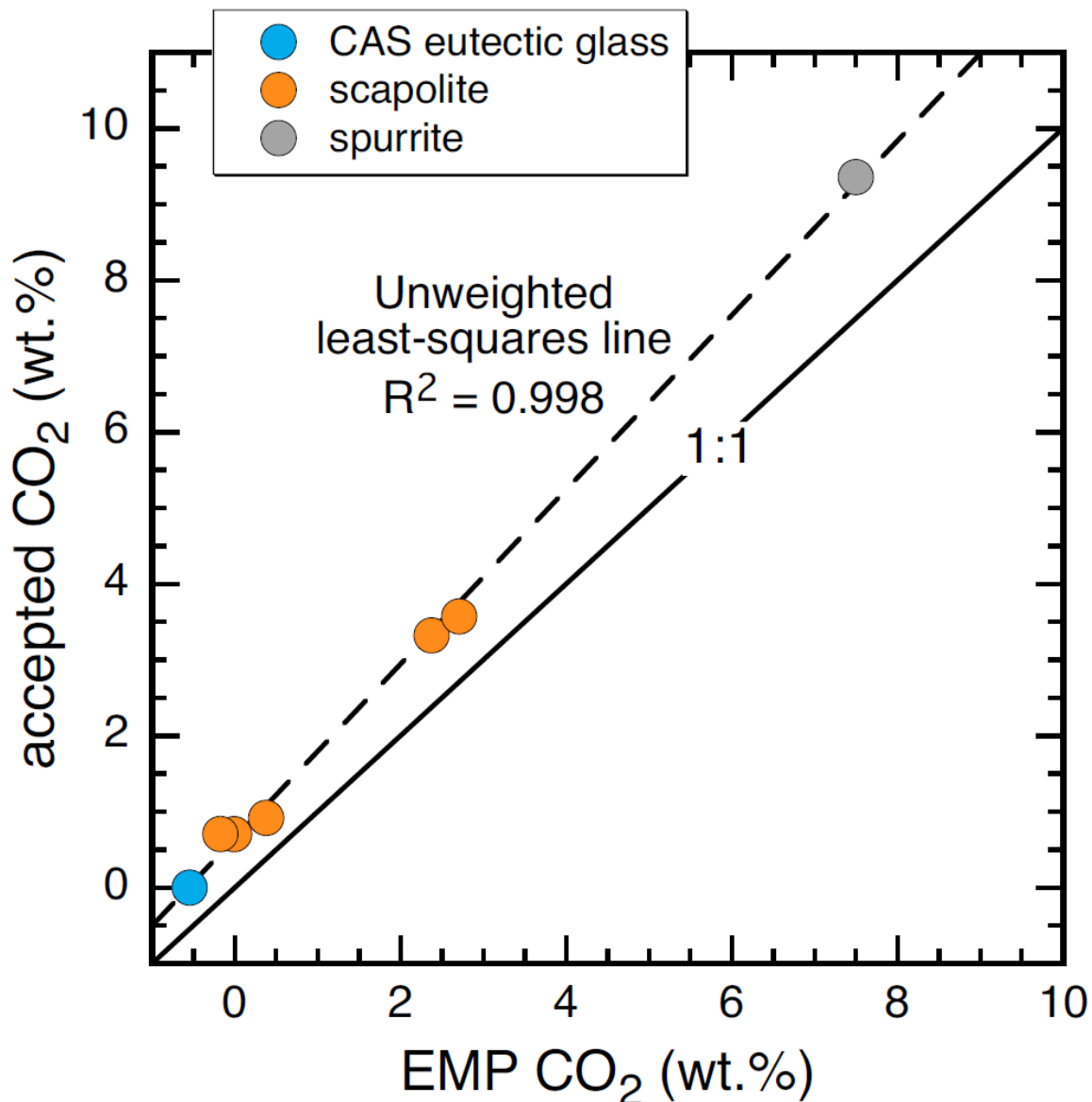
970



971

972 **Figure S7:** Signal retrieved by SIMS using a O⁻ primary beam at WHOI and Caltech Ion
 973 Probe facilities. Filled circle symbols show glasses used as standards for volatile analyses
 974 (marked as “Other glasses analysed” in Table 5) in addition to INSOL_MX1_BA and
 975 VILLA_YM whose volatile contents were determined as part of this study. Square symbols
 976 represent the new ND70 reference series plotted on the y-axes according to their expected
 977 (i.e., loaded) values. Data in Tables S6 and S7. Black dashed lines are the calibration lines
 978 while red dotted lines are linear regressions through the ND series glasses.

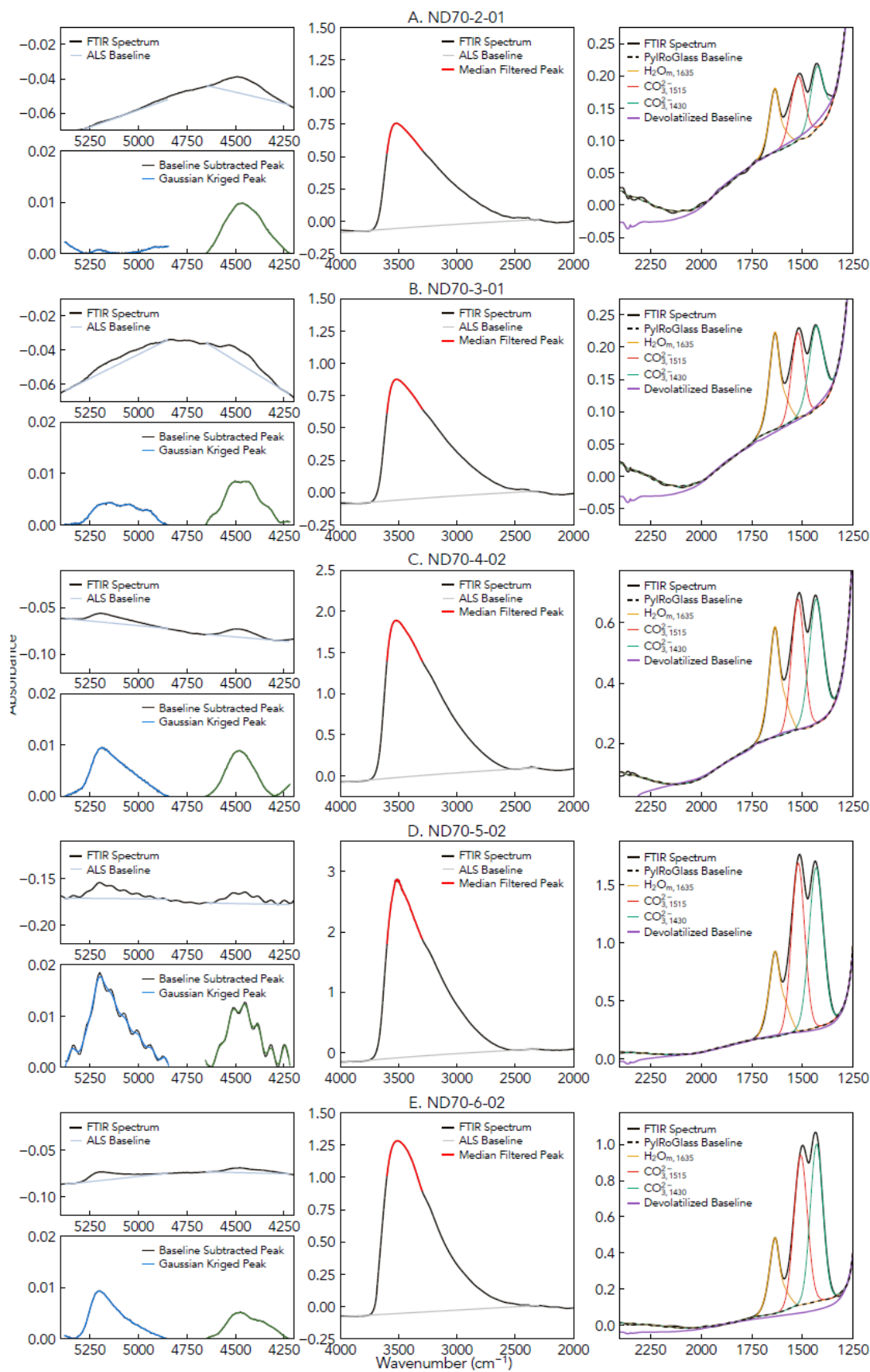
979



980

981 **Figure S8:** Electron microprobe CO₂ contents vs. accepted CO₂ contents (all in wt.%) for the
 982 secondary standards. The CaO-Al₂O₃-SiO₂ eutectic is bounded by the pseudowollastonite,
 983 anorthite, and tridymite liquidus fields; the glass was fused at 1-atm in air and is assumed to
 984 have a CO₂ content of zero. Scapolite CO₂ contents determined by NRA; the CO₂ content of
 985 the spurrite is based on mineral stoichiometry. The dashed line is an unweighted least-
 986 squares fit to the seven secondary standards.

987



988

989 **Figure S9:** FTIR spectra of ND70 series glasses and spectra fitting with the PyIRoGlass
 990 software (Shi et al., 2023).

991 **SUPPLEMENTARY TABLES**

992

993 *Table S1: Weight of all starting materials added to each experiment. 'ND70-4 Bulk Enriched' is a mixture of all the dry components, mixed for 1*
 994 *hour, and used as starting material for five of the experiments.*

Experiments and pre-mix	ND70 mix (g)	ND70-4 Bulk Enriched (g)	ND70 + 6wt% SiO ₂ Mix (g)	Water (g)	Calcite (g)	CaSO ₄ (g)	NaCl (g)	MgF ₂ (g)	Total (g)
ND70-4 Bulk Enriched	0.56770				0.00270	0.00510	0.00200	0.00210	0.57960
ND70-4-01		0.19200		0.00790					0.19990
ND70-4-02		0.19280		0.00840					0.20120
ND70-3-01	0.07310	0.07320		0.00470					0.15100
ND70-2-01	0.13080	0.06550		0.00450					0.20080
ND70-5-03	0.12468	0.01400		0.00550					0.14418
ND70-5-02			0.17790	0.01000	0.00470	0.00430	0.00180	0.00180	0.20050
ND70-6-02			0.16615	0.01250	0.00680	0.00860	0.00340	0.00330	0.20075

995

996

997

998 **Table S2:** Volatile and SiO₂ contents (normalised to 100%) of other glasses analysed.

Name	H ₂ O (wt.%)	CO ₂ (ppm)	F (ppm)	S (ppm)	Cl (ppm)	SiO ₂ (wt.%)	References
ND-70	1.015	76.5	148	880	184	50.4	Keller et al., 2008; Caulfield et al., 2012; Lloyd et al., 2013
Suprasil	0.0007±0.0002	0.65±0.35	0.19±0.05	0.15±0.03	1000-3000	100.0	Shimizu et al., 2021
BF73	0.72	2995				51.2	Brounce et al., 2021 and Almeev (unpublished)
BF76	0.67	2336				51.2	Brounce et al., 2021 and Almeev (unpublished)
BF77	0.70	935				51.2	Brounce et al., 2021 and Almeev (unpublished)
M15	1.54	60				50.5	Shishkina et al., 2010
M19	3.29	3277				50.4	Shishkina et al., 2010
M20	5.72	2421				50.4	Shishkina et al., 2010
M34	5.70	375				50.4	Shishkina et al., 2010
M35	4.20	1019				50.4	Shishkina et al., 2010
M40	3.07	2183				50.3	Shishkina et al., 2010
M43	2.62	3172				50.4	Shishkina et al., 2010
M48	0.77	176				51.0	Shishkina et al., 2010
KL2	0.02	5	177	8	26	50.1	Jochum et al., 2006; Rose-Koga et al., 2020
KE12	0.12		4200	210	3280	70.8	Mosbah et al., 1991 and Mandeville (unpublished); Rose-Koga et al., 2020
40428	0.85		650	890	494	51.0	Kamenetsky et al., 2000
47963	1.45		777	776	1356	48.9	Kamenetsky et al., 2000
N72	0.00	0				50.1	Shishkina et al., 2010
ALV519-4-1	0.17	165	95	950	53	49.1	Bryan & Moore, 1977; Hauri et al., 2002; Kumamoto et al., 2017 and Hauri (unpublished)
1846-12	1.58	90	288	981	400	50.8	Newman et al., 2000; Hauri et al., 2002; Kumamoto et al., 2017
80-1-3	0.57	295				48.9	Newman et al., 2000
1846-9	1.89	0	574	358	292	49.7	Newman et al., 2000; Kumamoto et al., 2017 and Hauri (unpublished)

NS-1	0.37	3154				50.4	Helo et al., 2011
VILLA_P2	3.92	835		3529	120	53.4	This study
INSOL_MX1_BA4	0.15	8207				52.6	This study
VG2	0.28	153	300	1424	298	50.8	Jarosewich et al., 1980; Rose-Koga et al., 2020
Run101	1.62					57.6	Mandeville et al., 2002
Run10	5.28					57.2	Mandeville et al., 2002
Vol-std-G_EPR-G3	0.22	269	147	1270	159	50.2	Shimizu et al., 2017
Vol-std-G_IND-G1	0.50	97	216	1048	97	50.1	Shimizu et al., 2017
Vol-std-G_Vol-3A	3.60		2957		2833	53.4	Shimizu et al., 2017
Vol-std-G_Vol-1B	0.94	4686	1018	592	1000	50.5	Shimizu et al., 2017
Vol-std-G_Vol-05A	0.54	3354	511	469	376	50.5	Shimizu et al., 2017
Vol-std-G_Vol-005B	0.10	479	55	51	55	49.8	Shimizu et al., 2017
Vol-std-G_MRN-G1	1.81		507	62	2517	70.2	Shimizu et al., 2017
Vol-std-G_MA42	4.79	1243				51.8	Shimizu et al., 2017
Vol-std-G_FJ-G2	0.23	307	151	1372	118	49.6	Shimizu et al., 2017
Vol-std-G_IND-G2	0.50	389	264	1023	113	50.3	Shimizu et al., 2017
Vol-std-G_vol-0B	0.02		8	1	12	48.4	Shimizu et al., 2017

1000 **Table S3:** Raw SIMS analyses from IMS 1280 at CNRS-CRPG Nancy using a Cs+ primary beam. All errors are given as one standard deviation
 1001 on repeat analyses or as one standard deviation from analytical error (whichever is the highest).

		SIMS (CNRS-Nancy) Cs+ primary beam																			
Experiment #	n	$^{12}\text{C}/^{30}\text{Si}$	\pm	$^{16}\text{O}^1\text{H}/^{30}\text{Si}$	\pm	$^{19}\text{F}/^{30}\text{Si}$	\pm	$^{32}\text{S}/^{30}\text{Si}$	\pm	$^{35}\text{Cl}/^{30}\text{Si}$	\pm	$^{12}\text{C}/^{18}\text{O}$	\pm	$^{16}\text{O}^1\text{H}/^{18}\text{O}$	\pm	$^{19}\text{F}/^{18}\text{O}$	\pm	$^{32}\text{S}/^{18}\text{O}$	\pm	$^{35}\text{Cl}/^{18}\text{O}$	\pm
ND 70_Degassed	2	0.0017	0.0002	0.0578	0.0012	0.0371	0.0022	0.0206	0.0010	0.0048	0.0003	0.0019	0.0001	0.0641	0.0016	0.0403	0.0004	0.0225	0.0001	0.0053	0.0000
ND70-2-01	3	0.0301	0.0024	4.3713	0.1936	1.6094	0.1119	0.8055	0.0434	1.1781	0.0666	0.0265	0.0006	3.9555	0.0437	1.4228	0.0162	0.7207	0.0029	1.0494	0.0045
ND70-3-01	2	0.0370	0.0029	5.3718	0.2615	2.1066	0.1490	1.0753	0.0591	1.3283	0.0789	0.0334	0.0006	4.9536	0.0399	1.9056	0.0232	0.9821	0.0036	1.2108	0.0038
ND70-4-01	2	0.0659	0.0052	7.4514	0.3509	5.2887	0.3632	2.7161	0.1416	3.2016	0.1763	0.0509	0.0010	5.8959	0.0509	4.1039	0.0434	2.1256	0.0139	2.5017	0.0109
ND70-5-02	2	0.1716	0.0156	8.9640	0.5286	15.4225	1.2157	7.6321	0.4503	9.0217	0.5759	0.1291	0.0034	6.9094	0.0465	11.6824	0.1666	5.8729	0.0246	6.8998	0.0253
ND70-5-03	2	0.0287	0.0022	6.6193	0.2875	0.6352	0.0416	0.2154	0.0106	0.4339	0.0231	0.0230	0.0004	5.4222	0.0601	0.5123	0.0051	0.1751	0.0013	0.3521	0.0015
ND70-6-02	2	0.1731	0.0144	12.7743	0.7299	27.6741	2.1188	14.0800	0.7245	16.8742	1.0217	0.1176	0.0026	8.8323	0.0859	18.8701	0.2968	9.7299	0.1092	11.6021	0.0616
Other glasses analyzed																					
ND-70 (Natural)	1	0.0051	0.0004	2.0414	0.0575	0.2716	0.0160	1.1220	0.0501	0.2579	0.0123	0.0047	0.0001	1.9267	0.0418	0.2528	0.0024	1.0512	0.0068	0.2413	0.0014
M34	3	0.0119	0.0008	10.9312	0.3698	0.2182	0.0117	0.0140	0.0007	0.0473	0.0024	0.0075	0.0002	6.9359	0.0813	0.1370	0.0012	0.0088	0.0001	0.0297	0.0003
M35	10	0.0287	0.0023	8.1092	0.3131	0.2083	0.0132	0.0133	0.0009	0.0433	0.0026	0.0191	0.0005	5.5323	0.0789	0.1401	0.0016	0.0089	0.0001	0.0292	0.0002
M40	10	0.0553	0.0038	6.4981	0.2218	0.2035	0.0119	0.0146	0.0008	0.0433	0.0023	0.0390	0.0008	4.6534	0.0716	0.1441	0.0014	0.0103	0.0001	0.0307	0.0002
M43	1	0.0801	0.0052	5.2770	0.1683	0.1883	0.0105	0.0060	0.0004	0.0384	0.0017	0.0591	0.0009	3.9509	0.0685	0.1395	0.0010	0.0044	0.0001	0.0286	0.0002
M48	10	0.0123	0.0012	1.5927	0.0447	0.1759	0.0114	0.0030	0.0003	0.0367	0.0023	0.0104	0.0004	1.3923	0.0358	0.1510	0.0017	0.0025	0.0001	0.0316	0.0002
KL2	10	0.0041	0.0004	0.0219	0.0007	0.1619	0.0110	0.0070	0.0004	0.0182	0.0012	0.0039	0.0002	0.0213	0.0005	0.1548	0.0022	0.0067	0.0001	0.0175	0.0002
KE12	10	0.0021	0.0003	0.2162	0.0098	8.4050	0.6110	0.2303	0.0118	3.2320	0.1966	0.0019	0.0001	0.2081	0.0025	7.9613	0.1329	0.2217	0.0017	3.0826	0.0170
40428	9	0.0066	0.0006	1.6951	0.0724	1.1336	0.0846	1.0777	0.0625	0.4579	0.0286	0.0067	0.0002	1.7806	0.0228	1.1611	0.0170	1.1142	0.0033	0.4723	0.0021
47963	10	0.0061	0.0005	2.4869	0.1206	1.8266	0.1300	0.8160	0.0479	1.2350	0.0758	0.0063	0.0002	2.5894	0.0262	1.8830	0.0251	0.8410	0.0027	1.2689	0.0061
N72	5	0.0049	0.0005	0.0335	0.0008	0.2143	0.0114	0.0047	0.0004	0.0380	0.0018	0.0040	0.0002	0.0281	0.0007	0.1762	0.0016	0.0039	0.0001	0.0314	0.0002
VG2	10	0.0102	0.0008	0.6600	0.0183	0.4403	0.0292	1.7624	0.0888	0.3069	0.0169	0.0098	0.0003	0.6536	0.0163	0.4263	0.0054	1.7223	0.0081	0.2989	0.0009

1002

1003

1004

1005 **Table S4:** Raw SIMS analyses from IMS 7f-GEO at Caltech using a Cs+ primary beam. All errors are given as one standard from analytical
 1006 error.

		SIMS (Caltech) Cs+ primary beam																			
Experiment #	n	$^{12}\text{C}/^{30}\text{Si}$	\pm	$^{16}\text{O}^1\text{H}/^{30}\text{Si}$	\pm	$^{19}\text{F}/^{30}\text{Si}$	\pm	$^{32}\text{S}/^{30}\text{Si}$	\pm	$^{35}\text{Cl}/^{30}\text{Si}$	\pm	$^{12}\text{C}/^{18}\text{O}$	\pm	$^{16}\text{O}^1\text{H}/^{18}\text{O}$	\pm	$^{19}\text{F}/^{18}\text{O}$	\pm	$^{32}\text{S}/^{18}\text{O}$	\pm	$^{35}\text{Cl}/^{18}\text{O}$	\pm
ND70-2-01	2	0.0478	0.0002	6.7317	0.0170	2.8197	0.0226	1.2384	0.0183	1.3360	0.0411	0.0274	0.0002	3.8655	0.0188	1.6202	0.0175	0.7144	0.0123	0.7708	0.0255
ND70-3-01	8	0.0752	0.0054	8.6127	0.3426	4.1524	0.1505	1.8058	0.0625	2.3865	0.0928	0.0391	0.0013	4.5398	0.2608	2.1764	0.0452	0.9468	0.0357	1.2517	0.0445
ND70-4-02	3	0.0843	0.0035	8.2648	0.2507	6.1457	0.2329	3.0092	0.0691	3.2802	0.0749	0.0584	0.0009	5.7656	0.0102	4.2917	0.0403	2.1238	0.0137	2.3185	0.0307
ND70-5-02	2	0.3262	0.0021	13.2015	0.1969	27.1263	0.0998	11.2017	0.0430	13.7957	0.1175	0.1476	0.0007	6.0019	0.1567	12.3280	0.1835	5.1213	0.0792	6.3053	0.1274
ND70-6-02	2	0.2958	0.0164	18.9729	1.2590	46.5657	2.3499	18.7704	0.2025	24.2523	0.3967	0.1269	0.0022	8.1747	0.2270	20.0705	0.2322	8.1458	0.2286	10.5244	0.2328
Other glasses analysed																					
ND-70 (Natural)	2	0.0054	0.0001	2.9097	0.1264	0.4307	0.0127	1.5644	0.0070	0.3944	0.0239	0.0033	0.0000	1.7813	0.0463	0.2637	0.0030	0.9605	0.0215	0.2420	0.0102
Suprasil	2	0.0000	0.0000	0.0013	0.0000	0.0002	0.0000	0.0000	0.0000	1.9023	0.0447	0.0000	0.0000	0.0008	0.0000	0.0001	0.0000	0.0000	0.0000	1.2669	0.0439
BF73	2	0.0957	0.0020	2.0744	0.0498	0.1612	0.0021	0.0001	0.0000	0.0798	0.0004	0.0602	0.0005	1.3135	0.0162	0.1015	0.0000	0.0001	0.0000	0.0503	0.0004
BF76	2	0.0996	0.0062	2.2367	0.1879	0.1336	0.0086	0.0003	0.0001	0.0815	0.0029	0.0570	0.0014	1.2869	0.0571	0.0764	0.0019	0.0002	0.0000	0.0467	0.0003
BF77	2	0.0335	0.0016	2.1690	0.1154	0.1254	0.0049	0.0006	0.0000	0.0773	0.0033	0.0205	0.0005	1.3339	0.0408	0.0766	0.0012	0.0004	0.0000	0.0473	0.0010
M15	2	0.0055	0.0003	4.4695	0.0615	0.2567	0.0040	0.0015	0.0003	0.0486	0.0004	0.0032	0.0001	2.5973	0.0324	0.1492	0.0016	0.0009	0.0001	0.0283	0.0005
M19	2	0.1005	0.0002	9.0987	0.0086	0.2719	0.0064	0.0076	0.0006	0.0532	0.0030	0.0540	0.0007	4.8984	0.0450	0.1465	0.0019	0.0041	0.0003	0.0288	0.0013
M20	2	0.0642	0.0010	14.2935	0.0897	0.2936	0.0007	0.0201	0.0003	0.0594	0.0001	0.0287	0.0003	6.4065	0.0023	0.1316	0.0005	0.0090	0.0002	0.0266	0.0001
M34	1	0.0106	0.0002	14.3829	0.1797	0.2767	0.0040	0.0135	0.0003	0.0530	0.0013	0.0051	0.0001	6.9973	0.0547	0.1347	0.0009	0.0066	0.0001	0.0258	0.0004
M35	2	0.0347	0.0021	11.0667	0.9776	0.2818	0.0101	0.0113	0.0001	0.0527	0.0001	0.0169	0.0007	5.3833	0.3833	0.1373	0.0024	0.0055	0.0002	0.0258	0.0005
M43	1	0.1132	0.0018	7.4751	0.0851	0.2707	0.0047	0.0041	0.0001	0.0541	0.0012	0.0604	0.0003	3.9914	0.0142	0.1445	0.0008	0.0022	0.0000	0.0289	0.0003
M48	1	0.0087	0.0001	2.2129	0.0203	0.2501	0.0034	0.0001	0.0000	0.0465	0.0009	0.0054	0.0001	1.3672	0.0064	0.1545	0.0006	0.0001	0.0000	0.0288	0.0003
ALV519-4-1	2	0.0077	0.0007	0.4490	0.0260	0.2550	0.0104	1.3248	0.0014	0.0734	0.0003	0.0059	0.0003	0.3438	0.0072	0.1951	0.0006	1.0234	0.0385	0.0567	0.0025
1846-12	2	0.0050	0.0001	3.6540	0.0268	0.6252	0.0128	1.4597	0.0264	0.5293	0.0107	0.0034	0.0000	2.4897	0.0160	0.4257	0.0024	1.0009	0.0026	0.3631	0.0017
80-1-3	2	0.0150	0.0011	1.5076	0.0055	0.7287	0.0087	1.3904	0.0159	0.0952	0.0012	0.0104	0.0009	1.0467	0.0104	0.5050	0.0003	0.9694	0.0224	0.0663	0.0016
1846-9	2	0.0003	0.0000	4.6133	0.1971	1.3004	0.0560	0.5399	0.0081	0.4284	0.0065	0.0002	0.0000	2.8100	0.0058	0.7901	0.0019	0.3305	0.0083	0.2625	0.0066
NS-1	3	0.1969	0.0106	1.1232	0.0394	0.3005	0.0064	0.0758	0.0034	0.0548	0.0033	0.1216	0.0048	0.6996	0.0155	0.1861	0.0048	0.0472	0.0025	0.0341	0.0023
VILLA_P2	2	0.0344	0.0024	11.4049	0.3284	0.6406	0.0226	8.3473	0.3511	0.2201	0.0090	0.0165	0.0006	5.6285	0.0236	0.3084	0.0011	4.1159	0.3091	0.1063	0.0010
INSOL_MX1_BA4	2	0.2957	0.0073	0.4497	0.0080	1.0520	0.0288	0.0128	0.0007	0.1404	0.0022	0.2117	0.0021	0.3262	0.0056	0.7595	0.0052	0.0094	0.0008	0.1026	0.0018

1007

1008

Table S5: Raw SIMS analyses from IMS 1280 at WHOI using a Cs+ primary beam. All errors are given as one standard from analytical error.

Experiment #	SIMS (WHOI) Cs+ primary beam										
	n	12C/30Si	±	16O1H/30Si	±	19F /30Si	±	32S /30Si	±	35Cl /30Si	±
ND70-2-01	3	0.0567	0.0013	4.9908	0.0825	2.3760	0.0294	1.0878	0.0068	1.0433	0.0213
ND70-3-01	2	0.0997	0.0029	5.6332	0.1643	2.9645	0.1933	1.3357	0.1003	1.4319	0.1657
ND70-4-01	3	0.1419	0.0023	8.9285	0.0868	7.7497	0.0527	3.5208	0.0274	4.2429	0.0406
ND70-4-02	3	0.1458	0.0010	8.1725	0.0150	7.3624	0.0271	3.5184	0.0232	3.7283	0.0346
ND70-5-02	3	0.4089	0.0086	11.3843	0.2507	24.3667	0.2252	10.6667	0.0273	12.6703	0.1309
ND70-5-03	3	0.0658	0.0010	8.2423	0.1151	0.9277	0.0155	0.2896	0.0039	0.5979	0.0132
ND70-6-02	3	0.3915	0.0024	15.5580	0.3396	44.5050	0.4786	19.7107	0.2466	23.8557	0.4052
Other glasses analysed											
ND-70 (Natural)	3	0.0056	0.0001	2.1747	0.0161	0.3684	0.0028	1.4098	0.0059	0.3185	0.0018
Suprasil	3	0.0006	0.0009	0.0078	0.0021	0.0075	0.0002	0.0002	0.0002	1.9159	0.0178
BF73	2	0.1145	0.0093	1.8283	0.0315	0.1505	0.0009	0.0006	0.0007	0.0708	0.0009
BF76	2	0.0977	0.0009	1.7173	0.0153	0.1142	0.0002	0.0004	0.0001	0.0675	0.0003
BF77	3	0.0362	0.0002	1.7300	0.0153	0.1140	0.0009	0.0007	0.0000	0.0662	0.0006
M15	3	0.0071	0.0012	3.5002	0.0535	0.2273	0.0016	0.0016	0.0001	0.0414	0.0006
M19	3	0.1212	0.0029	6.5289	0.0298	0.2316	0.0015	0.0064	0.0003	0.0414	0.0009
M20	3	0.0785	0.0020	12.3073	0.1822	0.2660	0.0026	0.0176	0.0003	0.0499	0.0012
M34	3	0.0155	0.0027	11.7937	0.0590	0.2563	0.0012	0.0125	0.0002	0.0479	0.0005
M35	3	0.0417	0.0013	9.4117	0.0320	0.2542	0.0031	0.0105	0.0003	0.0472	0.0007
M43	3	0.1266	0.0008	5.9117	0.0665	0.2360	0.0010	0.0037	0.0000	0.0450	0.0010
M48	3	0.0137	0.0073	1.6145	0.0207	0.2119	0.0017	0.0003	0.0002	0.0382	0.0007
KE12	3	0.0002	0.0001	0.3022	0.0169	12.8230	0.0459	0.3286	0.0102	4.6523	0.0382
ALV519-4-1	5	0.0098	0.0001	0.4117	0.0044	0.2708	0.0025	1.4244	0.0153	0.0802	0.0015
80-1-3	3	0.0255	0.0098	1.3997	0.0357	0.7085	0.0095	1.3856	0.0028	0.0955	0.0025
NS-1	3	0.1999	0.0077	0.8877	0.0229	0.2543	0.0028	0.0694	0.0009	0.0482	0.0006
VILLA_P2	3	0.0416	0.0012	9.4519	0.0758	0.5811	0.0041	7.7760	0.6566	0.1994	0.0036

INSOL_MX1_BA4	3	0.3703	0.0102	0.4441	0.0574	1.1063	0.0570	0.0176	0.0045	0.1534	0.0106
Run101@2.asc	3	0.0022	0.0001	3.6113	0.0404	1.0030	0.0281	0.5635	0.0188	0.9911	0.0370
Run10@2.asc	3	0.0009	0.0001	8.1861	0.1171	0.0166	0.0005	0.0400	0.0016	0.7018	0.0189
ALV_1846-9	4	0.0004	0.0000	3.8590	0.0445	1.1673	0.0093	0.5410	0.0053	0.4149	0.0064
ALV_1833-1	3	0.0007	0.0000	4.5644	0.1128	1.0142	0.0067	1.0499	0.0241	1.0283	0.0224
WOK28-3	3	0.0137	0.0002	1.1325	0.0089	0.4112	0.0025	1.4849	0.0155	0.0901	0.0012

1009

1010

1011 **Table S6:** Raw SIMS analyses from IMS 7f-GEO at Caltech using a O- primary beam. All errors are given as one standard from analytical
 1012 error.

Experiment #	SIMS (Caltech) O- primary beam				
	n	$^{12}\text{C}/^{30}\text{Si}$	\pm	$^{16}\text{O}^1\text{H}/^{30}\text{Si}$	\pm
ND70-2-01	2	9.32E-06	1.25E-07	9.86E-03	1.11E-04
ND70-3-01	2	1.38E-05	1.43E-06	1.25E-02	1.11E-04
ND70-4-02	2	2.35E-05	1.90E-06	1.42E-02	2.97E-04
ND70-5-02	2	6.83E-05	5.76E-07	1.74E-02	1.59E-04
ND70-6-02	2	8.16E-05	2.48E-07	2.17E-02	6.33E-04
Other glasses analysed					
Suprasil	1	0.00E+00	2.07E-06	0.00E+00	1.53E-08
M43	2	1.93E-05	2.99E-07	1.04E-02	9.22E-06
80-1-3	1	4.42E-06	1.69E-07	2.84E-03	1.05E-05
NS-1	2	2.90E-05	4.28E-07	1.82E-03	1.83E-04
INSOL_MX1_BA4	1	5.08E-05	1.12E-05	8.93E-04	2.52E-07

1013

1014 **Table S7:** Raw SIMS analyses from IMS 1280 at WHOI using a O- primary beam. All errors are given as one standard from analytical error.

Experiment #	SIMS (WHOI) O- primary beam										
	n	12C/30Si	±	16O1H/30Si	±	19F /30Si	±	32S /30Si	±	35Cl /30Si	±
ND70-2-01	3	1.72E-04	4.14E-06	1.37E-03	1.09E-05	2.42E-02	2.08E-04	1.56E-03	1.73E-05	5.49E-04	5.16E-06
ND70-3-01	5	2.26E-04	1.20E-05	1.70E-03	3.89E-05	3.44E-02	2.91E-04	1.86E-03	1.92E-05	9.77E-04	2.01E-05
ND70-4-01	5	4.67E-04	1.13E-05	2.12E-03	4.06E-05	6.83E-02	6.44E-04	2.90E-03	5.77E-05	1.93E-03	4.47E-05
ND70-4-02	3	4.31E-04	5.71E-06	1.82E-03	2.31E-05	6.22E-02	5.18E-04	2.82E-03	9.30E-06	1.61E-03	2.41E-05
ND70-5-02	3	1.41E-03	2.04E-05	2.33E-03	7.00E-05	1.90E-01	5.93E-03	6.40E-03	1.38E-04	5.11E-03	2.39E-04
ND70-5-03	3	2.15E-04	1.88E-06	1.91E-03	1.44E-05	8.23E-03	1.69E-04	9.08E-04	8.60E-06	2.74E-04	3.87E-06
ND70-6-02	3	1.59E-03	1.99E-05	3.07E-03	1.44E-04	3.65E-01	1.20E-02	1.10E-02	5.96E-04	1.04E-02	6.60E-04
Other glasses analysed											
ND-70 (Natural)	3	2.10E-05	2.16E-06	5.64E-04	1.76E-05	3.63E-03	6.44E-05	1.73E-03	3.48E-05	1.73E-04	4.53E-06
Suprasil	3	1.97E-06	6.47E-07	2.43E-06	1.05E-06	1.64E-06	5.55E-07	4.60E-07	1.71E-07	3.01E-04	1.99E-05
M20	3	2.39E-04	2.30E-06	2.76E-03	8.94E-05	2.04E-03	6.06E-05	6.50E-04	1.64E-05	4.84E-05	2.47E-06
M35	3	1.20E-04	3.70E-06	2.06E-03	1.95E-05	1.93E-03	5.58E-06	5.10E-04	1.47E-05	3.69E-05	1.27E-06
ALV519-4-1	3	2.85E-05	1.02E-06	1.03E-04	4.84E-06	2.65E-03	7.42E-05	1.83E-03	3.79E-05	5.41E-05	5.31E-06
NS-1	3	5.50E-04	7.34E-06	2.40E-04	3.43E-06	2.56E-03	5.11E-05	8.66E-04	2.83E-05	4.02E-05	3.77E-06
VILLA_P2	3	1.27E-04	3.12E-06	2.03E-03	8.22E-05	3.71E-03	1.31E-04	3.17E-03	1.32E-04	7.54E-05	4.91E-06
INSOL_MX1_BA4	3	9.55E-04	9.31E-05	1.15E-04	1.80E-05	1.22E-02	1.87E-03	7.98E-04	4.14E-05	1.10E-04	1.28E-05

1015

1016

1017 **Table S8:** Raw SIMS analyses from IMS 1280 at JAMSTEC Kochi Institute using a Cs+ primary beam. All errors are given as one standard
 1018 deviation on repeat analyses or as one standard deviation from analytical error (whichever is the highest).

1019

Experiment #	SIMS (JAMSTEC-Kochi) Cs+ primary beam										
	n	¹² C/ ³⁰ Si	±	¹⁶ O ¹ H/ ³⁰ Si	±	¹⁹ F/ ³⁰ Si	±	³² S/ ³⁰ Si	±	³⁵ Cl/ ³⁰ Si	±
ND 70_ Degassed	2	0.0003	0.0000	0.0672	0.0001	0.0581	0.0019	0.0649	0.0248	0.0231	0.0130
ND70-2-01	3	0.0535	0.0007	5.6850	0.0125	2.5715	0.0211	1.1908	0.0084	0.9936	0.0293
ND70-3-01	3	0.0851	0.0038	7.4538	0.0213	3.5139	0.0345	1.7151	0.0124	2.1524	0.0438
ND70-4-01	3	0.1311	0.0005	10.1917	0.0813	8.2971	0.0472	3.9268	0.0527	4.5143	0.0374
ND70-4-02	3	0.1394	0.0008	9.0278	0.0500	7.6666	0.0085	3.8328	0.0112	4.3001	0.0219
ND70-5-02	3	0.3922	0.0026	13.1235	0.0254	26.3081	0.0764	11.4754	0.0503	13.9327	0.0475
ND70-6-02	3	0.4716	0.0184	17.2664	0.2443	48.3145	0.5284	20.8799	0.7687	25.0239	0.6325
Other glasses (and minerals) analyzed											
ND-70 (Natural)	2	0.0079	0.0033	2.3344	0.0095	0.3683	0.0019	1.4617	0.0058	0.3477	0.0075
Vol-std-G_EPR-G3	5	0.0141	0.0004	0.5373	0.0030	0.4153	0.0020	2.0627	0.0163	0.2352	0.0022
Vol-std-G_SC-ol	1	0.0004	0.0000	0.0098	0.0003	0.0057	0.0001	0.0003	0.0000	0.0003	0.0000
Vol-std-G_ELA-qz	4	0.0002	0.0002	0.0058	0.0013	0.0022	0.0005	0.0002	0.0001	0.0004	0.0001
Vol-std-G_IND-G1	1	0.0082	0.0001	1.1270	0.0036	0.6087	0.0020	1.7418	0.0043	0.1548	0.0006
Vol-std-G_Vol-3A	1	0.1786	0.0007	7.2310	0.0174	9.9764	0.0203	1.6415	0.0404	4.7743	0.0084
Vol-std-G_Vol-1B	1	0.1791	0.0005	2.0724	0.0038	2.9762	0.0046	1.1141	0.0020	1.4706	0.0012
Vol-std-G_Vol-05A	1	0.1333	0.0006	1.2576	0.0042	1.4683	0.0035	0.8625	0.0027	0.5378	0.0012
Vol-std-G_Vol-005B	1	0.0201	0.0001	0.2120	0.0005	0.1640	0.0004	0.0742	0.0004	0.0637	0.0004
Vol-std-G_MRN-G1	1	0.0002	0.0000	3.3626	0.0081	1.6462	0.0044	0.0859	0.0005	4.0661	0.0085
Vol-std-G_MA42	1	0.0574	0.0004	10.1889	0.0263	0.2469	0.0006	0.0468	0.0005	0.2145	0.0008
Vol-std-G_FJ-G2	1	0.0172	0.0001	0.5344	0.0014	0.4193	0.0010	2.2429	0.0039	0.1808	0.0006
Vol-std-G_IND-G2	1	0.0191	0.0002	1.2013	0.0022	0.7376	0.0016	1.7335	0.0047	0.1593	0.0005
Vol-std-G_vol-0B	1	0.0003	0.0000	0.0509	0.0005	0.0185	0.0003	0.0020	0.0001	0.0012	0.0000

1020

1021
1022
1023
1024

Table S9: Data used to generate Figure 8.

Sample number	SiO ₂ (normalized)	CO ₂ (ppm)	H ₂ O	SIMS Cs+ Nancy	SIMS Cs+ Nancy	SIMS Cs+ Kochi	SIMS Cs+ WHOI	SIMS O- WHOI	SIMS Cs+ Caltech	SIMS Cs+ Caltech	SIMS O- Caltech	SIMS Cs+ Nancy	SIMS Cs+ Nancy	SIMS Cs+ Kochi	SIMS Cs+ WHOI	SIMS O- WHOI	SIMS Cs+ Caltech	SIMS Cs+ Caltech	SIMS O- Caltech	
				¹² C/ ³⁰ Si	¹² C/ ¹⁸ O	¹² C/ ³⁰ Si	¹² C/ ³⁰ Si	¹² C/ ³⁰ Si	¹² C/ ³⁰ Si	¹² C/ ¹⁸ O	¹² C/ ³⁰ Si	¹² C/ ¹⁸ O	¹² C/ ³⁰ Si	(¹² C/ ³⁰ Si)x SiO ₂ /CO ₂	¹² C/ ¹⁸ O/CO ₂	(¹² C/ ³⁰ Si)x SiO ₂ /CO ₂	(¹² C/ ³⁰ Si)x SiO ₂ /CO ₂	(¹² C/ ³⁰ Si)x SiO ₂ /CO ₂	(¹² C/ ³⁰ Si)x SiO ₂ /CO ₂	¹² C/ ¹⁸ O/CO ₂
ND 70_ Degassed	50.1			1.74E-03	1.86E-03	3.11E-04														
ND70-2-01	49.8	1560	2.4	3.01E-02	2.65E-02	5.35E-02	5.67E-02	1.72E-04	4.78E-02	2.74E-02	9.32E-06	9.61E-04	1.70E-05	1.71E-03	1.81E-03	5.49E-06	1.53E-03	1.76E-05	2.98E-07	
ND70-3-01	49.5	2637	3.1	3.70E-02	3.34E-02	8.51E-02	9.97E-02	2.26E-04	7.52E-02	3.91E-02	1.38E-05	6.96E-04	1.27E-05	1.60E-03	1.87E-03	4.25E-06	1.41E-03	1.48E-05	2.59E-07	
ND70-4-01	50.2	4161	4.1	6.59E-02	5.09E-02	1.31E-01	1.42E-01	4.67E-04												
ND70-4-02	48.7	4214	3.6			1.39E-01	1.46E-01	4.31E-04	8.43E-02	5.84E-02	2.35E-05			1.61E-03	1.68E-03	4.98E-06	9.74E-04	1.39E-05	2.71E-07	
ND70-5-02	50.3	12237	5.0	1.72E-01	1.29E-01	3.92E-01	4.09E-01	1.41E-03	3.26E-01	1.48E-01	6.83E-05	7.05E-04	1.05E-05	1.61E-03	1.68E-03	5.78E-06	1.34E-03	1.21E-05	2.80E-07	
ND70-6-02	49.2	15847	6.4	1.73E-01	1.18E-01	4.72E-01	3.91E-01	1.59E-03	2.96E-01	1.27E-01	8.16E-05	5.37E-04	7.42E-06	1.46E-03	1.22E-03	4.93E-06	9.18E-04	8.01E-06	2.53E-07	
ND-70 (Natural)	50.4	145	1.0	5.09E-03	4.71E-03	7.86E-03	5.60E-03	2.10E-05	5.37E-03	3.29E-03		1.77E-03	3.24E-05	2.73E-03	1.94E-03	7.30E-06	1.86E-03	2.26E-05		
BF73	51.2	2995	0.7				1.15E-01		9.57E-02	6.02E-02					1.96E-03		1.64E-03	2.01E-05		
BF76	51.2	2336	0.7				9.77E-02		9.96E-02	5.70E-02					2.14E-03		2.18E-03	2.44E-05		
BF77	51.2	935	0.7				3.62E-02		3.35E-02	2.05E-02					1.98E-03		1.84E-03	2.19E-05		
M15	50.5	60	1.5				7.08E-03		5.50E-03	3.19E-03					5.95E-03		4.62E-03	5.32E-05		
M19	50.4	3277	3.3				1.21E-01		1.01E-01	5.40E-02					1.87E-03		1.55E-03	1.65E-05		
M20	50.4	2421	5.7				7.85E-02	2.39E-04	6.42E-02	2.87E-02					1.64E-03	4.98E-06	1.34E-03	1.19E-05		
M34	50.4	375	5.7	1.19E-02	7.46E-03		1.55E-02		1.06E-02	5.13E-03		1.61E-03	1.99E-05		2.08E-03		1.42E-03	1.37E-05		
M35	50.4	1019	4.2	2.87E-02	1.91E-02		4.17E-02	1.20E-04	3.47E-02	1.69E-02		1.42E-03	1.88E-05		2.06E-03	5.93E-06	1.72E-03	1.66E-05		
M40	50.3	2183	3.1	5.53E-02	3.90E-02							1.27E-03	1.79E-05							
M43	50.4	3172	2.6	8.01E-02	5.91E-02		1.27E-01		1.13E-01	6.04E-02	1.93E-05	1.27E-03	1.86E-05		2.01E-03		1.80E-03	1.90E-05	3.06E-07	
M48	51.0	176	0.8	1.23E-02	1.04E-02		1.37E-02		8.71E-03	5.37E-03		3.56E-03	5.91E-05		3.97E-03		2.52E-03	3.05E-05		
ALV519-4-1	49.1	165	0.2				9.80E-03	2.85E-05	7.74E-03	5.88E-03					2.91E-03	8.49E-06	2.30E-03	3.56E-05		
1846-12	50.8	90	1.6						4.98E-03	3.38E-03							2.81E-03	3.76E-05		

80-1-3	48.9	295	0.6			2.55E-02	1.50E-02	1.04E-02	4.42E-06			4.23E-03	2.49E-03	3.52E-05	7.33E-07	
1846-9	49.7	0	1.9			4.30E-04	2.85E-04	1.72E-04								
NS-1	50.4	3154	0.4			2.00E-01	5.50E-04	1.97E-01	1.22E-01	2.90E-05		3.19E-03	8.79E-06	3.15E-03	3.86E-05	4.63E-07
Villa_YM	53.2	835	3.9			4.16E-02	1.27E-04	3.44E-02	1.65E-02			2.65E-03	8.12E-06	2.19E-03	1.97E-05	
INSOL_MX1 _BA4	52.6	8207	0.2			3.70E-01	9.55E-04	2.96E-01	2.12E-01	5.08E-05		2.37E-03	6.13E-06	1.90E-03	2.58E-05	3.26E-07
VG2	50.8	153	0.3	1.02E-02	9.80E-03						3.40E-03	6.41E-05				
ALV_1833-1	53.9	24	2.4			6.68E-04							1.50E-03			
WOK28-3	49.8	183	0.5			1.37E-02							3.74E-03			
Vol-std- G_EPR-G3	50.2	269	0.2			1.41E-02							2.63E-03			
Vol-std- G_IND-G1	50.1	97	0.5			8.17E-03							4.22E-03			
Vol-std- G_Vol-1B	50.5	4686	0.9			1.79E-01							1.93E-03			
Vol-std- G_Vol-05A	50.5	3354	0.5			1.33E-01							2.01E-03			
Vol-std- G_Vol-005B	49.8	479	0.1			2.01E-02							2.09E-03			
Vol-std- G_MA42	51.8	1243	4.8			5.74E-02							2.39E-03			
Vol-std- G_FJ-G2	49.6	307	0.2			1.72E-02							2.78E-03			
Vol-std- G_IND-G2	50.3	389	0.5			1.91E-02							2.47E-03			

1025 **REFERENCES**

- 1026 Brounce, M., Reagan, M. K., Kelley, K. A., Cottrell, E., Shimizu, K., & Almeev, R. (2021). Covariation of Slab Tracers, Volatiles, and
1027 Oxidation During Subduction Initiation. *Geochemistry, Geophysics, Geosystems*, 22(6), e2021GC009823.
1028 <https://doi.org/10.1029/2021GC009823>
- 1029 Bryan, W. B., & Moore, J. G. (1977). Compositional variations of young basalts in the Mid-Atlantic Ridge rift valley near lat 36°49'N. *GSA*
1030 *Bulletin*, 88(4), 556–570. [https://doi.org/10.1130/0016-7606\(1977\)88<556:CVOYBI>2.0.CO;2](https://doi.org/10.1130/0016-7606(1977)88<556:CVOYBI>2.0.CO;2)
- 1031 Caulfield, J., Turner, S., Arculus, R., Dale, C., Jenner, F., Pearce, J., et al. (2012). Mantle flow, volatiles, slab-surface temperatures and melting
1032 dynamics in the north Tonga arc–Lau back-arc basin. *Journal of Geophysical Research: Solid Earth*, 117(B11).
1033 <https://doi.org/10.1029/2012JB009526>
- 1034 Hauri, E., Wang, J., Dixon, J. E., King, P. L., Mandeville, C., & Newman, S. (2002). SIMS analysis of volatiles in silicate glasses: 1.
1035 Calibration, matrix effects and comparisons with FTIR. *Chemical Geology*, 183(1–4), 99–114. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2541(01)00375-8)
1036 [2541\(01\)00375-8](https://doi.org/10.1016/S0009-2541(01)00375-8)
- 1037 Helo, C., Longpré, M.-A., Shimizu, N., Clague, D. A., & Stix, J. (2011). Explosive eruptions at mid-ocean ridges driven by CO₂-rich magmas.
1038 *Nature Geoscience*, 4(4), 260–263. <https://doi.org/10.1038/ngeo1104>
- 1039 Jarosewich, E., Nelen, J. a., & Norberg, J. A. (1980). Reference Samples for Electron Microprobe Analysis*. *Geostandards Newsletter*, 4(1),
1040 43–47. <https://doi.org/10.1111/j.1751-908X.1980.tb00273.x>
- 1041 Jochum, K. P., Stoll, B., Herwig, K., Willbold, M., Hofmann, A. W., Amini, M., et al. (2006). MPI-DING reference glasses for in situ
1042 microanalysis: New reference values for element concentrations and isotope ratios. *Geochemistry, Geophysics, Geosystems*, 7(2).
1043 <https://doi.org/10.1029/2005GC001060>

- 1044 Kamenetsky, V. S., Everard, J. L., Crawford, A. J., Varne, R., Eggins, S. M., & Lanyon, R. (2000). Enriched End-member of Primitive MORB
1045 Melts: Petrology and Geochemistry of Glasses from Macquarie Island (SW Pacific). *Journal of Petrology*, 41(3), 411–430.
1046 <https://doi.org/10.1093/petrology/41.3.411>
- 1047 Keller, N. S., Arculus, R. J., Hermann, J., & Richards, S. (2008). Submarine back-arc lava with arc signature: Fonualei Spreading Center,
1048 northeast Lau Basin, Tonga. *Journal of Geophysical Research: Solid Earth*, 113(B8). <https://doi.org/10.1029/2007JB005451>
- 1049 Kumamoto, K. M., Warren, J. M., & Hauri, E. H. (2017). New SIMS reference materials for measuring water in upper mantle minerals.
1050 *American Mineralogist*, 102(3), 537–547. <https://doi.org/10.2138/am-2017-5863CCBYNCND>
- 1051 Lloyd, A. S., Plank, T., Ruprecht, P., Hauri, E. H., & Rose, W. (2013). Volatile loss from melt inclusions in pyroclasts of differing sizes.
1052 *Contributions to Mineralogy and Petrology*, 165(1), 129–153. <https://doi.org/10.1007/s00410-012-0800-2>
- 1053 Mandeville, C. W., Webster, J. D., Rutherford, M. J., Taylor, B. E., Timbal, A., & Faure, K. (2002). Determination of molar absorptivities for
1054 infrared absorption bands of H₂O in andesitic glasses. *American Mineralogist*, 87(7), 813–821. <https://doi.org/10.2138/am-2002-0702>
- 1055 Mosbah, M., Metrich, N., & Massiot, P. (1991). PIGME fluorine determination using a nuclear microprobe with application to glass inclusions.
1056 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 58(2), 227–231.
1057 [https://doi.org/10.1016/0168-583X\(91\)95592-2](https://doi.org/10.1016/0168-583X(91)95592-2)
- 1058 Newman, S., Stolper, E., & Stern, R. (2000). H₂O and CO₂ in magmas from the Mariana arc and back arc systems. *Geochemistry, Geophysics,*
1059 *Geosystems*, 1(5). <https://doi.org/10.1029/1999GC000027>
- 1060 Rose-Koga, E. F., Koga, K. T., Devidal, J.-L., Shimizu, N., Voyer, M. L., Dalou, C., & Döbeli, M. (2020). In-situ measurements of magmatic
1061 volatile elements, F, S, and Cl, by electron microprobe, secondary ion mass spectrometry, and heavy ion elastic recoil detection analysis.
1062 *American Mineralogist*, 105(5), 616–626. <https://doi.org/10.2138/am-2020-7221>
- 1063 Shi, S. C., Towbin, W. H., Plank, T., Barth, A., Rasmussen, D., Moussallam, Y., et al. (2023). PyIRoGlass: An Open-Source, Bayesian MCMC
1064 Algorithm for Fitting Baselines to FTIR Spectra of Basaltic-Andesitic Glasses. Retrieved from
1065 <https://eartharxiv.org/repository/view/6193/>

- 1066 Shimizu, K., Alexander, C. M. O., Hauri, E. H., Sarafian, A. R., Nittler, L. R., Wang, J., et al. (2021). Highly volatile element (H, C, F, Cl, S)
1067 abundances and H isotopic compositions in chondrules from carbonaceous and ordinary chondrites. *Geochimica et Cosmochimica Acta*,
1068 *301*, 230–258. <https://doi.org/10.1016/j.gca.2021.03.005>
- 1069 Shimizu, K., Ushikubo, T., Hamada, M., Itoh, S., Higashi, Y., Takahashi, E., & Ito, M. (2017). H₂O, CO₂, F, S, Cl, and P₂O₅ analyses of silicate
1070 glasses using SIMS: Report of volatile standard glasses. *Geochemical Journal*, *51*(4), 299–313. <https://doi.org/10.2343/geochemj.2.0470>
- 1071 Shishkina, T. A., Botcharnikov, R. E., Holtz, F., Almeev, R. R., & Portnyagin, M. V. (2010). Solubility of H₂O- and CO₂-bearing fluids in
1072 tholeiitic basalts at pressures up to 500 MPa. *Chemical Geology*, *277*(1–2), 115–125. <https://doi.org/10.1016/j.chemgeo.2010.07.014>
- 1073
- 1074