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1 **Raman spectroscopy to determine CO₂ solubility in mafic silicate melts at high**
2 **pressure: haplobasaltic, haploandesitic and approach of basaltic compositions**

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4 Julien Amalberti^{1,2}, Philippe Sarda^{1,3,4*}, Charles Le Losq², Nicolas Sator^{5,6}, Tahar Hammouda^{7,8,9},
5 Eva Chamorro-Perez^{3,4}, Bertrand Guillot^{5,6}, Sylvie Le Floch¹⁰ and Daniel R. Neuville²

6
7 ¹ Université Paris-Saclay, CNRS-GEOPS, Rue du Belvédère, Bât. 504, 91405 Orsay, France

8 ² CNRS-IPGP, Université de Paris, 1 rue Jussieu, Paris F-75005, France

9 ³ ENS de Lyon, Laboratoire de Géologie de Lyon, UMR 5276, 15 parvis René Descartes, F-69342
10 Lyon Cedex 07, France

11 ⁴ CNRS, F-69342 Lyon Cedex 07, France

12 ⁵ Sorbonne Universités, UPMC Univ. Paris 6, UMR 7600, LPTMC, Paris F-75005, France

13 ⁶ CNRS, Paris F-75005, France

14 ⁷ Université Blaise Pascal Clermont-Ferrand 2, Laboratoire Magmas et Volcans, UMR-CNRS 6524,
15 UMR-IRD 163, Clermont-Ferrand F-63038, France

16 ⁸ CNRS, Clermont-Ferrand F-63038, France

17 ⁹ IRD, Clermont-Ferrand F-63038, France

18 ¹⁰ Institut Lumière Matière, Université Lyon1 – CNRS, UMR 5306, Université de Lyon, 69622
19 Villeurbanne, France

20
21 * corresponding author: philippe.sarda@universite-paris-saclay.fr

22
23 Keywords: Carbon dioxide; basaltic melt; andesitic melt; solubility; high pressure; confocal micro-
24 Raman spectroscopy; molecular dynamics simulation

25
26 **Abstract:**

27 CO₂ degassing of mafic silicate melts is an important part of the terrestrial carbon cycle, at mid-
28 ocean ridges, oceanic hot spots, or in the middle of continents. Deeper CO₂-bearing mafic magmas
29 may also exist, such as those suspected in the D'' zone, and certainly existed in the magma ocean
30 of the early Earth. Knowledge of the CO₂ solubility in mafic melts at high pressure is therefore
31 important but unknown at present. Results from molecular dynamics simulation (e.g., Guillot and
32 Sator, 2011) predict that CO₂ solubility in basalt may be much higher than previously thought at
33 pressures and temperatures relevant to the upper mantle. But some recent models predict low
34 solubility at high pressure (e.g., Eguchi and Dasgupta, 2018). The present study thus
35 experimentally investigates the solubility of CO₂ in basalt and andesite in the pressure range 1.5-
36 8.5 GPa at 1820-2130 K in oxidizing conditions. Up to 4 GPa, the quenched samples are essentially
37 vitreous and CO₂-saturated. Their CO₂ contents are measured using confocal micro-Raman
38 spectroscopy, where we establish an internal calibration line relating CO₂ content to the area of the
39 Raman band assigned to the ν_1 stretching vibration of carbonate groups. This calibration appears
40 independent from the spectrometer, sample or experimentalist, thus enhancing confidence in this
41 method. At 5 and 8.5 GPa, the quenched samples are found partially crystallized. Their CO₂
42 abundance is estimated at micro-scale from Raman mapping, and at large scale from image

43 analysis and presence/absence of vesicles. Over the 1.5-8.5 GPa pressure range, obtained CO₂
44 concentrations vary between 1.8 and >13.6 wt.%. At 5 GPa and 1873 K, the CO₂ content in basalt
45 and andesite are similar. These findings experimentally confirm the ability of mafic melts to
46 accommodate large amounts of CO₂ at conditions prevailing in the deep Earth. A consequence is
47 that magmas issued from partial melting of carbonate-bearing silicate rocks may ascend with
48 significant quantities of CO₂ of several wt.% and more: when reaching shallower depths, they may
49 degas large quantities of CO₂. Present estimates of the global carbon flux to the atmosphere may
50 thus be underestimated, and implications to early magma ocean degassing may be considered.
51 Other consequences may concern the genesis of kimberlites and carbonatites. We finally speculate
52 that, if silicate melts exist in the D'' zone, significant amounts of carbon may be stored there, and
53 consequences may arise as to carbon sequestration in the core.

54

55 **1. Introduction**

56

57 CO₂ and H₂O are the two most abundant volatile species of the inner planets (Gerlach and
58 Nordlie, 1975). On the Earth, they constitute a great deal of several external reservoirs such as the
59 atmosphere, the oceans or the carbonates of the crust, and play a fundamental role in determining
60 past and present surface temperatures (Ringwood, 1966; Cameron, 1973). They are also important
61 in geodynamics because of their effects on the mantle solidus and liquidus as well as on the
62 properties of melts (Kushiro et al., 1968; Egglar, 1976; Kawamoto and Holloway, 1997; Dasgupta
63 and Hirschmann, 2006; Green et al. 2010; Pommier et al. 2012, Hammouda and Keshav, 2015).
64 Therefore, it is important to understand their behavior in planetary processes.

65 In this paper, we focus on CO₂. Since basalt is the main magma type resulting from melting of
66 the terrestrial interior, and probably other planetary interiors (Stanley et al., 2012), we study the
67 question of how much CO₂ can be dissolved in basaltic melts (and one intermediate).

68 At present, basaltic melts are produced mainly at mid-ocean ridges, subduction zones and hot
69 spots, but it has been suggested that melt could also be present close to the core, in the so-called
70 D'' zone between about 2800 and 2900 km depth (Labrosse et al., 2007).

71 Solubility of CO₂ in melt controls degassing, i.e., the way CO₂ exits the solid Earth, an important
72 part of the carbon cycle, past and present (Dasgupta and Hirschmann, 2010). In very ancient
73 geological times, degassing occurred massively as recorded by noble gas isotopes (e.g., Sarda et
74 al., 1985), probably in the shallow regions of a magma ocean (e.g., Elkins-Tanton, 2012). Such
75 degassing mainly released H₂O and CO₂ since this magma ocean was likely H₂O- and CO₂-rich
76 (e.g., Marty, 2012), contributing to establish the P,T conditions at the surface, which in turn
77 influenced magma ocean cooling (e.g. Lebrun et al., 2013; Hamano et al., 2013).

78 In these ancient times, the silicate Earth may have been completely molten (e.g., review in
79 Elkins-Tanton, 2012), hence the terrestrial magma ocean was possibly as deep as the present
80 core-mantle boundary (CMB). Work on heat in the Earth raised the hypothesis that the magma
81 ocean did not crystallize at great depth, thus generating the so-called basal magma ocean
82 (Labrosse, 2007; Coltice et al., 2011). That melt may have existed at such great depths raises the
83 question of how much carbon it could have contained, an important question for carbon partitioning
84 with iron (e.g., Chi et al., 2014), given that carbon could be among the light elements in the

85 present core (e.g., Wood, 1993). These matters are currently the subject of experiments and
86 discussions (e.g., Grewal et al., 2019), but knowledge of CO₂ solubility in melt at such very high
87 pressure is necessary to better understand carbon sequestration into the core during its early
88 differentiation.

89 At present, and for more recent geologic times, high pressure CO₂ solubility in melt is important
90 everywhere deep magmas may exist. One example is given by the low velocity seismic anomalies
91 evidenced in the D'' zone (e.g., Vinnik et al., 1998), just above the CMB, which may be explained
92 by the existence of silicate melts (e.g., Williams and Garnero, 1996; Coltice et al., 2011).

93 Other examples include the above-mentioned degassing of basaltic melts ascending at Mid-
94 Oceanic Ridges or subduction zones, witnessed by numerous CO₂ vesicles in samples (e.g. Moore,
95 1978; Sarda and Graham, 1990; Chavrit et al., 2014), continental magmatism, where degassed
96 CO₂ may be stored in sedimentary basins (e.g., Ballentine et al. 1991; Ballentine, 1997), the rare
97 occurrence of carbonatites in continental areas (Woolley and Church, 2005) and some oceanic
98 islands (Mourão et al., 2012), or else the existence of kimberlites (Sparks et al., 2006; Mitchell,
99 2008), which are derived from carbon-rich silicate melts (Brooker et al., 2011).

100 Concerning depth and pressure, the latter examples probably involve CO₂ melts in the first 100-
101 300 km of the Earth, i.e., pressures up to roughly 10 GPa, and studies of the magma ocean
102 degassing or of the D'' zone require knowledge of CO₂ solubility at much higher pressures, up to
103 ~100 GPa.

104 Solubility of CO₂ in silicate melts has been both documented in an experimental way and
105 approached in a theoretical way. On the experimental side, early studies reach relatively low
106 pressures and used silicic compositions because experiments are easier (see reviews in Blank and
107 Brooker, 1994; Ni and Kepler, 2013). More recently, higher pressures were reached but, for mafic
108 compositions, few studies achieve pressures higher than 1 GPa, and very few higher than 3 GPa
109 (review in Iacono-Marzano et al., 2012). On the theoretical side, often to interpret experimental
110 data, a first approach developed classical models based on macroscopic thermodynamics yielding a
111 very abundant literature (e.g., Khitarov et Kadik, 1973; Dixon et al., 1995; Papale, 1999; Behrens
112 et al. 2004; Iacono-Marzano et al., 2012). These models are essentially empirical and include
113 parameters that are adjusted to reproduce experimental data.

114 Another theoretical approach is molecular dynamics (MD), where the very atoms are simulated
115 in their relations with all the other atoms of their environment, allowing their interactions and their
116 bonds to be reproduced from basic principles (e.g., Genge et al., 1995 for carbonate melt).
117 Although ab initio calculation is in principle possible, it is practically difficult to be used for the
118 complex silicate melts, demanding short simulation times and small numbers of atoms, but being
119 possible in the case of crystals (e.g., Gerin et al., 2017). Whereas pioneering studies of silicate
120 melts by ab initio calculations exist (Vuilleumier et al., 2015), current simulations are based on a
121 force field determined previously (Guillot and Sator, 2007a,b), and constantly refined (e.g., Dufils
122 et al., 2017).

123 A molecular dynamics simulation study (Guillot and Sator, 2011) has shown that the CO₂
124 amount a silicate melt can dissolve at high pressure far exceeds the amount predicted by the
125 Henry's law constrained by low-pressure data, e.g., ~20 wt.% CO₂ in MORB at 8 GPa and 1873K,
126 as compared to ~4 wt.%. The simulation of Guillot and Sator (2011) also confirms that the high-
127 pressure CO₂ solubility increases with increasing number of non-bridging oxygen atoms (NBOs) in

128 the melt (e.g., Verweij et al., 1977; Brooker et al., 2001a). Though these simulation results agree
129 with the few solubility data for mafic compositions available at moderate pressures of 1-2 GPa
130 (Mattey, 1991; Pan et al., 1991; Stanley et al., 2012; Li et al., 2017) and more recently up to 3
131 GPa (Stanley et al., 2011; Eguchi and Dasgupta, 2017), experimental data at pressure above ~3
132 GPa is still lacking. Moreover, the recent model of Eguchi and Dasgupta (2018) contradicts the
133 simulation of Guillot and Sator (2011) in predicting low CO₂ concentrations at pressures above ~5
134 GPa. Only one recent study exists for pressures higher than 3 GPa, that of Kim et al. (2018) at 6
135 GPa, where 15 wt.% CO₂ was measured using Nuclear Magnetic Resonance (NMR) spectroscopy,
136 and it agrees with the very high CO₂ solubilities suggested by the simulations, although it is for an
137 albitic composition.

138 To extend the pressure range where the solubility of CO₂ in basaltic melts is known, we
139 performed high pressure - high temperature experiments on CO₂-bearing mafic and intermediate
140 samples in the pressure range 1.5-8.5 GPa, at about 1820 - 2130 K, and in oxidizing conditions.
141 This is a challenging task because very high temperatures must be reached and maintained at high
142 pressure. Of course, the melts used here are not natural melts, but are as close as possible, with
143 the techniques used. We are aware that our results only approach the behavior of natural melts,
144 but we are confident that they must be quite close as indicated by comparison with previous
145 experimental results or with theoretical simulations (section 4).

146 At pressures higher than ~1 GPa, the amount of dissolved CO₂ is larger than 1 wt.%. At such
147 concentrations, Fourier transform infrared (FTIR) spectroscopy, which is routinely used to measure
148 CO₂ solubility (e.g., Stolper and Holloway, 1988; Dixon et al. 1995; Eguchi and Dasgupta, 2017),
149 becomes difficult to use because most of the IR photons are absorbed by the sample, which
150 demands samples to be vanishingly thin (see Brooker et al., 1999).

151 The alternative we use here is Raman spectroscopy. Indeed, Raman spectroscopy has
152 demonstrated its efficiency to quantify various volatiles in silicate glass, such as H₂O (Thomas,
153 2000; Chabiron et al., 2004; Behrens et al., 2006; Mercier et al., 2010; Le Losq et al. 2012), SO₄²⁻
154 (Manara et al., 2007; Lenoir et al., 2009, 2010) or N₂ (Roskosz et al., 2006). About CO₂, Raman
155 spectroscopy was recently used to measure the density of CO₂ in bubbles present in melt inclusions
156 of minerals, and, coupled with optically measured vesicularity, to yield the CO₂ concentration in the
157 inclusion (Capriolo et al. 2020). For direct measurement of CO₂ present in silicate melt or glass
158 using Raman spectroscopy, feasibility studies appeared first (Sarda et al., 2009; Amalberti et al.,
159 2011a,b) and Morizet et al. (2013) more recently published a calibration for this method.

160 In the present work, we thus use Raman spectroscopy to measure the CO₂ content of glasses
161 synthesized at high pressure, that were saturated in CO₂ as indicated by the presence of a bubble.
162 For partially crystallized samples synthesized at $P \geq 4$ GPa, analysis of microscope images or the
163 absence of any vesicle allows estimating the fraction of dissolved CO₂. To discuss those
164 experimental data, we also report results from a molecular dynamic simulation of CO₂-bearing
165 silicate melts, using the force field of Guillot and Sator (2011).

166

167 **2. Experimental set up**

168

169 **2.1. Starting materials and high-pressure experiments**

170 In this study, we focus on mafic melts and tried to approach basaltic and andesitic
171 compositions. Of course, the prepared samples approach basalt and andesite as close as possible,
172 but, as explained below, it is impossible to experiment on compositions rigorously identical to
173 basalt and andesite. In the following, we may use the terms basalt and andesite, keeping in mind
174 that the reported experiments used starting compositions, given in Table 1, that differ to some
175 extent.

176 *Internal calibration of Raman analysis for CO₂*

177 For this work, internal calibration is based on two kinds of samples. One is potassium silicate
178 glass prepared at ambient pressure, for which dissolved CO₂ was previously quantified and
179 published. We used two potassium silicate glass aliquots, dubbed KS here, obtained by Bourgue
180 and Richet (2001). One of these is without CO₂. The other was prepared by melting a mixture of
181 powdered SiO₂ and K₂CO₃. Dissolved CO₂ of the latter sample was quantified by these authors
182 using a LECO® cell, giving a CO₂ concentration of 3.6 wt.% (Bourgue and Richet, 2001) More
183 details are given in section 2.3.

184 The other kind of sample used for internal calibration is a selection of our studied samples, for
185 which H₂O was also quantified by Raman spectroscopy following the method of Le Losq et al.
186 (2012), and the CO₂ was then deduced from the budget of all the major elements plus water (Table
187 2 and section 2.3).

188

189 *Basaltic natural and synthetic samples exposed to pressures up to 5 GPa with a Belt-type press*

190 For high temperature - high pressure (HT-HP) experiments with pressure in the range 1.5–4
191 GPa, a CO₂-bearing starting material close to the basaltic composition was prepared by mixing a
192 tholeiite glass from the South Atlantic Ocean labeled EW9309 14D-4g (Douglass et al., 1999) with
193 an amount of powdered calcite, large enough for the resulting basaltic melt to be CO₂-saturated at
194 such pressures (> 10 wt.% CO₂). The corresponding samples are named BPhE2 and BPhE3 in
195 Tables 1 and 2.

196 For comparison, and to avoid iron loss to the platinum capsule (e.g., Gudmundsson and
197 Holloway, 1993), an iron-free starting material was prepared by mixing appropriate amounts of
198 high purity powdered oxides (SiO₂, TiO₂, Al₂O₃ and MgO) and carbonates (CaCO₃ and Na₂CO₃), the
199 composition of the resulting HT-HP melt being haplo-tholeiitic (samples BPhE10, BPhE11 and
200 BPhE12 in Tables 1 and 2). The resulting CO₂ concentration was calculated to be ~10.8 wt.% CO₂,
201 large enough to saturate the silicate melt in CO₂ at pressures of 1.5-4 GPa. Of course, iron has
202 important influence on physical properties of melts (e.g., Chevrel et al., 2013 about rheology), but
203 our results on these compositions are only a tentative approach of reality. However, we recall that
204 Fe²⁺, in contrast to K⁺, Na⁺ and Ca²⁺, is a cation that has the weakest influence on CO₂ solubility
205 together with Mg (Brooker et al., 2001a).

206 All the above samples were placed into a platinum capsule that was arc-electrically welded.
207 They were exposed to high pressures using a Belt-type press at Institut Lumière Matière,
208 Université Claude Bernard Lyon1, France (e.g., Toulemonde et al., 2005). The cell assembly
209 includes a pyrophyllite sleeve, with two pyrophyllite gaskets and two steel plugs (see Fig.2 in San
210 Miguel and Toulemonde, 2005), that receives the sample assembly composed of a graphite
211 furnace, a periclase sleeve and the sample capsule. Pressure is not measured but known from

212 laboratory calibration with an estimated 1σ error of 5% (Table 2). Melting basaltic compositions
213 under such high pressures requires very high temperatures of 1500°C-1800°C, depending on
214 pressure, which are difficult to obtain. An assembly minimizing heat loss, including a graphite
215 furnace and a periclase sleeve receiving the platinum capsule, was thus especially designed, and
216 realized for these experiments (Supplement, Fig. S1).

217 With this press, the assembly rapidly creeps at high pressure when exposed to such high
218 temperatures. Therefore, experiments did not last more than 30 min. Heating was interrupted by
219 turning off electrical power, which is expected to chill melt into glass with minimum crystallization.
220 The observed cooling rate is ~ 2 degrees/s, a relatively slow value compared to the multi-anvil
221 press also used in this study (see below), probably due to the pyrophyllite sleeve acting as a
222 thermal insulator (also reported in Liu et al., 2015). Pressure was then slowly brought back to
223 ambient, to avoid cracks as far as possible.

224 The assembly has no routine thermocouple, and, because of creeping, it is impossible to
225 calibrate temperature up to the values reached in our experiments. Because temperature should
226 have a weak influence on CO₂ solubility, our intention was to obtain complete melting, even if
227 temperature was not accurately known. We thus initially used temperature estimates available in
228 the laboratory from applied electrical power. Later, we performed careful experiments dedicated to
229 temperature calibration using S-type Pt10%Rh-Pt thermocouples up to $\sim 1000^\circ\text{C}$ and extrapolated
230 to the highest power values. The temperatures obtained for BPhE samples have an estimated 1σ
231 error of $\sim 50^\circ\text{C}$ and are reported in Table 2. They are higher than initially assumed by up to 200
232 degrees. Therefore, the platinum capsules were probably very soft. Indeed, we observed that, in
233 most of the BPhE experiments, a cavity is present within the Pt metal at the top of the capsule,
234 certainly the remnant of a CO₂ bubble (e.g., Fig. S2A for BPHE11). Although known with some
235 uncertainty, such high temperatures give supplementary assurance that the starting material
236 indeed melted completely, and these cavities suggest that melts were indeed CO₂-saturated.

237

238 *Basaltic and andesitic synthetic samples up to 8.5 GPa with a multi-anvil press*

239 Another series of experiments were carried out using a multi-anvil press at pressures from 5 to
240 8.5 GPa. Two other glasses were synthesized from reagent grade powders of MgO, Al₂O₃ and SiO₂
241 mixed in the right proportions to obtain, after melting at 1923 K, a first glass with 63 mol.% SiO₂,
242 18 mol.% Al₂O₃, and 19 mol.% MgO, and a second glass with 76 mol.% SiO₂, 17 mol.% Al₂O₃, and
243 7 mol.% MgO. To ensure getting glass with no vestige of any crystal, the initial mixture was melted
244 in air at 1350°C for 12 hours and up to 1650°C for 2 additional hours, then quenched, grinded, and
245 melted again, such a cycle been repeated no less than 4 times (Neuville et al., 2008).

246 To these compositions was added a carbonate mixture of reagent grade powders of MgCO₃,
247 CaCO₃ and Na₂CO₃ to obtain, respectively, a basaltic glass powder (samples 1010 and 1011), and
248 an andesitic glass powder (sample 1090), both with excess CO₂. This CO₂ excess was calculated to
249 be ~ 13.6 wt.% for samples 1010 and 1011, and ~ 9.0 wt.% for sample 1090 (see Table 1).

250 The multi-anvil press allowed us to achieve higher pressures than the Belt press. These
251 experiments were performed at the "Laboratoire Magmas et Volcans" in Clermont-Ferrand
252 (France). A Pt capsule contains the sample and is closed by electric arc welding. This Pt capsule is
253 placed into a cell assembly that includes a ceramic octahedron, a ZrO₂ sleeve used as thermal

254 insulator, a LaCrO₃ furnace, and an MgO sleeve around the Pt capsule (Hammouda, 2003). This cell
255 assembly is then placed into a multi-anvil press (Kawai and Endo, 1970) with a Walker-type
256 module (Walker et al., 1990). Pressure is not measured but known from laboratory calibration with
257 a 1 σ error of 0.25 GPa (Table 2). During each experiment, temperature was monitored by a W-Re
258 thermocouple routinely placed above the Pt capsule and was regulated at 1873 \pm 1 K (1 σ).
259 Temperature gradient across the assembly is estimated to \pm 50°C so that the 1 σ uncertainty on
260 sample temperature is estimated to be 25°C (Table 2). Experiments ran for several hours, making
261 it safer that equilibrium was reached. After having been exposed to HT-HP conditions, the melt was
262 quenched by turning off electrical power, where the cooling rate is on the order of 100 K/s
263 (Hammouda, 2003).

264

265 *Redox state estimate*

266 We did not attempt to measure the redox state in our samples. For all the experiments, samples
267 were contained in a platinum capsule. No reduced material was at the contact with capsules during
268 runs: in BPhE experiments, the carbon furnace was always outside the platinum capsule, separated
269 from it by the periclase sleeve, and, in experiments run with the multi-anvil press, the capsule was
270 located in a MgO sleeve, while the furnace around it is made of LaCrO₃, both being surrounded by a
271 ZrO sleeve and a MgO octahedron, all these being oxidized compounds.

272 No attempt was done to vary the redox state in the present experiments. Hence, we believe our
273 samples remained in a relatively oxidizing state, i.e., close to that of a natural basalt from Mid-
274 Ocean Ridges with an oxygen fugacity of \sim FMQ – 0.4 (e.g., Bézou and Humler, 2005; FMQ is the
275 fayalite-magnetite-quartz buffer).

276 This conclusion is supported by the Raman spectra of our iron-bearing samples, where the raw
277 spectra leave no doubt as to the presence of iron as Fe³⁺ in the melt (see below, section 2.3.; e.g.,
278 Magnien et al., 2006, 2008; Roskosz et al., 2008; Cochain et al., 2012; Le Losq et al., 2019). Our
279 measured CO₂ concentrations do not contradict this conclusion, since, according to Li et al. (2017),
280 our *lowest* value (\sim 1.6 wt.%) points to $\log f_{\text{O}_2}$ being above \sim IW + 2.5 (roughly 1.3 logs units
281 below the MORB value of Bézou and Humler, 2005).

282

283 *Measurements on samples brought back to ambient pressure*

284 The CO₂ contents in the samples back from HP-HT were determined by Raman spectroscopy,
285 since FTIR is difficult to use at such high CO₂ concentrations (Table 2). The chemical composition of
286 the run products (Table 2) was obtained from electron microprobe analyzes performed at
287 Clermont-Ferrand for BPhE samples, and at University Pierre et Marie Curie, in Paris, for samples
288 1010, 1011 and 1090.

289

290 **2.2. Raman spectroscopy analyzes**

291

292 *Raman spectrometry*

293 Raman spectra were recorded using a triple grating T64000 Jobin-Yvon® Raman spectrometer
294 equipped with a confocal system, a 1024 charge-coupled device (CCD) detector cooled by liquid
295 nitrogen and an Olympus® microscope. The optimal spatial resolution is 1-2 μm^2 with an x100

296 Olympus® objective, and the spectral resolution is 0.7 cm⁻¹. A Coherent® laser 70-C5 Ar⁺, having a
297 wavelength of 514.532 nm, is used as the excitation line, with a laser power of 150 to 250 mW. No
298 damage caused by the laser was observed, even for high iron content samples (Magnien et al.,
299 2006). All spectra were acquired in the 15-4000 cm⁻¹ frequency-range, with an exposure time of
300 300 s in 3 repetitions. For an optimum signal/noise ratio, the Raman spot was focalized at 10 μm
301 below sample surface (Behrens et al., 2006). Raw Raman spectra are given in supplement Fig. S3.

302

303 *Preliminary treatment of Raman spectra*

304 After acquisition, all spectra were corrected for temperature and excitation line effects by
305 applying the Long correction (Shuker and Gammon, 1970; Long, 1977; Galeener and Sen, 1978;
306 Mysen et al., 1982). Then, background was subtracted following the protocol described in Le Losq
307 et al. (2012). The background is defined by a generalized cross-validation cubic spline baseline
308 (Craven and Wahba, 1979; Woltring, 1986) that is fitted to portions of Raman spectra devoid of
309 signal (Fig. 1a and Fig. S3). After baseline subtraction, spectra were normalized to their maximum
310 intensity, and these successive steps are illustrated in Fig. 1a. Then, as described next, a
311 deconvolution procedure was applied to the region of interest to extract the carbonate peak (Fig.
312 1b). For clarity, these four successive stages of treatment are also illustrated in Fig. S4 for one
313 spectrum.

314

315 **2.3. CO₂-related Raman peaks and calibration**

316

317 *Raman peaks and their deconvolution*

318 When CO₂ dissolves into a silicate melt, it is incorporated either under the molecular form (CO₂)
319 or as carbonate ion (CO₃²⁻). By analogy between Raman and infrared spectra of fluid CO₂ and
320 carbonates, the Raman bands due to CO₂ and CO₃²⁻ present in silicate glasses have been known for
321 long (Verweij et al., 1977; Sharma, 1979; Mysen and Virgo, 1980; Rai et al., 1983; Brooker et al.,
322 1999; Bourgue and Richet, 2001): a weak band at ~ 650 cm⁻¹ corresponds to a bending mode of
323 CO₃²⁻ (out of the molecule plane), a strong band at ~ 1080–1090 cm⁻¹ is associated with the
324 symmetric stretching mode (ν₁) of CO₃²⁻ and a doublet in the region of 1400-1500 cm⁻¹ is due to
325 the asymmetric stretching vibrations (ν₃) of CO₃²⁻ (Fig. 1a); molecular CO₂ generates a doublet in
326 the 1286-1388 cm⁻¹ range (see Burke and Lustenhouwer, 1987). For comparison, the molecular
327 CO₂ doublet in gas hydrates is at 1274-1382 cm⁻¹ (Nakano et al., 1998). In silicate glasses of
328 basaltic composition, it is believed that CO₂ is dissolved essentially under the form of carbonate
329 ions (Stolper and Holloway, 1988; Matthey, 1991; Pan et al., 1991; Dixon et al. 1995; Brooker et
330 al., 1999, 2001a,b) and, besides, we found no evidence for molecular CO₂ in any of the Raman
331 spectra of our quenched samples (e.g., Fig. 1a). Therefore, we use the intense peak assigned to
332 symmetric stretching vibrations of the carbonate ion at 1080-1090 cm⁻¹ to quantify the global CO₂
333 content in the samples.

334 However, contrary to the peak assigned to O-H stretching in hydrous glasses that allows
335 quantification of water (Fig. 1a), the ~1085 cm⁻¹ peak is mixed with signals from T-O (T=Si, Al)
336 stretching vibrations in Qⁿ units (i.e., SiO₄ and AlO₄ tetrahedra with *n* bridging oxygens (Schramm
337 et al., 1984). We thus need to separate the peak due to CO₃²⁻ symmetric stretching from the

338 signals generated by T-O stretching. To do so, corrected-normalized Raman spectra are fitted using
 339 a combination of Gaussian bands, as documented in Mysen et al. (1982) (see also Mysen, 1990;
 340 Neuville, 2006 and Le Losq et al., 2014). Fig. 1b shows examples of this deconvolution procedure
 341 (more examples are given in Fig. S5). The number of peaks depends on the glass chemical
 342 composition, i.e., on its initial depolymerization: obtained peaks at wavenumbers of 800, 880, 950,
 343 1100 and 1150-1200 cm^{-1} are assigned to Si-O symmetric stretching in Q^0 , Q^1 , Q^2 , Q^3 and Q^4 units
 344 respectively (Brawer and White, 1975, 1977; Virgo et al., 1980; Mysen et al., 1982; McMillan,
 345 1984). One peak near 1050 cm^{-1} is also obtained, that can be assigned to asymmetric stretching of
 346 Si-O bonds in Q^n units (Le Losq et al., 2014 and references therein).

347 We remark that the peak at $\sim 1000 \text{ cm}^{-1}$ in Fig. 1b that is assigned to Q^3 is in fact a combination
 348 of Q^3 and Fe^{3+} (e.g. Magnien et al., 2006, 2008; Roskosz et al., 2008; Cochain et al., 2012; Le
 349 Losq et al., 2019) and this is seen on the subtle shoulder of the raw spectrum in this region. The
 350 occurrence of Fe^{3+} indicates the oxidized state of our samples (see discussion above).

351 Then, the area of all the peaks found are measured and that assigned to CO_3^{2-} is normalized to
 352 the sum of the areas of *all* the deconvoluted peaks, including CO_3^{2-} itself, as illustrated by relation
 353 (1):

$$354 \quad A_{\text{CO}_3^{2-}} = \frac{a(\text{CO}_3^{2-})}{\sum_{i=0}^4 a(Q^i) + a(\text{CO}_3^{2-})} \quad (1)$$

355 where $A_{\text{CO}_3^{2-}}$ is the carbonate normalized peak area, $a(\text{CO}_3^{2-})$ is the raw carbonate peak area,
 356 and $a(Q^0), a(Q^1), a(Q^2), a(Q^3), a(Q^4)$ are the raw areas of the silicate peaks. Obtained values of the
 357 $A_{\text{CO}_3^{2-}}$ normalized area are given in Table S1 for samples BPhE3, BPhE10, and 1010.

358

359 *Calibration of CO_2 measurement (Fig. 2)*

360 The peak area is proportional to the number of vibrators. We thus assume a linear relationship
 361 between the CO_3^{2-} normalized peak area and the concentration of dissolved CO_2 , noted C_{CO_2} ,

$$362 \quad A_{\text{CO}_3^{2-}} = a \times C_{\text{CO}_2} (\text{wt. \%}) . \quad (2)$$

363 For calibrating relation (2), we first have the two KS samples (section 2.1) for which the CO_2
 364 concentration was determined by Bourgue and Richet (2001) to be zero (base melt $\text{KS}_{1.3}$ in
 365 (Bourgue and Richet, 2001)) and 3.6 wt.% (sample K2-1 in (Bourgue and Richet, 2001)). We
 366 remark that the CO_3^{2-} band in KS samples was found at 1046 cm^{-1} , not at 1080 cm^{-1} , certainly
 367 related to the particular chemical composition of these samples.

368 As other standard glasses, we use the basaltic samples BPhE2, BPhE3, BPhE10, BPhE12 and
 369 1010, for which we used another part of the recorded Raman spectra to determine their water
 370 contents using the Raman-based method of Le Losq et al. (2012). These water values are given in
 371 Table 2 and are the average of several determinations across each sample. The water
 372 determinations for each spectrum of each sample are given in Table S1. Averaged over all the
 373 measurement spots, these H_2O values are between 0.5 and 2.6 wt.% (Table 2), and, adding them
 374 to the sum of the major element concentrations obtained by electron microprobe, the CO_2 content
 375 was determined by difference to 100% for each of the Raman spots. We then calculate, for each
 376 sample, the average of these CO_2 concentrations, and couple it to the average of the CO_3^{2-}
 377 normalized peak areas measured for the several spots. For sample 1010, this procedure was

378 performed on 12 spots, and compared to two additional spots, giving three reasonably well
379 grouped points (Fig. 2).

380 We thus have 7 samples for calibration (Table 2): zero, KS, BPhE2, BPhE3, BPhE10, BPhE12 and
381 1010, with CO₂ values between zero and ~6 wt.% (9 points when using the three points of sample
382 1010). These points are reasonably aligned when plotting CO₂ concentration versus CO₃²⁻
383 normalized peak area, thus defining a calibration line for CO₂ measurement (Fig. 2). The slope of
384 this line yields a value of 0.063453±0.002156 (1σ) for calibration coefficient *a*. This technique was
385 presented in abstract form (Sarda et al., 2009; Amalberti et al., 2011a,b), and, at this time, we
386 considered this calibration as preliminary because it included only three points.

387 Morizet et al. (2013) also reported on quantifying CO₂ in silicate glasses using Raman
388 spectroscopy. They obtained a very similar (identical within error) calibration line with a value of
389 0.0659±0.0007 (1σ) for coefficient *a* (see eq.1). But those authors have 143 data points, as well
390 as samples with various chemical compositions and up to 16 wt.% CO₂. We remark that Morizet et
391 al. (2013), in describing their procedure, indicate they normalize the CO₃²⁻ peak area to the sum of
392 the Qⁿ silicate peaks only. The almost identical calibration lines obtained here and by Morizet et al.
393 (2013) suggest that Morizet et al. (2013) normalize in reality to the sum of the areas of all the
394 deconvoluted peaks including the CO₃²⁻ peak, as we do here. We also remark that the calibration of
395 Morizet et al. (2013) was slightly modified by Morizet et al. (2017).

396 The calibration line thus appears independent on the chemical composition of samples and
397 independent on the Raman spectrometer (particularly its detector). The former is explained by the
398 fact that the silicate and CO₂ peaks are affected in the same way by the changes in acquisition
399 conditions that could be induced by variable chemical composition, so that their ratio is
400 independent of them. The latter is explained by the fact that the silicate and CO₂ signals lie in the
401 same frequency range, and hence, are affected in the same way by the specifications of the
402 spectrometer. This is not the case for water measurement, because of the large frequency
403 difference between the signals from silicate vibrations and O-H stretching (Fig. 1 and Le Losq et al.,
404 2012). In addition, the strong similarity of these calibrations further suggest that results are also
405 independent on the experimentalist.

406 We estimate the global uncertainty on normalized peak area determination to lie within 10 to
407 20%, depending on the sample. This is equivalent to 2-σ and thus, we use a conservative 1-σ value
408 of 10% for all our peak area data, which we then propagate in a quadratic manner through
409 equation (2): as the 1-σ error on our obtained calibration coefficient is of 3.3%, the 1-σ error on
410 the obtained CO₂ concentration is dominated by the error on peak area, and it is on the order of
411 10%. In three cases, as discussed below, we made several measurements on the same sample to
412 obtain a cartography of the CO₂ concentration: sample BPhE10 exhibits a large dispersion of the
413 CO₃²⁻ concentration showing a distribution characterized by a 1-σ value of 51%, while other
414 samples are much more homogeneous such as BPhE3, with a 1-σ of 5.9%, and sample 1010, with
415 a 1-σ of 8.9%. Such a variable dispersion is a real feature, due to variable sample heterogeneity.
416 Therefore, Raman measurement of CO₂ concentrations is quite accurate, in the sense that it yields
417 a value close to the true one, and we estimate this accuracy to about 1%. On the other hand, there
418 may be an up to 10% 1-σ uncertainty on the precision of the CO₂ concentration, expressing the

419 dispersion due to the measurement technique itself. Of course, these values do not take sample
420 heterogeneity into account, which is a natural feature.

421 From an analytical point of view, Raman spectroscopy thus appears to be a useful way of
422 measuring CO₂ in silicate glasses for relatively elevated CO₂ concentrations (e.g., Morizet et al.,
423 2014; Morizet et al., 2020). The possibility of such a measurement relies on the detection and
424 measurement of the carbonate peak that depends on the how well this peak can be separated from
425 the bulge in the spectrum due to the Qⁿ and Fe³⁺ peaks. We empirically estimate a lower detection
426 limit of 0.5 - 1 wt.% CO₂, depending on the silicate matter investigated. When possible,
427 quantification of CO₂ is rapid, does not depend on acquisition conditions and glass composition, and
428 as suggested by comparison with other laboratories, on the type of Raman spectrometer.

429

430

431 **3. Results**

432

433 **3.1. CO₂ concentrations in vitreous samples**

434

435 *Silicate melt and CO₂ bubbles*

436 CO₂ contents were determined by Raman spectroscopy (Table 2) for samples BPhE2 and BPhE3
437 (a MORB composition doped in CO₂, exposed to 2 and 3 GPa respectively and ~1920-2000 K),
438 BPhE10, 11 and 12 (an iron-free haplobasalt composition doped in CO₂, exposed to 1.5, 2 and 4
439 GPa respectively and 1820-2130 K), and sample 1010 (an iron-free haplobasaltic glass doped in
440 CO₂, exposed to 5 GPa and 1873 K).

441 A visual inspection of these samples shows the presence of cavities, either within the bulk
442 silicate sample in contact with the Pt capsule (e.g., samples BPhE2 in Fig. 3a and 1010 in Fig. 3b),
443 or frequently inside the platinum capsule for BPhE samples (see BPhE11 in Fig. S2A; see section
444 2.1 about temperature in BPhE experiments). Only for samples BPhE3 and BPhE10 was no such a
445 bubble seen, but, for BPhE10, we surmise a bubble is located inside the platinum mass and was not
446 revealed by the abrasion procedure, and, for BPhE3, pictures of the abraded capsule strongly
447 suggest it was lost (Fig. 4b).

448 Reported partial melting experiments with carbonate-supplemented mafic compositions (Yaxley
449 and Brey, 2004; Dasgupta et al., 2004, 2005, 2006; Gerbode and Dasgupta, 2010; Kiseeva et al.,
450 2012) show that this type of assemblage is fully molten at 2-5 GPa and 1873 K if their initial CO₂
451 content is sufficiently high, i.e. > 5 wt.%. The silicate liquid formed at HT-HP, when CO₂-saturated,
452 is expected to coexist either with a CO₂ vapor, or with a carbonatitic liquid immiscible with it, or
453 both. On quenching, the silicate liquid transforms into glass with some crystallites, while the
454 carbonatitic liquid, if present, tends to crystallize. This carbonatitic liquid must then be clearly
455 visible in the texture of the run products as *crystallized* globules, features that we never saw in our
456 samples. Therefore, in these experiments, we likely had a CO₂-bearing silicate liquid coexisting
457 with a CO₂ supercritical fluid.

458 The frequently observed cavities must thus have been CO₂ bubbles at HP-HT. Care was exerted
459 to check that these bubbles, when present, are located at the top of the capsule, and this was
460 indeed found to be the case. For samples loaded with natural basalt, the carbonate powder was

461 initially placed at the bottom of the capsule, then covered by silicate material above it, and the
462 bubble was yet systematically found at the top of the capsule. These CO₂ bubbles thus indicate that
463 the samples were saturated with respect to CO₂ (as known for H₂O-bearing samples, e.g., Burnham
464 and Jahns, 1962).

465

466 *Samples and crystallites*

467 When glass was obtained by quenching, the samples prepared from natural basalt appeared
468 black, whereas the hand-prepared iron-free samples, turned out to be transparent, as expected. In
469 some cases, the latter samples have a milky, whitish aspect indicating the presence of crystals in
470 them.

471 For the whitish samples obtained using the Belt press (BPhE), a further analysis by scanning
472 electron microscopy (SEM) reveals that the texture of most of them is essentially vitreous with the
473 presence of extremely small crystallites of micron size. This is likely related to the relatively low
474 quenching rate (section 2.1. above). When such crystallites are abundant enough, i.e., for
475 pressures higher than 3 GPa, they may give a whitish general aspect, such as in BPhE11, where
476 these crystallites have variable abundance throughout the sample, and are arranged in a way that
477 generates several visible globules (Fig. S2a). From the SEM examination of BPhE11, the crystallites
478 are silicate, and one can see that the globules are only regions with more abundant crystallites
479 (Fig. S2b, magnification 2000).

480 For the samples obtained using the multi-anvil press, sample 1010 (5 GPa, 1873 K) is nicely
481 vitreous, but samples 1090 (5 GPa, 1873 K) and 1011 (8.5 GPa, 1873 K) are partially crystallized.
482 The latter two samples are discussed below (sections 3.3. and 3.4.).

483

484 *Chemical composition of glass regions*

485 The chemical composition, on a CO₂-free basis, of glass zones in samples retrieved after HP-HT
486 experiments are close, but not identical, to those of the initial silicate blends (see Tables 1 and 2).
487 The final dissolved CO₂ contents measured in the quenched samples are systematically lower than
488 their initial concentrations. This corroborates the interpretation that bubbles were present in
489 samples that were CO₂-saturated.

490

491 *Raman mapping of CO₂*

492 An advantage of Raman spectroscopy is to allow quantifying the distribution of CO₂ (CO₃²⁻)
493 throughout the sample at the micron scale. Such Raman mapping revealed that significant
494 variations of CO₂ content may occur across samples. For those samples where such mapping was
495 done, we calculate the average of the individual measurements, and it is these average
496 concentrations that are reported in Table 2, with an uncertainty corresponding to the observed
497 dispersion.

498

499 *Appropriate values for global samples*

500 Such mapping was performed on sample BPhE10, 2 GPa, with 19 Raman spots (see Fig. 4a),
501 and revealed a strong heterogeneity in CO₂ concentrations from 0.29 to 2.37 wt.%, with an
502 average value of 1.56±0.80 wt.%. Moreover, as can be seen on Fig. 4a, the CO₂ concentrations are

503 weak at the bottom of the capsule, although the carbonate powder was initially placed at the
504 bottom, and they increase toward the top (where we guess a cavity is perhaps located inside the
505 platinum, or the bubble was lost). This argues for a complete redistribution of CO₂ in the capsule
506 during the experiment.

507 The same systematic is observed for sample 1010 (5 GPa) from 12 Raman spots, giving less
508 variable CO₂ concentrations ranging between 5.03 and 6.94 wt.% and averaging 5.97±0.53 wt.%,
509 where Raman mapping reveals an increase of the CO₂ concentration towards the top of the capsule
510 where the bubble is located (Fig. 3b).

511 These samples have perhaps not reached equilibrium for CO₂. Sample BPhE10 remained 32
512 minutes at 2 GPa and 1920K, while sample 1010 spent 3 hours at 5 GPa and 1873K. Therefore, it
513 is likely that CO₂ concentrations are never homogeneous in such kind of samples but are variable
514 due to CO₂ migration driven by the exsolution process that generates the bubble. These
515 observations indicate that the kinetics of such CO₂ migration is slow in the experimental conditions
516 with respect to the duration of the experiments. That sample 1010 appears more homogeneous
517 than BPhE10 is probably due to the much longer duration of the experiment, 3 hours vs. 32
518 minutes.

519 For these durations, we can calculate the typical diffusion length of a carbonate ion in melt if we
520 know the diffusion coefficient, using the formula $x = \sqrt{6Dt}$. For sample 1010, using the value of 4
521 10⁻¹⁰ m²/s for CO₃²⁻ in a MORB melt at 2 GPa and 1873 K from the simulations of Guillot and Sator
522 (2011, their Table 3), one gets 5 mm. At 5 GPa, the diffusion coefficient must be slightly smaller by
523 some tens of percent. However, these authors indicate that their values are probably
524 overestimated by a factor of 10. Their review of literature shows that the CO₂ molecular diffusion at
525 ambient pressure does not clearly depend on melt composition (see also Baker et al., 2005) and
526 that the data yields a linear trend in an Arrhenius plot (their figure 12). Extrapolating this trend to
527 1873 K gives a value of 7 10⁻¹¹ m²/s, which allows estimating a length of ~2 mm. For sample
528 BPhE10, at 1920K, we extrapolate to roughly the same value of the diffusion coefficient, and, in 32
529 minutes, the diffusion length is 0.9 mm. Given that our capsules are roughly 2 mm tall, these
530 calculations suggest that several hours may be necessary to reach CO₂ homogeneity in the melt.

531 It is also possible that the better homogeneity of sample 1010 compared to sample BPhE10
532 would be related to the higher cooling rate for the multi-anvil press than for the Belt press (section
533 2.1.), thus better freezing a possible re-solution of some gas from the bubble on cooling, but this is
534 yet too speculative.

535 The simplest way of interpreting these observations is probably to assume equilibrium at the
536 scale of the whole capsule between CO₂ dissolved in melt and CO₂ of the bubble, the melt being not
537 completely homogenized. It is thus probable that the values obtained for whole samples by
538 averaging several measurements are trustable only when the number of Raman spots is sufficient.

539 In contrast, sample BPhE3 (3 GPa) appears more homogeneous, with an average value of
540 4.21±0.25 wt.% CO₂, but we have only 6 spots for this sample (only 4 spots are shown on Fig. 4b).
541 This sample spent 33 minutes at 3 GPa and 2000K, thus it is possible that this apparent better
542 homogeneity is due to this higher temperature. We also remark that the relatively short duration of
543 the experiment here does not appear to have prevented homogeneity, hence probably equilibrium,
544 from being reached. However, given that we have only 6 points, it is still possible that zones with

545 lower or higher CO₂ concentrations have been missed, so that the average value for this sample is
546 perhaps not accurate. But we shall see below that, compared to theoretical values obtained by
547 molecular dynamics (section 4.1.), the result for BPhE3 is likely correct within experimental error.

548 Finally, the global values obtained for samples BPhE2 with 2 spots and BPhE12 with one
549 measurement spot are possibly not accurate. Sample BPhE12 (1.5 GPa, 1825 K) gives the same
550 value within experimental error as reported previously by Matthey (1991) and by Stanley et al.
551 (2011, 2012). This result is also consistent with the theoretical values. In contrast, sample BPhE2
552 (2 GPa, 1920 K) gives a clearly too high value when compared to previous results or to theory (see
553 section 4).

554

555

556

557

558 **3.2. Partially crystallized sample BPhE11 (4 GPa)**

559

560 Sample BPhE11 (4 GPa and 2130 K) shows a large cavity inside the platinum at the top of the
561 capsule. This sample is not completely vitreous, with whitish regions sometimes taking the form of
562 globules (Fig. S2a). For this sample, SEM analysis shows that the global texture is that of a glass
563 bearing very abundant silicate crystallites. Therefore, it is impossible to have the Raman spot
564 located on pure glass, but it always includes some crystallites, which must lower the measured CO₂
565 concentration. Thus, for this sample, we selected only the highest CO₂ results, using them to
566 obtain a rough value of its global CO₂ content (Table 2).

567

568 **3.3. Partially crystallized sample 1090 (5 GPa)**

569

570 The andesitic sample 1090, exposed to 5GPa, partially crystallized upon quenching (Fig. S6).
571 Raman analysis showed that the phenocrysts are aragonite, the high-pressure high-temperature
572 polymorph of CaCO₃ (Suito et al., 2001; Ivanov and Deutsch, 2002; Spivak et al., 2012), identified
573 by the three low frequency peaks at 155, 180 and 205 cm⁻¹ (lattice modes), and the narrow peaks
574 at 700 and 1085 cm⁻¹ (Fig. 5, to compare with Gillet et al., 1993). We found no spectral signatures
575 revealing crystalline silicates or other carbonates. The aragonite crystals are dispersed throughout
576 a vitreous silicate matrix (Fig. S6b) of dacitic-like composition (see microprobe analysis of vitreous
577 regions in Table 2).

578

579 *Mean CO₂ content from optical estimate of phenocryst proportion*

580 We estimated the volume proportion, V_c (in vol.%), of aragonite phenocrysts from an optical
581 photography of the whole sample (not shown). We found $V_c = 18 \pm 2$ vol.% (see supplement).

582 Deriving the corresponding CO₂ content needs knowledge of densities of aragonite and glass
583 (see supplement). Using densities at ambient conditions yields a CO₂ content of 9 ± 1 wt.%. It
584 would perhaps be more appropriate to use density values effective during the quench, at higher
585 pressure and higher temperature, but they are unknown. Furthermore, we did not consider any

586 possible deviation from the assumed identity between area proportion and volume proportion, 2D
587 vs. 3D.

588 This rough evaluation neglects the CO₂ still dissolved in the vitreous regions of the sample.
589 Nevertheless, the obtained value suggests that all the initial CO₂, i.e., 9 wt.% (Table 1), was
590 dissolved in this andesitic melt at 5 GPa. This sample was thus CO₂-saturated or slightly
591 undersaturated, consistent with the fact that no CO₂ bubble is seen in it (Fig. S6a).

592

593 *Micrometric scale Raman mapping of groundmass*

594 Crystallization of this sample prevents using Raman spectroscopy to determine its global CO₂
595 content. An estimate can be obtained by summing up the fraction of CO₂ in glass, determined with
596 Raman data, with that found in aragonite crystals.

597 A Raman mapping at micrometric scale revealed that very small aragonite crystallites of less
598 than a few microns are dispersed in the glass in most regions of sample 1090 (Fig. 5). Aragonite is
599 characterized by sharp peaks at 155, 180, 205, 700 and 1085 cm⁻¹. Glass presents broad bands
600 near 100, 500, 800, 1000 cm⁻¹, with the doublet assigned to dissolved CO₃²⁻ at 1300-1600 cm⁻¹,
601 while the ν₁ stretching mode of dissolved CO₃²⁻ at 1085 cm⁻¹ is buried under the silicate shoulder
602 located at 1000-1200 cm⁻¹. The Raman signal of aragonite is thus superimposed to that of vitreous
603 silicate (see the sharp 1085 cm⁻¹ peak shown in green in the spectrum of the glass + crystallites
604 mixture, Fig. 5).

605 We measured the area, named A₁₀₈₅, of the CO₃²⁻ sharp peak seen in the glass + crystals
606 mixture (Fig. 5), and the area, named A₁₀₈₅^{aragonite}, of the same peak in a large aragonite crystal
607 chosen in the sample. The ratio $R_{1085} = A_{1085}/A_{1085}^{\text{aragonite}}$ is then related to the CO₂ concentration
608 borne by crystallites by a simple linear relation (see supplement) because the intensity of a
609 vibration band is proportional to the concentration of vibrators per unit volume seen by the laser
610 beam.

611 Averaged over a surface of 30 X 30 micrometers, this mapping gives $R_{1085} = 0.1137$. Using the
612 relationship between R_{1085} and CO₂ concentration (see supplement), the derived mean CO₂
613 concentration in glass is 8.1 wt.%, this value representing the contribution of the aragonite
614 crystallites.

615

616 *Evaluation of CO₂ concentration in sample 1090*

617 Two analyzes at very different scales, optical image analysis and Raman mapping (Fig. 5), give
618 similar results, indicating that sample 1090 contains 8 to 9 wt.% CO₂. The optical analysis does not
619 take into account the residual CO₂ dissolved in glass, which is revealed by the presence of the
620 doublet at 1350-1600 cm⁻¹. In zones where no aragonite Raman signal is visible near 1085 cm⁻¹,
621 the CO₃²⁻ vibration band of CO₂ dissolved in glass is completely masked by the intense and broad
622 band of silicate in this frequency range (Fig. 5). As the total CO₂ content cannot be larger than the
623 9.0 wt.% of initial CO₂, the concentration of residual CO₂ in glass is at most equal to the difference
624 $9.0 - 8.1 = 0.9$ wt.%. If we use the Raman calibration line (Fig. 2) to get the corresponding Raman
625 signal via Eq. (2) and report this value into the Raman spectrum of the glass (Fig. 5), we see that
626 the corresponding dissolved CO₃²⁻ band at 1080-1090 cm⁻¹ indeed cannot emerge from the large
627 silicate shoulder. Consequently, the CO₂ concentration in glass cannot exceed 0.9 wt.%, and the

628 total CO₂ may be as large as the initial amount of 9.0 wt.%. We thus again reach the conclusion
629 that sample 1090 is undersaturated or just saturated, in agreement with the absence of any
630 bubble.

631 Altogether, the global CO₂ concentration is between 8.1 and 9.0 wt.%. We thus report an
632 intermediate value of 8.5±0.9 wt.% in Table 2 for the bulk CO₂ of sample 1090.

633

634 **3.4. Partially crystallized sample 1011 (8.5 GPa)**

635

636 Basaltic sample 1011, exposed to 8.5 GPa, yields a quenched structure made of an intergrowth
637 of silicate and carbonate crystals, with some proportion of glass (Fig. 6). To our knowledge, no
638 report of pure glass obtained at such a high pressure exists for such compositions in the literature,
639 so that high pressure likely just prevents from getting glass with a classical quenching procedure
640 (quench rate ~100K/s).

641 A quick Raman mapping of this sample allows identifying garnets (grossular and mostly pyrope)
642 and carbonates (Fig. 7), as well as glass regions dispersed throughout. In the spectra taken from
643 glass regions, one can clearly distinguish the Raman shifts corresponding to the stretching modes
644 of dissolved carbonate ions (see in Fig. 7 – glass, the broad band at ~1090 cm⁻¹ and the doublet at
645 1350-1600 cm⁻¹) and those generated by solid carbonates (see in Fig. 7 – glass, the narrow peak
646 at 1103 cm⁻¹). The narrow peak at 1103 cm⁻¹, instead of 1085 cm⁻¹ in aragonite, is characteristic of
647 the ν_1 stretching mode of CO₃²⁻ in mineral eitelite, Na₂Mg(CO₃)₂ (see Shatskiy et al., 2013).
648 Indeed, the microprobe analyzes of glass regions reveals a strong enhancement of Na with respect
649 to the initial composition (see Tables 1 and 2), suggesting that, during the quench, a large
650 proportion of Na⁺ ions migrated together with CO₃²⁻ ions to form eitelite crystals.

651 Sample 1011 does not show any bubble, indicating that CO₂ was mostly dissolved in melt at HP-
652 HT, and generated carbonate minerals on quenching. Accordingly, this sample must have retained
653 all the 13.6 wt.% CO₂ put in the capsule. A quick optical analysis of the picture presented in Fig. 6
654 with the protocol used for sample 1090 indicates that the area fraction of white parts (crystals) is
655 of 23-24%, leading to CO₂ values close to 12 wt.%, assuming all crystals are eitelite. Considering
656 the uncertainties in such an analysis (on densities, different crystalline phases, only one image was
657 analyzed...), this result corroborates the fact that the initial 13.6 wt.% CO₂ was quantitatively
658 dissolved at 8.5 GPa. Since we observe neither any evidence of a leak in the platinum capsule, nor
659 any bubble in the bulk material, we can thus assume that the basaltic melt at 8.5 GPa and 1873 K
660 can integrate 13.6 wt.% CO₂, still being not saturated.

661

662 **4. Discussion**

663

664 **4.1. CO₂ solubility in basaltic and andesitic melts up to 8.5 GPa**

665

666 *Breaking of Henry's law at high pressure*

667 The measured CO₂ contents of the studied samples globally exhibit a strong increase with
668 increasing pressure (Fig. 8). Above 2 GPa, the CO₂ solubility in basaltic and andesitic melts
669 increases much faster than what is expected from an extrapolation of the Henrian behavior known

670 at lower pressure (e.g. Pan et al., 1991; Matthey, 1991; Stanley et al., 2011, 2012). Deviations
671 from Henry's law at high pressure have already been pointed out, for rare gases toward low
672 solubility (Schmidt and Keppler, 2002; Sarda and Guillot, 2005; Guillot and Sarda, 2006; Bouhifd
673 and Jephcoat, 2006), and for CO₂ toward high solubility but only on theoretical grounds (Guillot
674 and Sator, 2011).

675

676 *Comparison to previous data and accuracy of results*

677 In detail, when compared to the seldom data reported in the literature for mafic compositions
678 between 1 and 3 GPa (e.g., Pan et al., 1991; Matthey, 1991; Stanley et al, 2011, 2012; Eguchi and
679 Dasgupta, 2017), our experimental results are compatible with Pan et al. (1991) and Stanley et al.
680 (2011, 2012) at 1.5 GPa within error for sample BPhE12 (although slightly higher), and with Matthey
681 (1991) and Stanley et al. (2011, 2012) at 2 GPa for sample BPhE10 (Fig. 8). We remark that the
682 results of Stanley et al. (2011, 2012) are for iron-rich Martian-like basalt compositions and are
683 slightly lower than ours but very close.

684 The experimental results of Eguchi and Dasgupta (2017) for andesite at 1-3 GPa are
685 significantly lower than the rest of presently available data, but their experiments were conducted
686 at graphite saturation and are therefore not comparable. Their thermodynamic model (Eguchi and
687 Dasgupta, 2018) for CO₂ solubility in silicate melts fits relatively well the low-pressure data (Fig.
688 S8), but as seen on Fig. 8, their curve goes down when pressure increases above ~5 GPa. In
689 addition, their model appears quite sensitive to chemical composition (Fig. 8 and S7).

690 Our 2 GPa sample BPhE2 gives clearly a too high CO₂ concentration. As discussed above, the
691 samples are heterogeneous, and we have not enough Raman spots for this sample so that the
692 obtained result is likely too high (compare BPhE2 and BPHE10 in Table 2 and see Fig. 4a for
693 BPhE10 at 2 GPa). The result for BPhE2 must thus be rejected and is not shown on Fig. 8. We keep
694 the rest of our results as representative of the CO₂-P evolution at various temperatures (Fig. 8).

695 Finally, the result of Kim et al. (2018) at 6 GPa, although for albite melt, is ~15 wt.%, an
696 extremely elevated value that agrees well with our measurements for basalt and andesite
697 compositions. A comparison with simulation below allows appreciating this datum better.

698

699 **4.2. Molecular dynamics approach**

700

701 *Simulation of CO₂ solubility in mafic melts*

702 A number of solubility models have been proposed in the literature to describe the CO₂ solubility in
703 silicate melts as function of pressure, composition, and (more recently) redox state (e.g., Khitarov
704 and Kadik, 1973; Dixon et al., 1995, Papale et al., 2006, Iacono-Marziano et al., 2012, Eguchi and
705 Dasgupta, 2018). These models being empirical in nature, their parameters cannot be a priori
706 deduced and are adjusted to reproduce at best some solubility data set. When it comes to the
707 question of applying these models to predict the carbon solubility for thermodynamic conditions
708 and/or for silicate composition not spanned by the experimental data basis used for
709 parametrization, the results are generally poor. In particular, most of these solubility models have
710 been parametrized at relatively low pressure (< 2 GPa), and as shown hereafter, they are unable
711 to reproduce the present HP experiments and disagree with the MD calculations. In contrast, MD

712 calculations are based on a first principles approach, and once the force field has been set up, no
713 adjustment of parameters is needed to describe the CO₂ solubility in silicate melts of various
714 composition at any thermodynamic conditions.

715 For having theoretical guidance in this study, we compare our data to the molecular dynamics
716 simulation study published by two of us (for technical details, see Guillot and Sator, 2011). In Fig.
717 8 is reported the solubility of CO₂ in a MORB melt at 1673K, 1873K and 2273K as function of
718 pressure, as calculated by MD, as well as that for an andesitic melt at 1873K. The general trend
719 predicted by the MD calculation, a strongly nonlinear increase of solubility at high pressure, is
720 supported by present experimental data, which also supports the validity of Raman spectroscopy
721 as a measurement technique of CO₂ concentration in silicate material (Fig. 8).

722

723 *Using MD simulations to discuss Raman CO₂ results*

724 The theoretical lines we have, permit to discuss the accuracy of the measured values.

725 At 1.5 GPa and 1820K, sample BPhE12 gives a value slightly higher than, but consistent with
726 those of Pan et al. (1991) and Stanley et al. (2011, 2012) within error. Our value is also consistent
727 with the simulations within error, but slightly high (Fig. 8 and S7). This sample was perhaps
728 relatively homogeneous, but again, had only one Raman measurement spot.

729 At 2 GPa and 1920K, sample BPhE2 gives clearly a too high value (not shown on Fig. 8), while
730 sample BPhE10, at the same pressure and temperature, gives a result perfectly consistent with
731 Matthey (1991), Stanley et al. (2011, 2012) and the MD lines at 1673 – 2273K (Fig. 8). Sample
732 BPhE2 is rejected due to sample heterogeneity having not been measured, 2 measurement points
733 versus 19 points).

734 At 3 GPa, sample BPhE3 was heated at ~2000 K and turns out to be quite homogeneous, which
735 may be due to the temperature, higher than for BPhE2 and BPhE10 by ~100K. It gives a value
736 consistent, within error, with the MD line at 1873K, which supports the validity of this experimental
737 result (Fig. 8 and S7).

738 At 4 GPa and 2130K, sample BPhE11, although partially crystallized, gives a value consistent
739 with the MD line at 2273K, supporting the significant effect of the high temperature in lowering the
740 CO₂ solubility seen by MD (Fig. 8).

741 At 5 GPa and 1873K, the haplo-basaltic sample 1010 gives a value that is consistent, within
742 error, with the MD line at 2273K for MORB, but relatively low for a MORB at 1873K. In the same
743 (P,T) conditions, the haplo-andesite 1090 gives a value perfectly consistent within error with the
744 MD line for an andesite at 1873K (Fig. 8).

745 At 8.5 GPa and 1873K, the undersaturated sample 1011 accommodates 13.6 wt.% CO₂, the
746 maximum possible, a value that does not contradict the MD result of ~25 wt.% for a saturated
747 MORB at 1873K (Fig. 8).

748 The global agreement between data and simulation thus suggests that the CO₂ solubility curve
749 in basaltic and andesitic melts is well constrained up to 5 GPa, and, based on sample 1011,
750 probably up to 8.5 GPa. The strong increase in CO₂ solubility above ~2 GPa is confirmed.

751 The consistency of the result by Kim et al. (2018) for albite melt with our results and
752 simulations (Fig. 8) further supports these conclusions.

753

754 **4.3. Influence of melt composition**

755

756 *Molecular vs. ionic solubility*

757 Comparing results for samples 1090 (5 GPa, 1873 K) and 1010 (same P, T) shows that the
758 solubility of CO₂ in a haploandesitic melt is similar to that in a haplobasaltic composition in these
759 conditions (Fig. 8). To check whether this observation holds over a large pressure range, we have
760 evaluated by MD simulation the CO₂ solubility curve at 1873K, from 1 to 10 GPa, in a silicate liquid
761 having the andesitic composition of sample 1090 (the force field, MD code and simulation
762 parameters are those used in Guillot and Sator (2011): the obtained solubility curve for andesite is
763 quite close to but slightly below that for MORB (Fig. 8). This similarity is due to a subtle energy-
764 entropy compensation when CO₂ is incorporated into a silicate melt (Guillot and Sator, 2011). In
765 polymerized melts, the number of NBO (non-bridging oxygen atoms) is too low to stabilize an
766 important fraction of carbonate groups, but the work to spend for inserting a CO₂ molecule into the
767 silicate network is weaker than in depolymerized melts because of a less compact structure.
768 Therefore, the CO₂ solubility is similar in basalt and andesite at 1873 K, and the MD calculation
769 takes this feature into account.

770 We note that this result contradicts several previous studies performed at lower pressure, where
771 it was observed that the CO₂ solubility was significantly higher in basalt than in andesite (e.g.,
772 Mysen, 1976; Dixon, 1997; Brooker et al., 1999, 2001a,b; King et Holloway, 2002; Lesne et al.,
773 2011; Iacono-Marziano et al., 2012), increasing with increasing NBO/T (here T means the number
774 of tetraordinated elements Si and Al). Of course, we do not claim that there is no influence of the
775 NBO/T, i.e., chemical composition, but things are probably subtler at high T and P because of the
776 interplay of carbonate ions and molecular CO₂, the solubility of which are extremely sensitive to
777 experimental conditions (T, P and H₂O content).

778 The experimental results are possibly influenced by changes occurring during quenching, where
779 cooling could trigger CO₂ conversion into CO₃²⁻, a phenomenon already experimentally documented
780 (Morizet et al., 2002; Nowak et al., 2004; Korschak and Keppler, 2014) and theoretically described
781 by Guillot and Sator (2011). Korschak and Keppler (2014) show that this speciation effect is much
782 stronger for depolymerized melts and strongly increases at low temperature, especially close to the
783 glass transition temperature, T_g . Therefore, it appears important that future experiments rather
784 attempt to perform measurements *in situ* at high pressure and high temperature.

785

786 *Relation to melt properties and solvation structure.*

787 We saw above that CO₂ solubility in basaltic and andesitic melt can reach similar and high
788 values. However, such high amounts of dissolved CO₂ only slightly lower the glass transition
789 temperature (T_g) of silicate melts (an example of such data is illustrated in Fig. S8) or their
790 viscosity (not shown; e.g., Bourgue and Richet, 2001; Morizet et al., 2002; Di Genova et al.,
791 2014), the effect on viscosity being, as expected, essentially visible close to T_g , when viscosity is
792 high enough (Bourgue and Richet, 2001). In contrast, solubilization of water (Richet et al., 1996;
793 Vetere et al., 2006; Whittington et al., 2000) or Na₂O (Poole, 1949; Neuville, 2006; Le Losq et al.,
794 2019) has a much stronger influence on both properties (Fig. S8). In addition, the CO₂ solubility is
795 significantly lower than that of H₂O by one order of magnitude (e.g., Papale et al., 2006).

796 This weak influence of CO₂ on melt properties can be explained as follows (Guillot and Sator,
797 2011). Upon dissolution in a liquid silicate, a significant fraction of CO₂ turns into carbonate ion by
798 linking to available non-bridging oxygen atoms, a smaller fraction links to bridging oxygen atoms
799 without breaking the two Si-O bonds (contrary to H₂O), and the rest, a non-negligible fraction of it,
800 finds interstitial sites where it stabilizes as a molecule, the higher the degree of polymerization the
801 larger the fraction of molecular CO₂. In short, CO₂ links to the network as a parasite, without
802 disturbing it.

803 In Raman spectra of the present study, the Raman band at ~1080 cm⁻¹ is the signature of the
804 solvation structure of the CO₃²⁻ ion in the silicate network. Indeed, as seen in Fig. 1.b, the
805 frequency of this band is 1046 cm⁻¹ in the KS samples, as compared to 1084-1086 cm⁻¹ in the
806 basaltic and andesitic samples: this is due to the different way the CO₃²⁻ ion links to these different
807 silicate networks. In the same way, we notice a slight frequency change at 5 GPa between andesite
808 and basaltic composition. However, for basaltic glasses, we do not observe any change in this
809 frequency with changing pressure, which suggests that the solvation structure of the carbonate ion
810 is essentially the same, whatever the pressure up to 8 GPa.

811

812 **4.5. Consequences for CO₂ geochemistry**

813 We present here an open tentative list of domains where our findings about high CO₂ solubility
814 in melts with compositions close to (as possibly close as) natural mafic melts may be important.
815 We discuss only few of them.

816 *Mantle melting, volcanism, carbonatites and kimberlites*

817 The present work may have consequences on our understanding of the transport of CO₂ at
818 depth in the mantle, and hence of Earth degassing as a whole. One of them concerns mantle
819 melting. When incipient melting occurs in the carbonate-bearing asthenosphere, at very low melt
820 fraction ($\leq 0.1\%$), the initial composition of the melt is carbonatitic (e.g., Dasgupta and
821 Hirschmann, 2006; Hammouda and Keshav, 2015) and it then evolves toward a basaltic
822 composition during magma ascent and increasing silicate melting.

823 If basaltic-like magmas can carry so much carbon, this is probably another piece of evidence in
824 favor of continuity between pure silicate melt and pure carbonate melt (see e.g., Gudfinnsson and
825 Presnall, 2005). During magma ascent toward the surface, carbonate and silicate melt will likely
826 separate when conditions for immiscibility are met (e.g., Fischer et al. 2009), thus leading to a
827 carbonatitic melt again with probably some silicate dissolved in it, and a silicate melt significantly
828 charged in dissolved CO₂ (for a scenario of magma ascent, see Gaillard et al., 2020).

829 The increase in melt fraction during melting must eventually induce a decrease in CO₂
830 concentration. After separation, the resulting silicate-rich melt will have a CO₂ concentration
831 determined by the evolution of the CO₂ solubility with melt composition and pressure during
832 melting. We show that basaltic magmas can transport high quantities of CO₂ (several wt.%) before
833 degassing. For instance, at 8.5 GPa our data show that a basaltic melt is able to accommodate
834 more than 13.6 wt.% CO₂ before starting degassing and as shown in Fig. 8, probably ~25wt.%
835 (Guillot and Sator, 2011). We speculate that, if such melts could be generated at such high
836 pressures and migrate up to the surface, their degassing could lead to explosive eruptions.

837 There is many evidence for a deep-sea explosive volcanism on the oceanic crust characterized
838 by pyroclastic deposits with very high vesicularity or showing CO₂-rich melt inclusions (e.g.,
839 Schminke et al., 1978; Smith and Batiza, 1989; Hekinian et al., 2000; Pineau et al., 2004; Sohn et
840 al., 2008; Helo et al., 2011). A part of these explosive episodes could be triggered by CO₂-rich
841 magmas reaching CO₂ saturation in the pressure range 1-5 GPa (Aubry et al., 2013).

842 Other occurrences of CO₂-rich volcanism include, for example, the *petit spots*, a large number of
843 oceanic submarine volcanoes, which appear on the ocean floor close to subduction zones (Hirano et
844 al., 2013). These volcanoes were shown by Okumura and Hirano (2013) to erupt lavas as rich as 5
845 to 10 wt.% CO₂. These authors estimate they carry a flux of CO₂ out of the Earth of 0.6 to 1.2 10¹⁰
846 mole CO₂/year, a significant fraction of the MOR CO₂ degassing flux of 1-5 10¹² mole CO₂/year
847 (Dasgupta & Hirschmann, 2010). This flux may be higher when considering degassing not related
848 to eruptions.

849 Another consequence of such high CO₂ solubility in silicate magmas at high pressure may be the
850 occurrence of CO₂-rich fluids in the relatively shallow mantle, as witnessed by the numerous CO₂-
851 H₂O fluid inclusions found in peridotite minerals (Frezzotti and Touret , 2014), possibly a record of
852 a general, unfocussed, mantle CO₂ continuous degassing.

853 Altogether, the CO₂ flux from the interior of the Earth to the atmosphere may well be more
854 important than several previous estimates, when considering (i) the high end of estimates for the
855 Mid-Oceanic Ridge flux of 5-6 10¹² mole/year, in full agreement with popping rocks (e.g., Sarda
856 and Graham, 1990; Dasgupta and Hirschmann, 2010), (ii) the flux coming via the large number of
857 *petit spots* and their degassing (Okumura and Hirano, 2013) and (iii) the general continuous
858 mantle degassing (Frezzotti and Touret, 2014). Such CO₂ has not yet been directly identified, and
859 part of it may be released via deep-sea hydrothermal activity.

860 About the carbonate melt possibly generated by immiscibility during ascent, it may play a role in
861 the genesis of carbonatites and kimberlites, since such a melt will inevitably rise upward in the
862 mantle (e.g., Russell et al., 2012; Kamenetsky and Yaxley, 2015), but this subject is still debated,
863 and is beyond the scope of the present work.

864

865 *Core-mantle boundary*

866 Finally, let us recall that the D'' zone, at the bottom of the mantle, may include liquid remnants
867 of the primordial magma ocean (Williams and Garnero., 1996; Vinnik et al., 1998; Labrosse et al.,
868 2007; Coltice et al., 2011). Although at much higher pressure than in this study, if we extrapolate
869 the logic evidenced here, we speculate that such melt might contain high amounts of CO₂.
870 Therefore, carbon may also play an important role in very deep mantle processes, such as in
871 mantle – core interactions occurring in the D'' zone. This could also relate to carbon being one of
872 the light elements having entered the core when it formed (e.g., Wood, 1993; Poirier, 1994;
873 Blanchard et al., 2015; Solomatova et al., 2019), a possibility supported by carbon being found as
874 carbide in some iron meteorites (Scott, 1971). Clearly, data at higher pressures should be
875 generated to follow-on the solubility curves of Fig. 8 and contribute to answer the question of CO₂-
876 rich melts existing at such great depths, a challenge for the future.

877

878

879

880 **6. Conclusion**

881

882 New data have been acquired on the solubility of CO₂ in silicate melts close to basaltic and
883 andesitic compositions at pressures up to 8.5 GPa in oxidizing conditions. Although the solubility of
884 CO₂ in such melts is weak at low pressures (500-1,000 ppmw at 1 kbar, Dixon et al., 1995;
885 Botcharnikov et al., 2006), our data show that it increases with increasing pressure much more
886 rapidly than expected from Henry's law (e.g., $C_{CO_2} = 7-8$ wt.% at 5 GPa as compared to 2.5-3
887 wt.% from Henry's law), confirming previous inferences from theoretical work (e.g., Guillot and
888 Sator, 2011). At 8.5 GPa, we obtain a minimum CO₂ concentration of 13.6 wt.% as compared to
889 ~25 wt.% from molecular dynamics. That such silicate melts may contain such high amounts of
890 CO₂ may have important consequences on our understanding of CO₂ transport at depth in the
891 mantle, such as when mantle melts in the asthenosphere, and, more globally, our understanding of
892 Earth degassing, especially at the magma ocean stage. Other consequences are tentatively
893 suggested, such as about the origin of carbonatites or kimberlites, and about the core - mantle
894 boundary.

895 From the experimental point of view, the present study highlights the usefulness of Raman
896 spectroscopy for analyzing silicate glasses in a quick and non-destructive fashion. Quantification of
897 CO₂ is possible in glasses, does not depend on acquisition conditions and glass composition, and as
898 suggested by comparison with existing studies, on the type of Raman spectrometer.

899 A major problem of the experimental method used in this study is to deal with a sample issued
900 from quenching the liquid phase, which has therefore experienced undesirable structural changes
901 (crystallites) and possible chemical variations. As seen here, a mixture of silicate and carbonate
902 exposed to pressures above 5 GPa is unlikely to quench to pure glass. Moreover, the establishment
903 of an equilibrium between silicate liquid and CO₂ gas was observed here to produce significant
904 heterogeneities of the CO₂ concentration in the silicate liquid observed as a quench. We thus
905 believe that a breakthrough in this field will arise from *in situ* spectroscopies running at
906 superliquidus temperatures and high pressure.

907

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1411 **Table 1**

1412 Starting compositions in wt.%; numbers in parentheses stand for CO₂-free composition, other
 1413 numbers represent the complete composition, including added CO₂. Note that, for the samples in
 1414 the 2nd column, the added carbonate was not weighted. The natural MORB is from the South
 1415 Atlantic Ocean, labeled EW9309 14D-4g (Douglass et al., 1999), and its composition was kindly
 1416 communicated by Jean-Guy Shilling.

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Sample type	MORB (natural)	MORB (synthetic)	Haplo-basalts	Haplo-andesite
Sample name	BPhE2, BPhE3	BPhE10, BPhE11, BPhE12	1010, 1011	1090
SiO ₂	(50.81)	50.40 (56.49)	41.66 (49.22)	54.93 (62.70)
TiO ₂	(1.59)	1.63 (1.83)	0 0	0 0
Al ₂ O ₃	(15.04)	14.93 (16.73)	20.20 (14.06)	20.85 (20.60)
FeO	(9.68)	0 0	0 0	0 0
MnO	(0.14)	0 0	0 0	0 0
MgO	(8.33)	8.26 (9.26)	11.98 (21.09)	3.39 (3.14)
CaO	(11.27)	11.18 (12.53)	9.87 (12.50)	8.10 (9.17)
Na ₂ O	(2.83)	2.82 (3.16)	2.73 (3.13)	4.34 (3.73)
K ₂ O	(0.28)	0 0	0 0	0 0
P ₂ O ₅	(0.16)	0 0	0 0	0 0
Total silicate	(100)	(100)	(100)	(100)
CO ₂ (added)	> 10	10.78	13.56	9.00
Total with CO ₂	-	100	100	100

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1433 **Table 2**

1434 Listed are experimental run conditions (P,T), major element microprobe analyzes of *vitreous*
 1435 regions in quenched samples (wt.%), and CO₂ contents, as well as H₂O where measured, both
 1436 obtained by Raman spectroscopy (wt.%). Typical 1 σ errors on temperature are ~50°C for BPhE
 1437 samples (due to an important extrapolation for Belt press experiments) and 25°C for the other
 1438 samples (temperature is measured in multi-anvil press experiments). Knowledge of pressure is
 1439 precise to about 5% (1 σ) for the Belt press, and about 0.25 GPa (1 σ) for the multi-anvil press.
 1440 Electron microprobe conditions are the following: for BPhE samples, Clermont-Ferrand, Cameca
 1441 SX100: acceleration tension: 15 kV, beam current: 8 nA, spot size: 20 micrometers, counting time:
 1442 10 s on peak. For 1010, 1011 and 1090, Camparis, Cameca SX100: 30 kV, 30 nA, 5 s on peak.
 1443 Results for CO₂ rely on the calibration shown in Fig. 2 and correspond to the average concentration
 1444 for each sample. Those samples used to establish the calibration are those for which H₂O was
 1445 measured (with the method of Le Losq et al., 2012) and these H₂O results are reported here.
 1446 Analytical uncertainties at 1 σ are typically 1% for major elements and are reported here for CO₂
 1447 and H₂O. Notice that, for samples 1011 and 1090, the major element data is likely perturbed by
 1448 sample non-homogeneity. *u.s.* : undersaturated.

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Sample	BPhE2	BPhE3	BPhE10	BPhE11	BPhE12	1010	1011	1090
P(GPa)	2	3	2	4	1.5	5	8.5	5
1 σ P	0.1	0.15	0.1	0.2	0.08	0,25	0,25	0,25
T(K)	1920	2003	1920	2128	1824	1873	1873	1873
1 σ T	48	54	48	65	41	25	25	25
SiO ₂	48.87	47.52	54.38	53.57	53.89	42.90	55.57	67.29
TiO ₂	1.56	1.46	1.65	1.68	1.75	0.05	0.03	0.03
Al ₂ O ₃	15.45	15.00	17.01	16.33	17.02	20.05	19.09	26.63
FeO	5.29	2.29	0.01	0.02	0.01	0.02	0.02	0.04
MnO	0.17	0.16	0.01	0.01	0.02	0.02	0.01	0.01
MgO	7.77	7.40	7.81	7.41	7.58	15.94	8.07	4.56
CaO	13.81	16.13	11.85	11.40	11.82	11.46	8.68	0.49
Na ₂ O	2.47	2.31	2.77	2.60	2.81	3.46	8.19	0.44
K ₂ O	0.29	0.30	0.03	0.06	0.04	0.13	0.27	0.03
P ₂ O ₅	0.15	0.17	0.06	0.04	0.07	0	0	0
SrO	0	0	0	0	0	0.02	0.06	0.03
GeO ₂	0	0	0	0	0	0.02	0.04	0.08
Total	95.89	92.74	95.58	93.14	95.02	93.34	100.02	99.62
CO ₂ ^{Raman}	2.65	4.21	1.56	4.67	1.78	5.97	>13.6 (<i>u.s.</i>)	8.5
1 σ CO ₂	0.28	0.25	0.80	0.47	0.19	0.53	-	0.85
H ₂ O	1,24	2,55	2,25	n.m.	2,62	0,54	-	-

1 σ H ₂ O	0,02	0,43	0,74	-	0,26	0,17	-	-
sum	99.77	99.49	99.38	> 97.81	99.50	99.84	-	-

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1456 **Figure captions**

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1458 Figure 1a: Raman spectra of a basalt glass, from top to bottom (i) uncorrected, (ii) after the Long
1459 correction, and (iii) baseline-corrected and normalized. Note the baseline shown in the second
1460 spectrum. a.u.: arbitrary units. Bands in the 20-1200 cm^{-1} portion of the spectra are assigned to
1461 vibrations of the SiO_4 and AlO_4 tetrahedral network of the basalt glass (see the review of Neuville
1462 et al., 2014, and references therein), the peak at $\sim 1085 \text{ cm}^{-1}$ and the doublet at $\sim 1400\text{-}1600 \text{ cm}^{-1}$
1463 are respectively assigned to the symmetric and asymmetric stretching mode of the CO_3^{2-} groups
1464 (Verweij et al., 1977; Mysen and Virgo, 1980; Rai et al., 1983; Brooker et al., 1999), and the band
1465 extending between 3000 and 4000 cm^{-1} is assigned to O-H stretching in $\text{H}_2\text{O}_{\text{mol}}$ and OH^- groups
1466 (Walrafen, 1975; Stolen and Walrafen, 1976; Walrafen et Samanta, 1978; Mysen et al., 1980,
1467 Mysen and Virgo, 1986; McMillan and Remmele, 1986).

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1469 Figure 1b: Examples of deconvolution on Raman spectra in the region 800 - 1200 cm^{-1} , which
1470 includes the several peaks of the Q^n tetrahedral species ($n = 0$ to 4) and the peak due to the C-O
1471 symmetric stretching of CO_3^{2-} located at 1070-1090 cm^{-1} in basaltic compositions and 1046 cm^{-1} in
1472 KS samples. Spectra A and B were taken from basaltic sample BPhE11, C and D from KS samples,
1473 where D is the KS with 3.6 wt.% CO_2 that is used in the calibration shown in Fig. 2.

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1475 Figure 2: Calibration of the Raman method of CO_2 measurement in silicate material. Area of the
1476 $\sim 1085 \text{ cm}^{-1}$ CO_2 Raman peak vs. CO_2 concentration. Shown are our potassium silicate (KS)
1477 samples, our natural MORB samples with added carbonate (BPh) and our artificial basaltic sample,
1478 1010). For BPhE and 1010 samples, CO_2 concentrations were determined by difference to 100% of
1479 the sum of the major elements obtained by electron microprobe analysis and H_2O by Raman
1480 spectroscopy. The best straight line passing through these points has a slope of
1481 0.063453 ± 0.002156 (correlation coefficient of 0.966), identical within error to that determined by
1482 Morizet et al., 2013).

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1484 Figure 3: a) Polished section of sample BPhE2, a natural basalt loaded with calcium carbonate and
1485 exposed to 2 GPa, showing the occurrence of a bubble at the top of the capsule after quench, while
1486 the carbonate powder was loaded at the bottom of the capsule. This bubble suggests this sample is
1487 saturated in CO_2 . The height of the capsule is 2.5 mm.

1488 b) Raman map of basaltic sample 1010 (5 GPa) showing CO_2 concentrations in wt.%. Note the
1489 bubble in the right-hand side bottom corner of the picture, highlighted by a dashed line, and the
1490 variations of CO_2 increasing toward the bubble. The top of the capsule, when at high pressure, was
1491 on the right side.

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1493 Figure 4: Raman mapping, with CO_2 concentrations reported in wt.%, of a) basaltic sample
1494 BPhE10, 2 GPa) with 19 measurement spots, showing the strong CO_2 heterogeneity of this sample,
1495 where a bubble is probably located inside the platinum at the top of the capsule or was lost in the
1496 experiment, and b) sample BPhE3 (3 GPa), showing the relative CO_2 homogeneity of this sample, a
1497 variability of about 0.2 % for the 4 spots shown (6 spots are available). Note that the global CO_2

1498 concentration obtained for BPhE10 is very different from the lowest and the highest values, but
1499 identical to that reported by Matthey (1991) for a similar composition and the same pressure,
1500 pointing to the interest to realize such a sample mapping.

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1502 Figure 5: Raman mapping of a 30 μm x 30 μm area of sample 1090. The probed depth was $\sim 2\mu\text{m}$
1503 and the spot of the laser beam $\sim 1\text{-}2\ \mu\text{m}^2$. On the left are shown a Raman spectrum from one of
1504 the aragonite crystals, a spectrum from the glass alone, and a spectrum from the aragonite-glass
1505 mixture (with the $\sim 1080\ \text{cm}^{-1}$ peak shown in green). The color-scale represents the intensity of the
1506 $\sim 1080\ \text{cm}^{-1}$ CO_3^{2-} stretch peak from aragonite microcrystals in the glass normalized to the
1507 maximum intensity found in the aragonite crystal at the bottom left-hand side of the map. We
1508 assume, here, that this normalized intensity of the crystalline CO_3^{2-} peak depends linearly on the
1509 fraction of nano- and micro-crystals present in the glass.

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1511 Figure 6: photograph of a section of sample 1011 (8.5 GPa) in reflected light. The circle shows
1512 where the Raman spectrum shown in Fig. 7 was taken.

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1514 Figure 7: From top down are displayed Raman spectra taken in sample 1011 for one glass region
1515 and one silicate crystal, then the reference Raman spectrum for the silicate mineral pyrope, a
1516 garnet, the spectrum of carbonate mineral eitelite, $\text{Na}_2\text{Mg}(\text{CO}_3)_2$, and the spectrum of aragonite.
1517 The thin peaks generated by eitelite microcrystals are visible in the spectrum of glass.

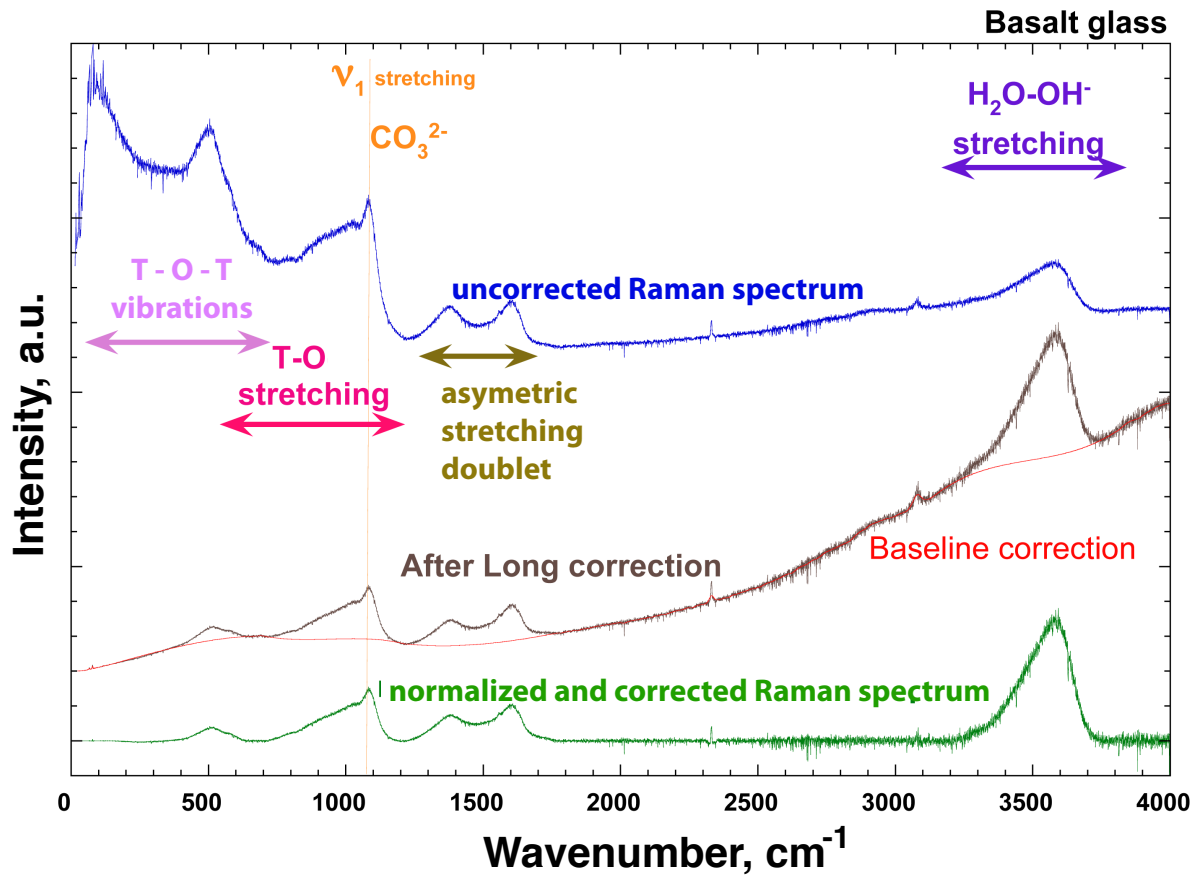
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1519 Figure 8: CO_2 concentration (weight ratio) in various mafic melts plotted as a function of total
1520 pressure in GPa, with 1- σ experimental errors. Shown are the experimental data generated in this
1521 work, as well as several curves obtained by molecular dynamics simulations for similar
1522 compositions (name of composition and temperatures indicated). Sample BPhE2 was omitted since
1523 it has a too small number of measurements (see text). These data correspond to melts saturated
1524 with CO_2 , thus solubility, except for the triangle with an arrow showing that the true value for
1525 sample 1011 is higher because this sample was clearly under-saturated at 8.5 GPa. Also shown
1526 are, using open symbols, some experimental results for similar compositions in the range 0 – 2.5
1527 GPa published previously by Pan et al. (1991), Matthey (1991) and Stanley et al. (2011). Other data
1528 in the pressure range between 0 and 0.5 GPa are impossible to show at this scale, including Stolper
1529 and Holloway (1988), Pawley et al. (1992), Dixon et al. (1995), Jendrzewski et al. (1997),
1530 Botcharnikov et al. (2005), Shishkina et al. (2010) and others, but are consistent with each other.
1531 The empty circle at 6 GPa is from Kim et al (2018) for albite melt. The dashed-dotted straight line
1532 is an extrapolation of the Henry's law proposed by Dixon et al. (1995) based on the shown data of
1533 Pan et al. (1991) and Matthey (1991). The dashed-dotted curves labeled 'Eguchi & Dasgupta 2018'
1534 are from the thermodynamic model of Eguchi and Dasgupta (2018) where the higher curve is for a
1535 composition of MORB and the lower curve for a haplo-basalt. A zoom on the low-pressure region of
1536 this figure is presented in the supplement (Fig. S7).

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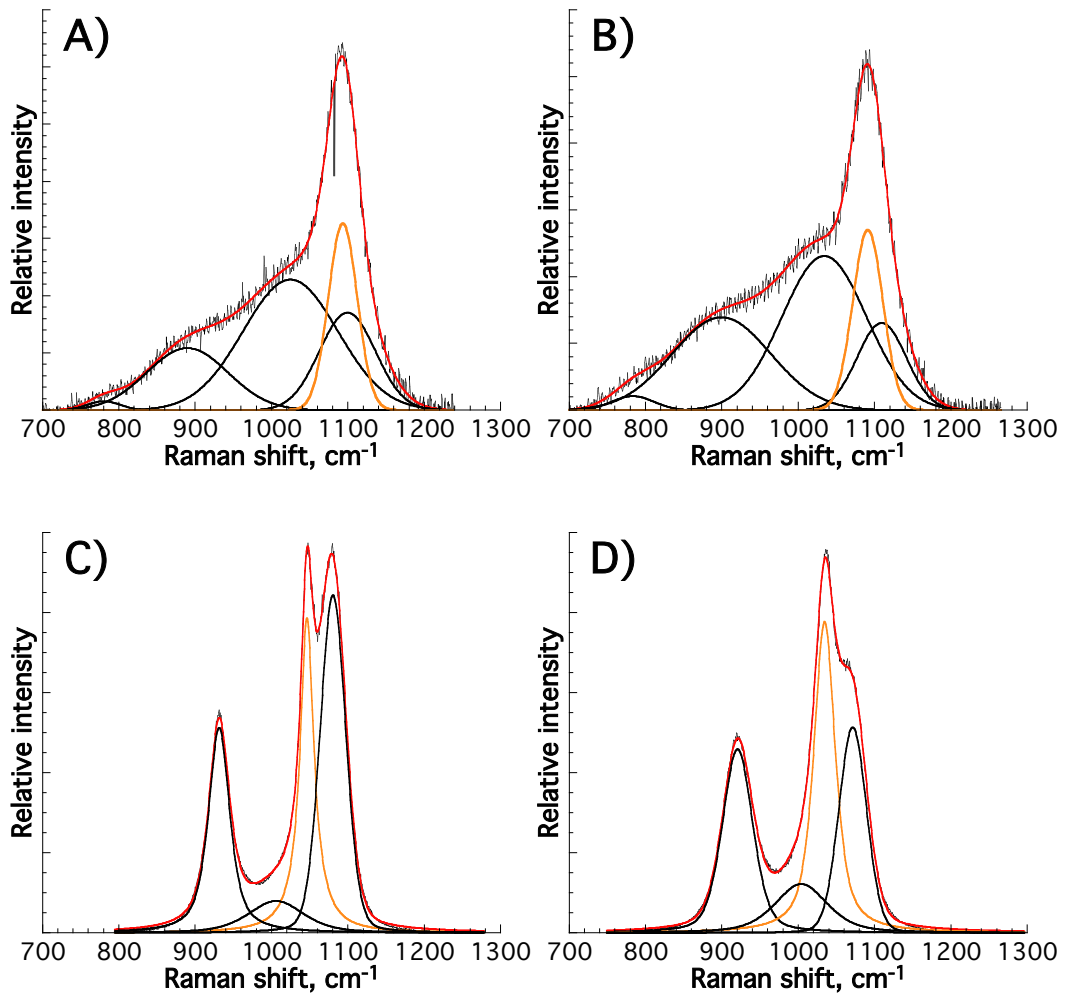
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Figure 1a

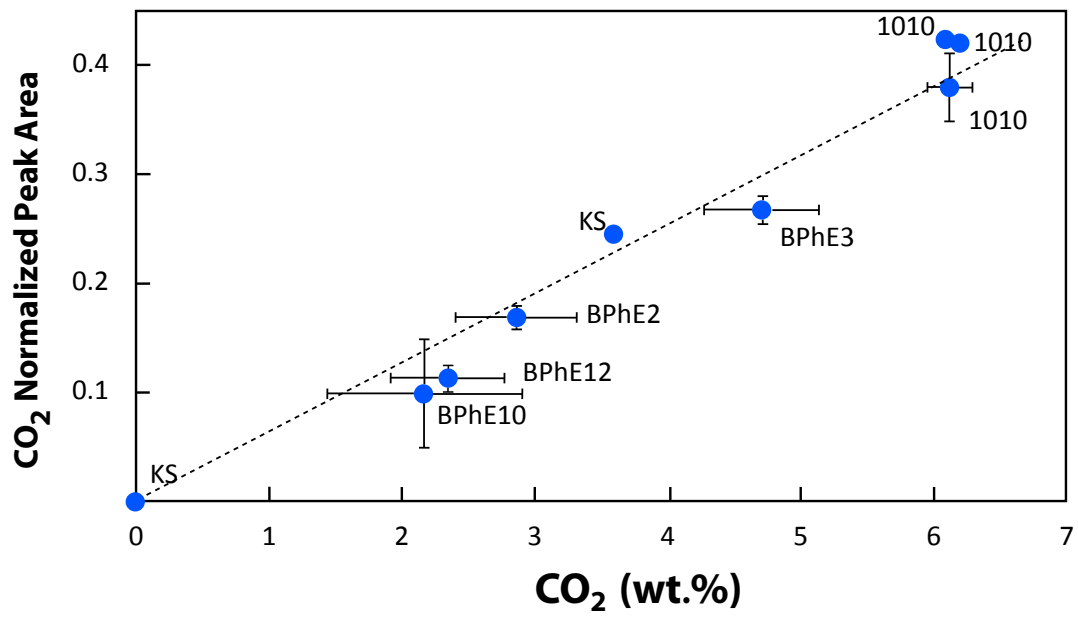
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Figure 1b

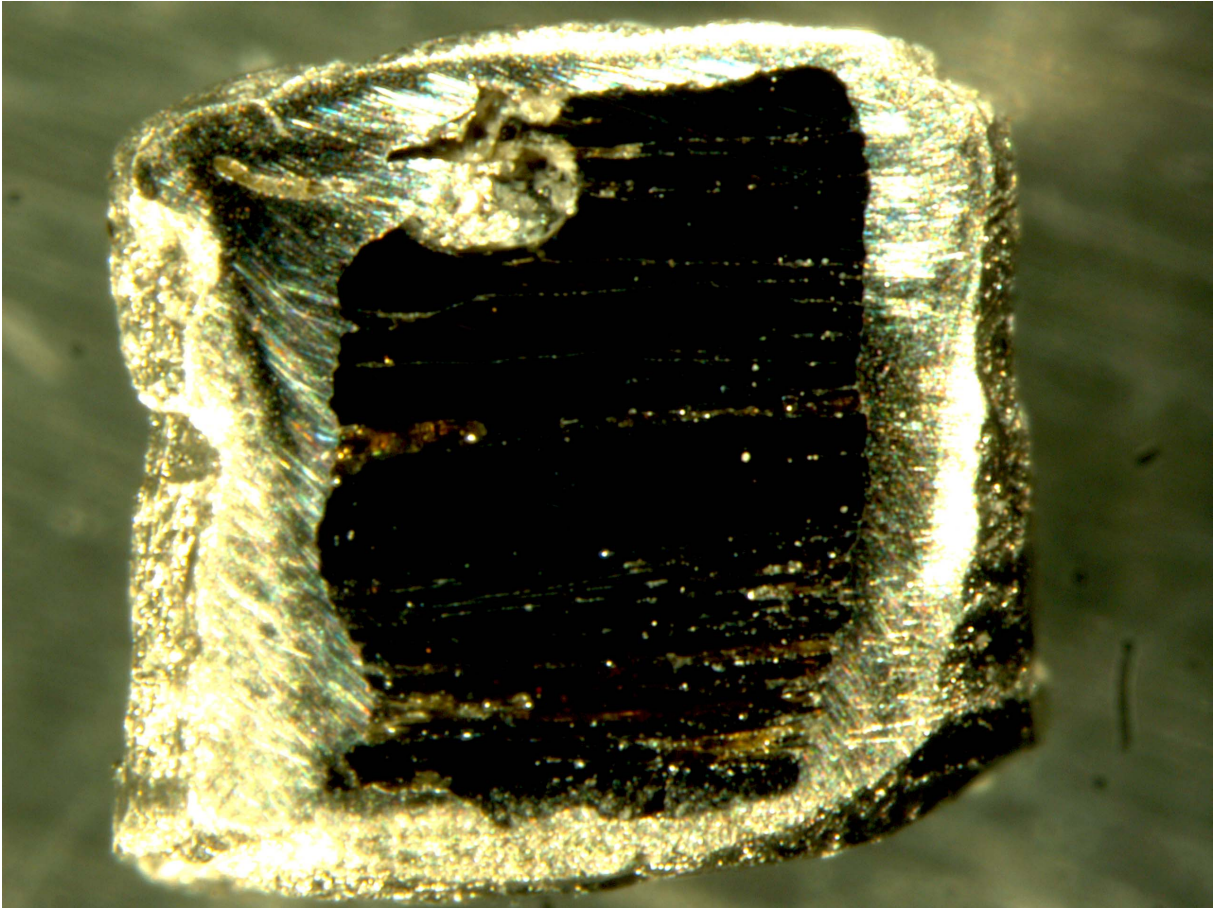
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Figure 2

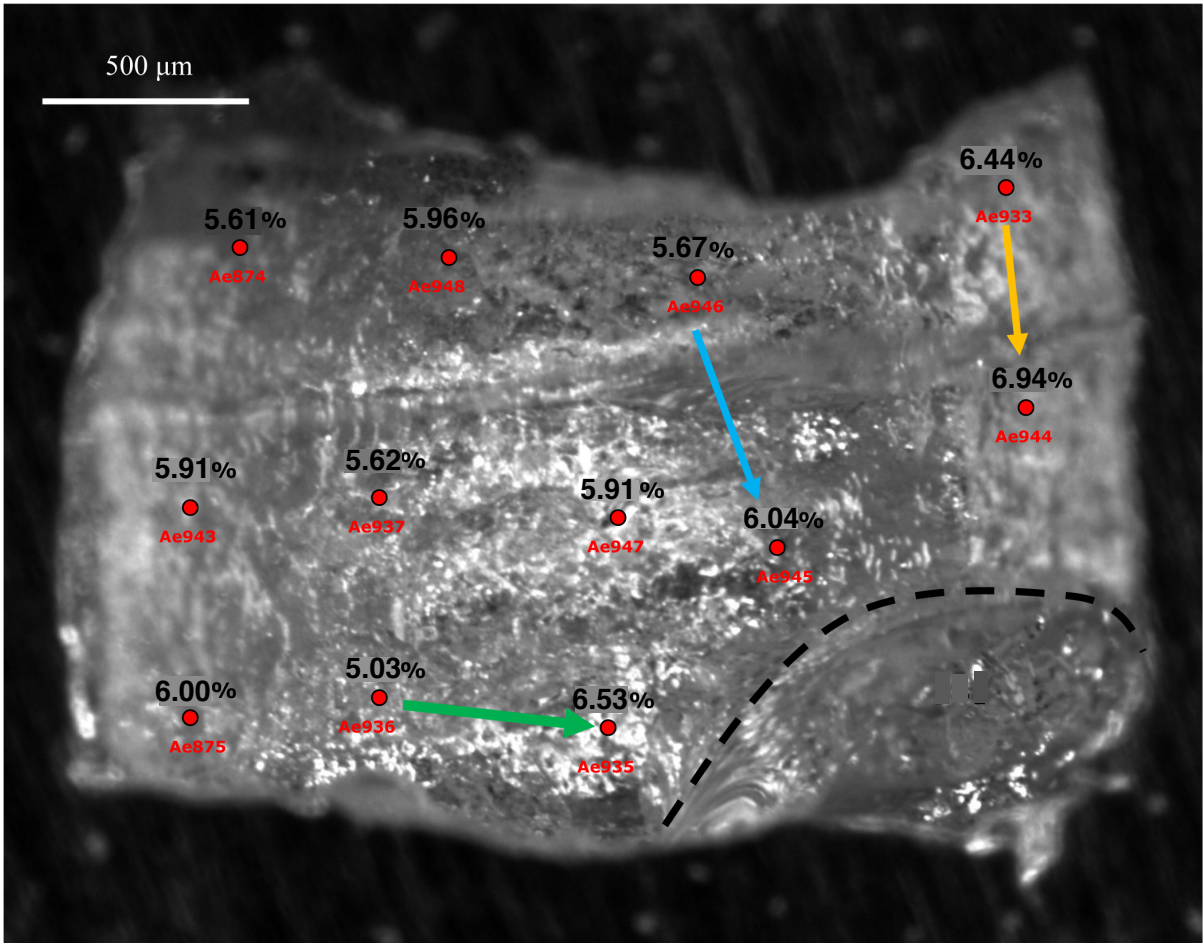
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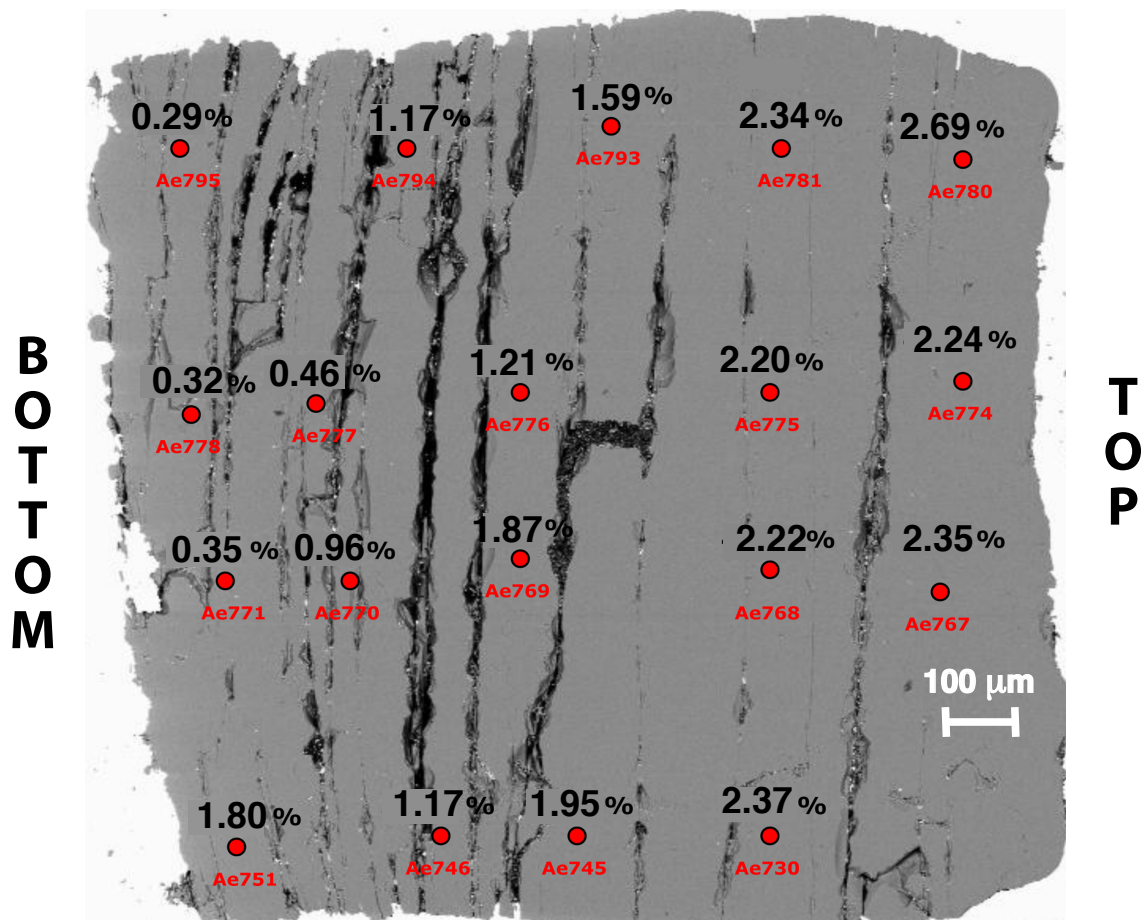
Figure 3a

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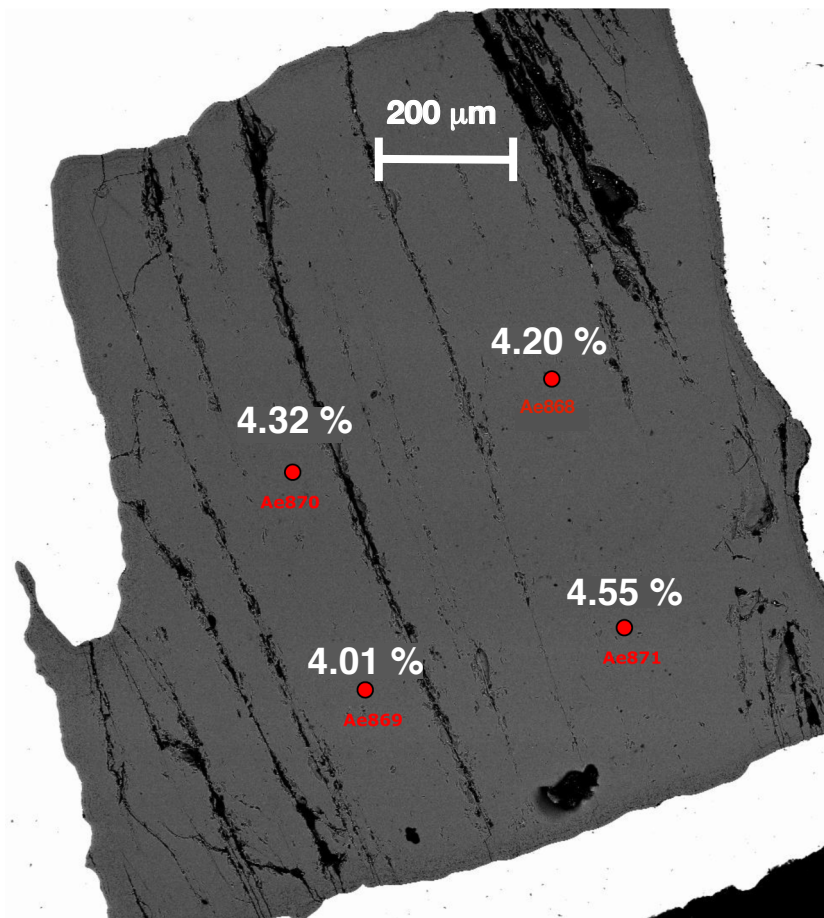
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Figure 3b



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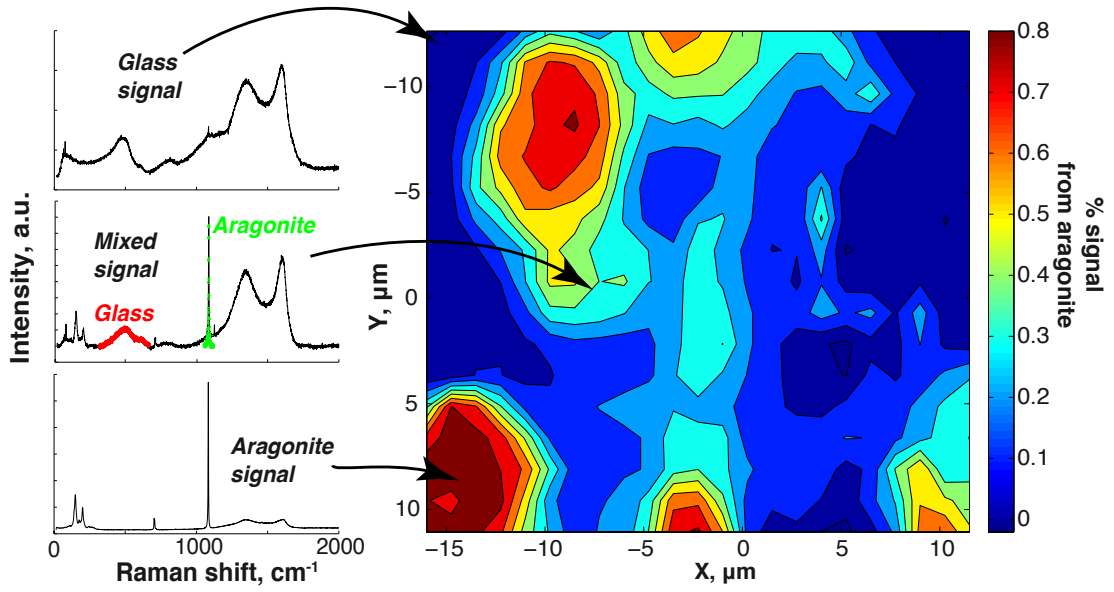
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Figure 4b

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Figure 5

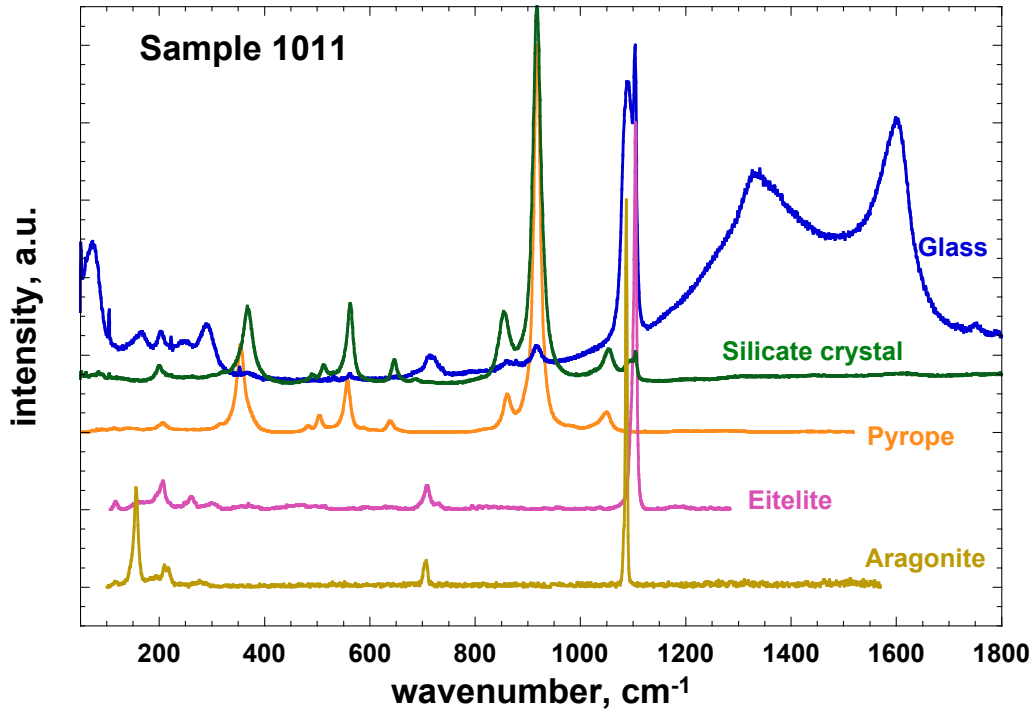
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Figure 6

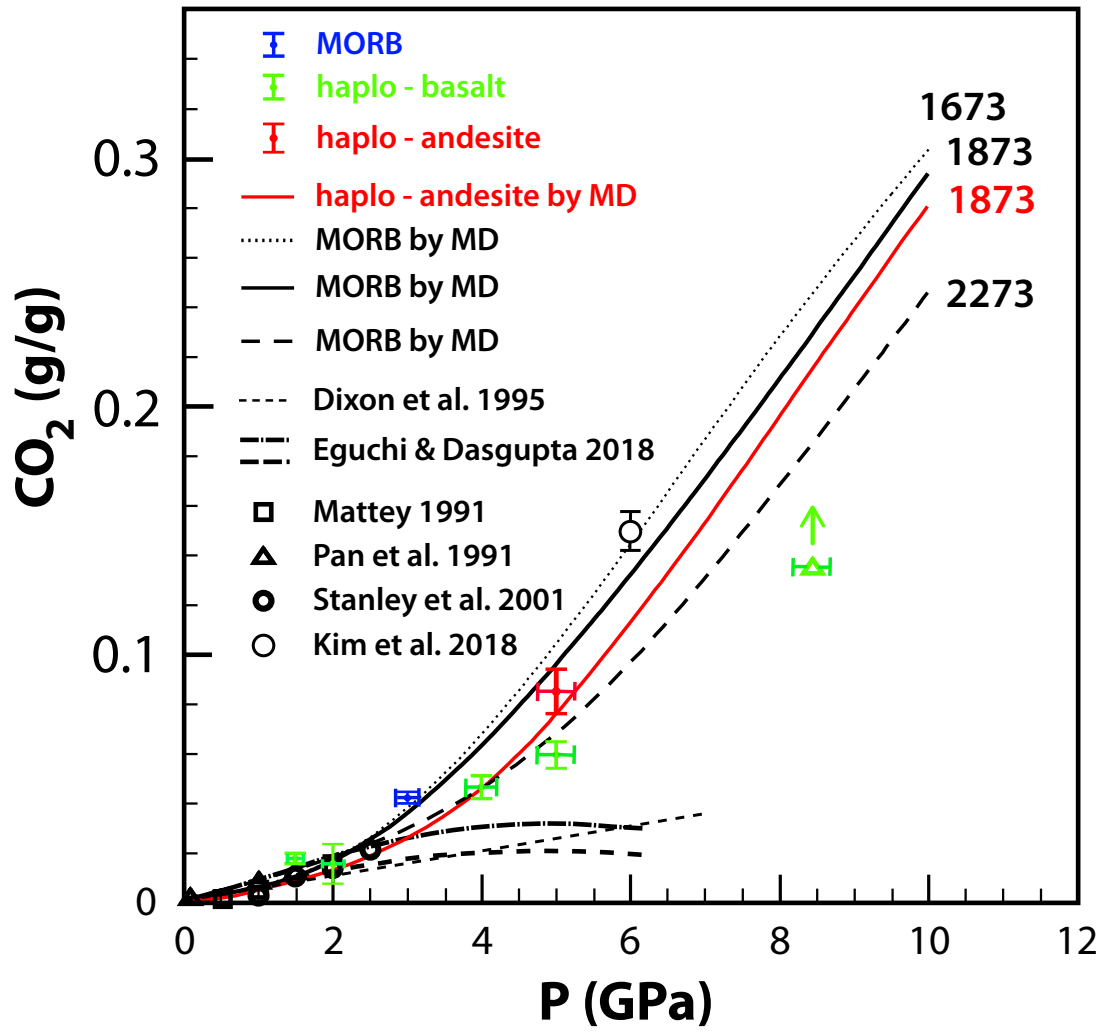
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Figure 7

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Figure 8

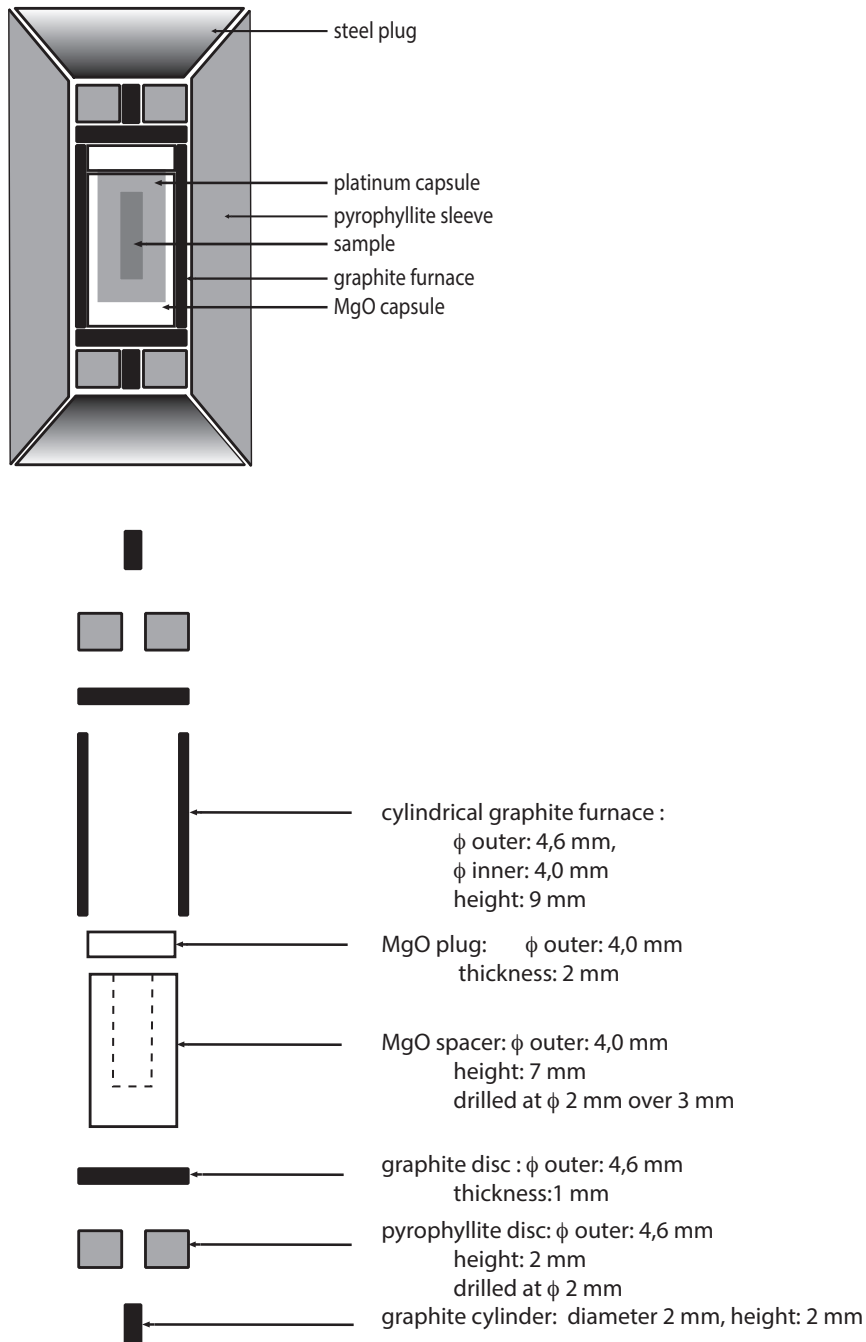
1770 Supplement to

1771 **Raman spectroscopy to determine CO₂ solubility in mafic silicate melts at high**
1772 **pressure: haplobasaltic, haploandesitic and approach to basaltic compositions**

1773

1774 **2. Experimental set up**

1775 **2.1. Starting materials and high-pressure experiments**

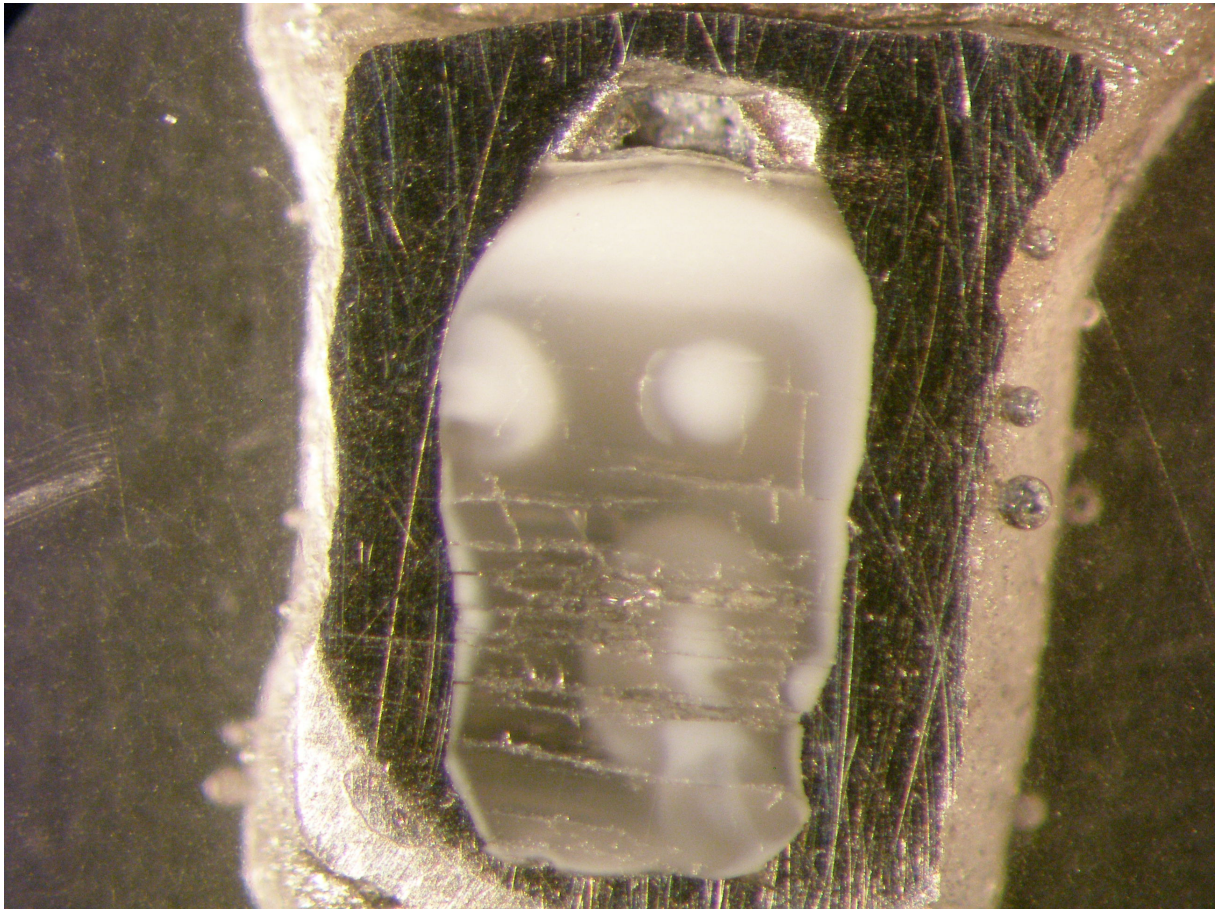


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1777 **Figure S1:** schematic cross section (top) and layout (bottom) of the high-pressure cell used in the
1778 Belt press for BPhE samples.

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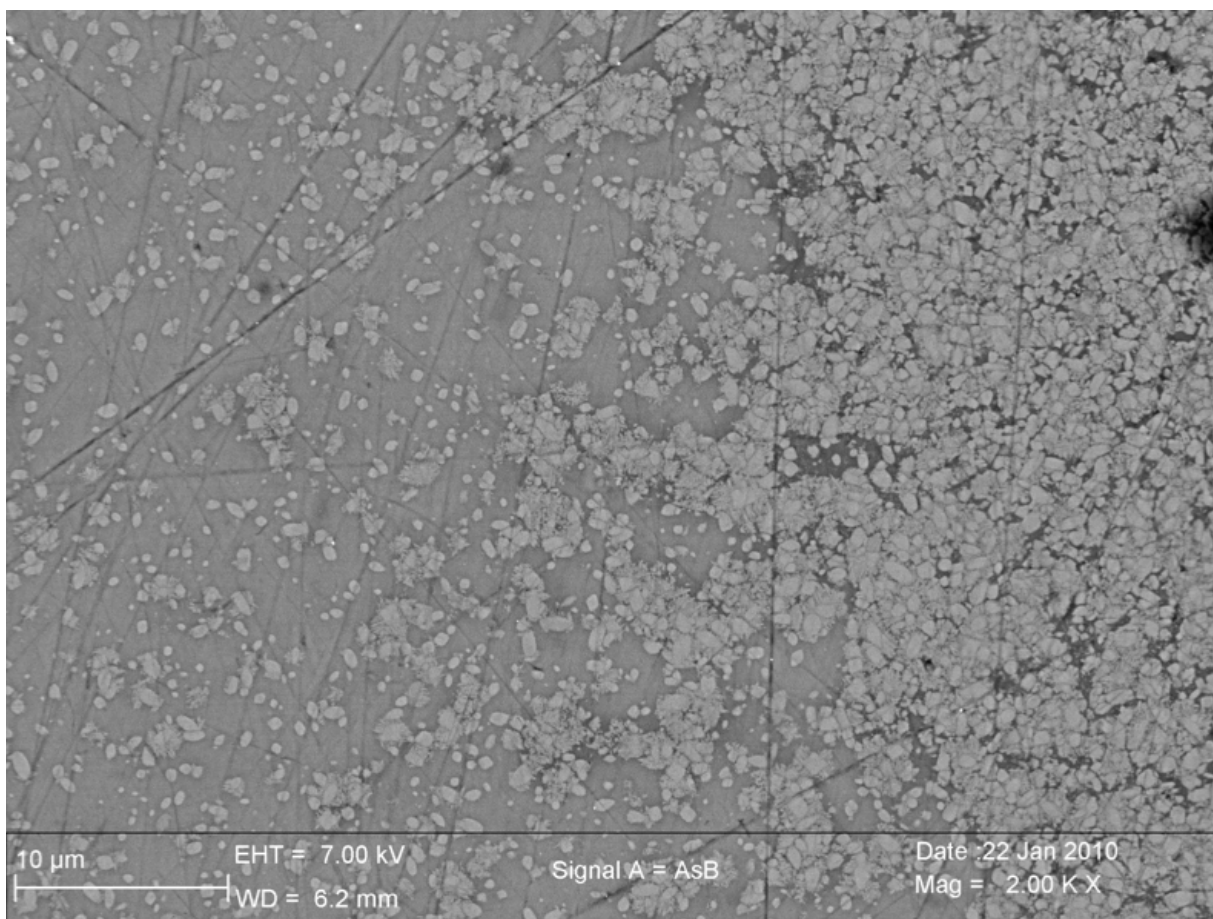
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Figure S2a: Photograph of polished capsule BPhE11 (4GPa, 2130K), showing a cavity inside the platinum, at the top of the sample, opened by abrasion. This cavity must have been filled with fluid CO₂ at high P and high T.

Analysis with SEM shows that the texture is that of a glass, bearing abundant and very small crystallites (micron size), which generate the visible whitish regions sometimes with globule forms. These crystallites are not carbonate, but silicate crystals. The height of the capsule is roughly 1.5 mm.

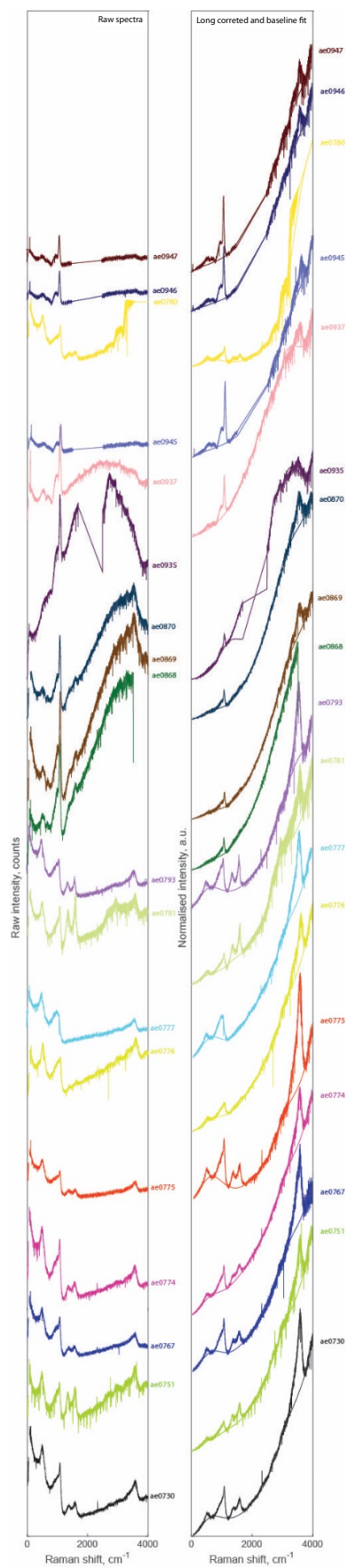


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Figure S2b: MEB image of sample BPhE11 at the limit of a globule (the globule is on the right side). The structure is that of a glass with micron-sized crystallites. The globule is only a region with more crystallites. Magnification is 2000.

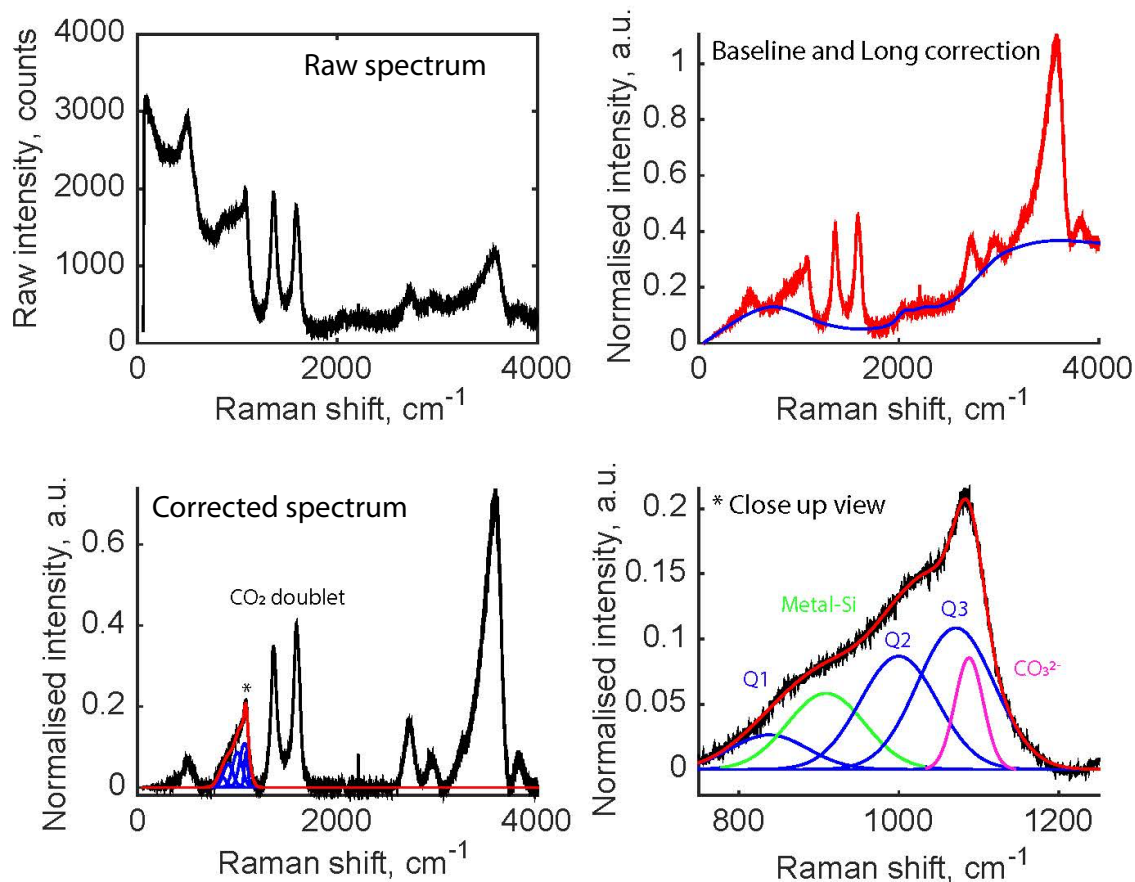
2.2. Raman spectroscopy analyzes

Raman spectrometry



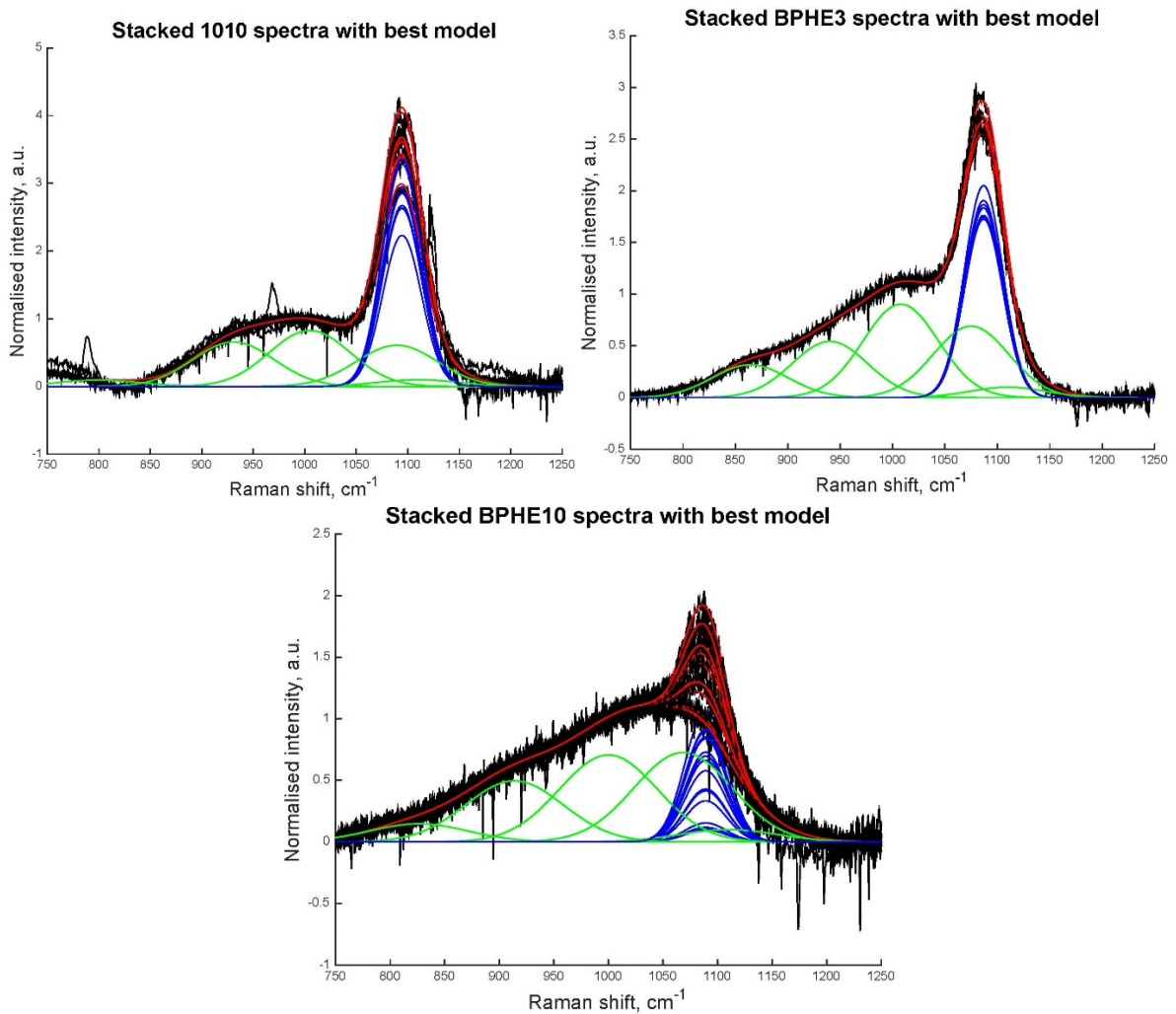
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Figure S3: raw Raman spectra and spectra after the Long correction and baseline fit.



1807
 1808 **Figure S4:** illustration of the four main stages of a typical spectrum treatment. Shown are the raw
 1809 data (top left), on which the Long correction and baseline determination are applied (top right).
 1810 The spectrum resulting from baseline subtraction is shown on the bottom left corner. Finally, a
 1811 close-up view on the 800 – 1200 cm^{-1} Raman wavenumber range (star) is displayed on the bottom
 1812 right showing the Q^n species, the metal-Si stretching mode and the CO_3^{2-} peak representing the
 1813 CO_2 concentration in the sample.
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1838 **2.3. CO₂-related Raman peaks and calibration**



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Figure S5: Close up look at the 800-1250 cm⁻¹ Raman wavenumber range for samples 1010, BPHE3 and BPHE10. All the spectra and their deconvolution are stacked for each sample. The green peaks represent the Qⁿ species and the stacked blue peaks the CO₃²⁻, for which different peak heights are related to different CO₃²⁻ concentrations at various places in the samples.

Sample BPhE3 (3 Gpa, 2003 K)			Sample BPhE10 (2 Gpa, 1920 K)			Sample 1010 (5 Gpa, 1873 K)		
Spectrum label	H ₂ O (wt.%)	CO ₂ relative area (a.u.)	Spectrum label	H ₂ O (wt.%)	CO ₂ relative area (a.u.)	Spectrum label	H ₂ O (wt.%)	CO ₂ relative area (a.u.)
ad4498	2.1901	0.26969	ae0795	1.3441	0.018681	ae0874	0.43054	0.35598
ad4499	2.3095	0.25679	ae0794	1.3229	0.074502	ae0948	0.50306	0.37804
ad4502	2.6353	0.2588	ae0793	1.6143	0.10062	ae0946	0.50564	0.35994
ae0871	2.065	0.28874	ae0781	3.4	0.14837	ae0933	0.86748	0.40856
ae0869	2.9206	0.25467	ae0780	3.1284	0.17085	ae0943	0.85069	0.37496
ae0870	3.1626	0.27394	ae0778	2.7967	0.020315	ae0937	0.40289	0.35671
			ae0777	1.8005	0.029012	ae944	0.84705	0.44013
			ae0776	2.8326	0.076898	ae0947	0.53026	0.37532
			ae0775	2.0979	0.13983	ae0945	0.47636	0.38297
			ae0774	1.9007	0.14208	ae0875	0.50322	0.38063
			ae0771	1.6017	0.022478	ae0936	0.54746	0.31947
			ae0770	1.9941	0.060812	ae0935	0.35416	0.41422
			ae0769	2.3624	0.11894			
			ae0768	1.7992	0.1408			
			ae0767	1.8418	0.14943			
			ae0751	3.4366	0.11393			
			ae0746	3.6465	0.074404			
			ae0745	1.5936	0.12386			
			ae0730	2.2122	0.15033			

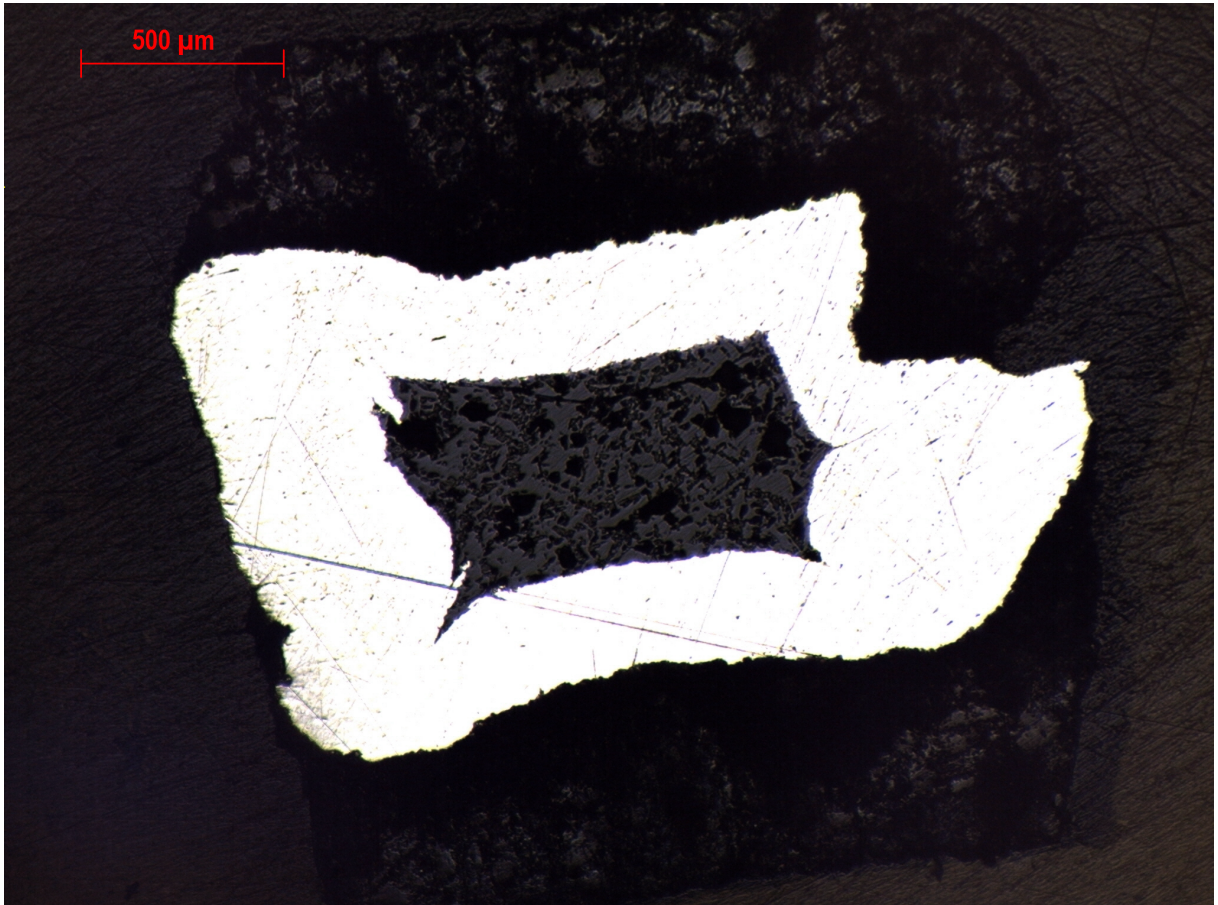
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Table S1: H₂O (wt.%) results and CO₂ normalized area (arbitrary units) for each Raman spot on 3 samples.

1867 **3.3. Partially crystallized sample 1090 (5 GPa)**

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1869 *Mean CO₂ content from optical estimate of phenocryst proportion*

1870 After subtracting the black glitches due to sample polishing (Fig. S6), we converted the grey-
1871 scale picture in a black and white picture, with a threshold chosen to discriminate glass from
1872 crystals. We obtained the area fraction of aragonite phenocrysts that we assume to be close to the
1873 volume fraction, V_c .



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1875 **Figure S6a:** Picture of sample 1090 in reflected light. No nubble is seen.
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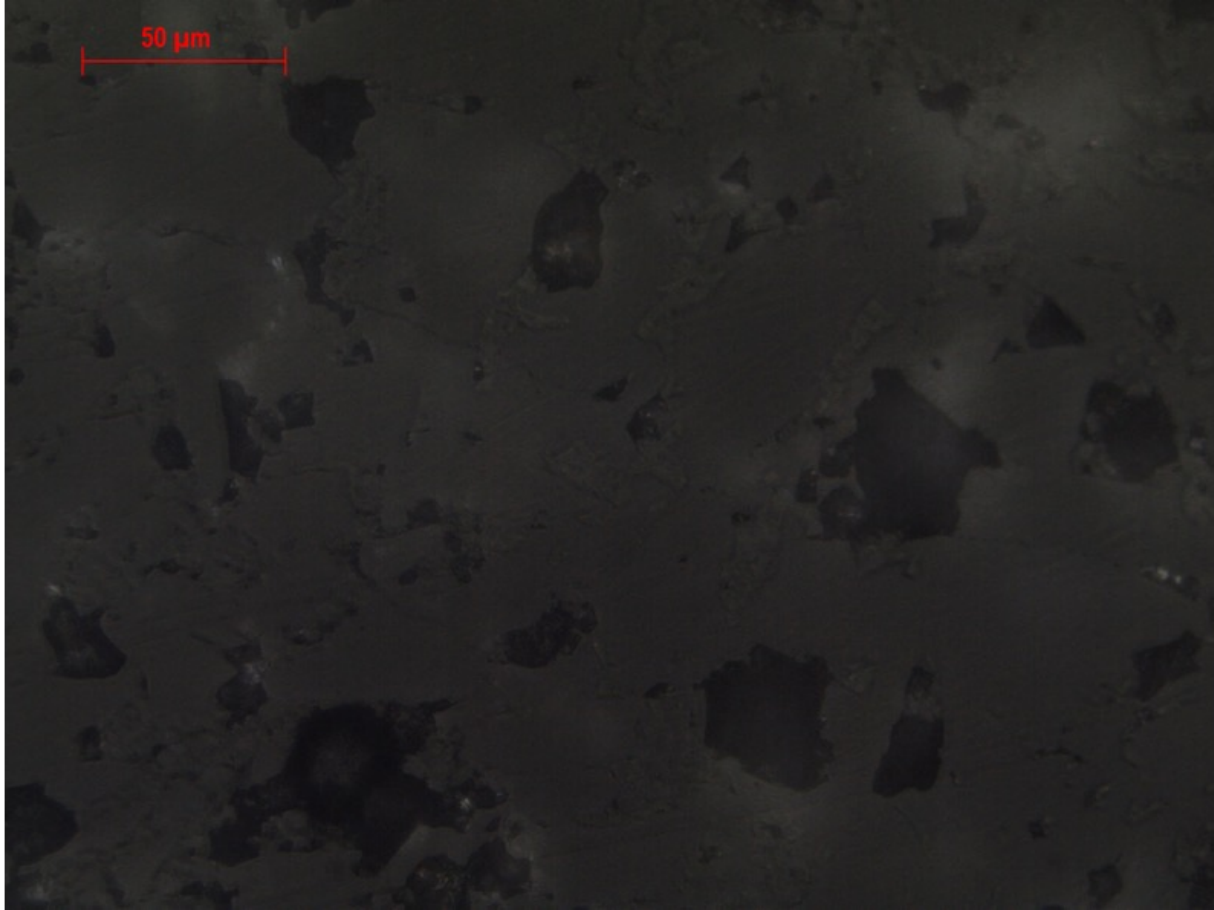


Figure S6b: Close-up of sample 1090 in reflected light. The black zones are glitches due poor polishing. One can see glass and crystals intermingled. Crystals appear slightly clearer than glass.

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The corresponding CO₂ content can then be deduced by the following relationship,

$$C_{CO_2}(\text{wt.}\%) = 100 \times \frac{n_{CaCO_3} \times \left(\frac{M_{CO_2}}{M_{CaCO_3}} \right)}{n_{CaCO_3} + n_{glass} \times \left(\frac{1-V_c}{V_c} \right)} \quad (\text{S3})$$

1884 where n_{CaCO_3} is the density of aragonite, M_{CO_2} the molar mass of CO₂, M_{CaCO_3} the molar mass of
1885 CaCO₃, n_{glass} the density of the glass.

1886 At atmospheric pressure, the density of aragonite is 2.93 g/cm³ at 300 K, and that of glass,
1887 assuming the chemical composition listed in Table 2, is ~2.49 g/cm³ at 300 K using Lange and
1888 Carmichael (1987). We found $V_c = 18 \pm 2$ vol% yielding a CO₂ content of 9 ± 1 wt.%.

1889

Micrometric scale Raman mapping of groundmass

1891 We measured the area, named A_{1085} , of the CO₃²⁻ sharp peak seen in glass (the carbonate
1892 vibration in aragonite at 1085 cm⁻¹), and the area, named $A_{1085}^{\text{aragonite}}$, of the same peak in a large
1893 aragonite crystal chosen in the sample (Fig. 5). Because the intensity of a vibration band is
1894 proportional to the concentration of vibrators per unit volume, the ratio $R_{1085} = A_{1085}/A_{1085}^{\text{aragonite}}$ is
1895 then related to the CO₂ concentration borne by crystallites by the following relation

$$C_{CO_2}(\text{wt.}\%) = 100 \times R_{1085} \times \left(\frac{M_{CO_2}}{M_{melt}} \right) \quad (\text{S4})$$

1896

1897 where M_{CO_2} is the molar mass of CO_2 and M_{melt} that of the melt. This is because the intensity of
1898 a vibration band is proportional to the concentration of vibrators per unit volume seen by the laser
1899 beam.

1900 Our evaluation gives $R_{1085} = 0.1137$ by averaging over a 30 micrometers X 30 micrometers
1901 region. To calculate the molar mass of melt, we should use the starting chemical composition of
1902 this sample including the initial CO_2 charge of 9.0 wt.% (Table 1): we find a value of 62.04 g/mol
1903 (64.66 g/mol for the pure silicate). Using the latter value, the derived CO_2 abundance amounts to
1904 8.1 wt.%, this value representing the carbonate microcrystals in the groundmass.

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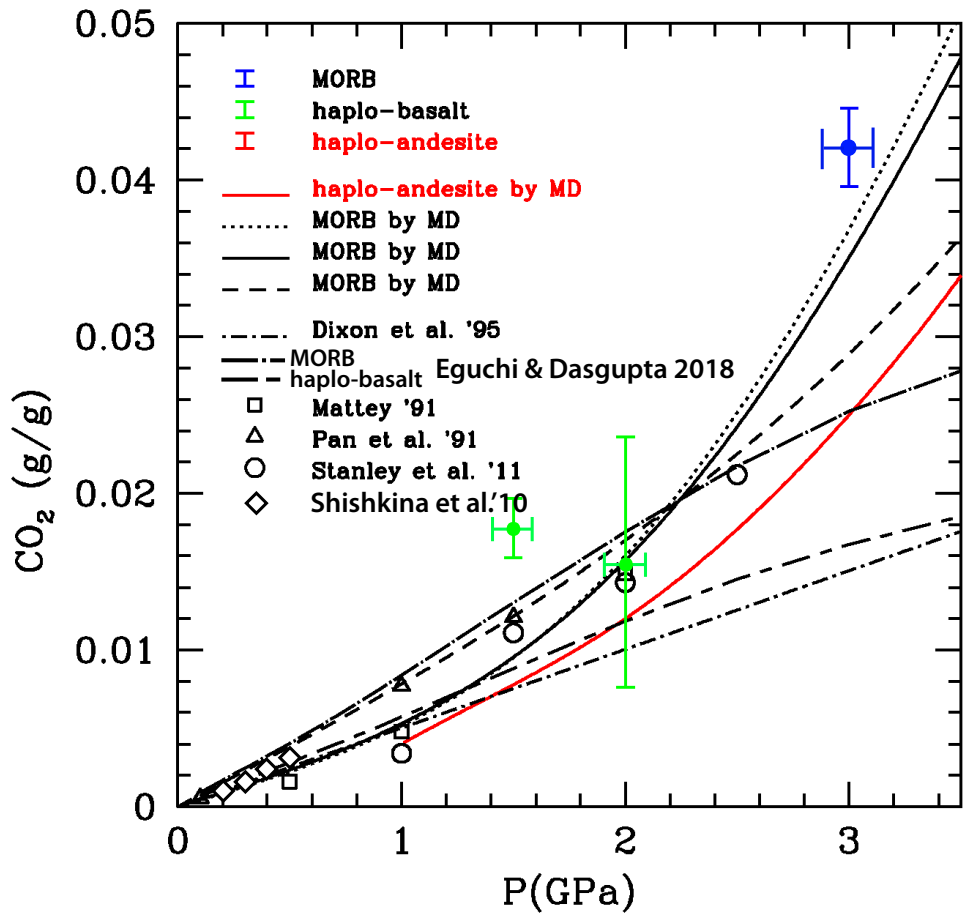
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1908 **4. Discussion**

1909 **4.1. CO₂ solubility in basaltic and andesitic melts up to 8.5 GPa**

1910 *Comparison to previous data and accuracy of results*



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1912 **Figure S7:**

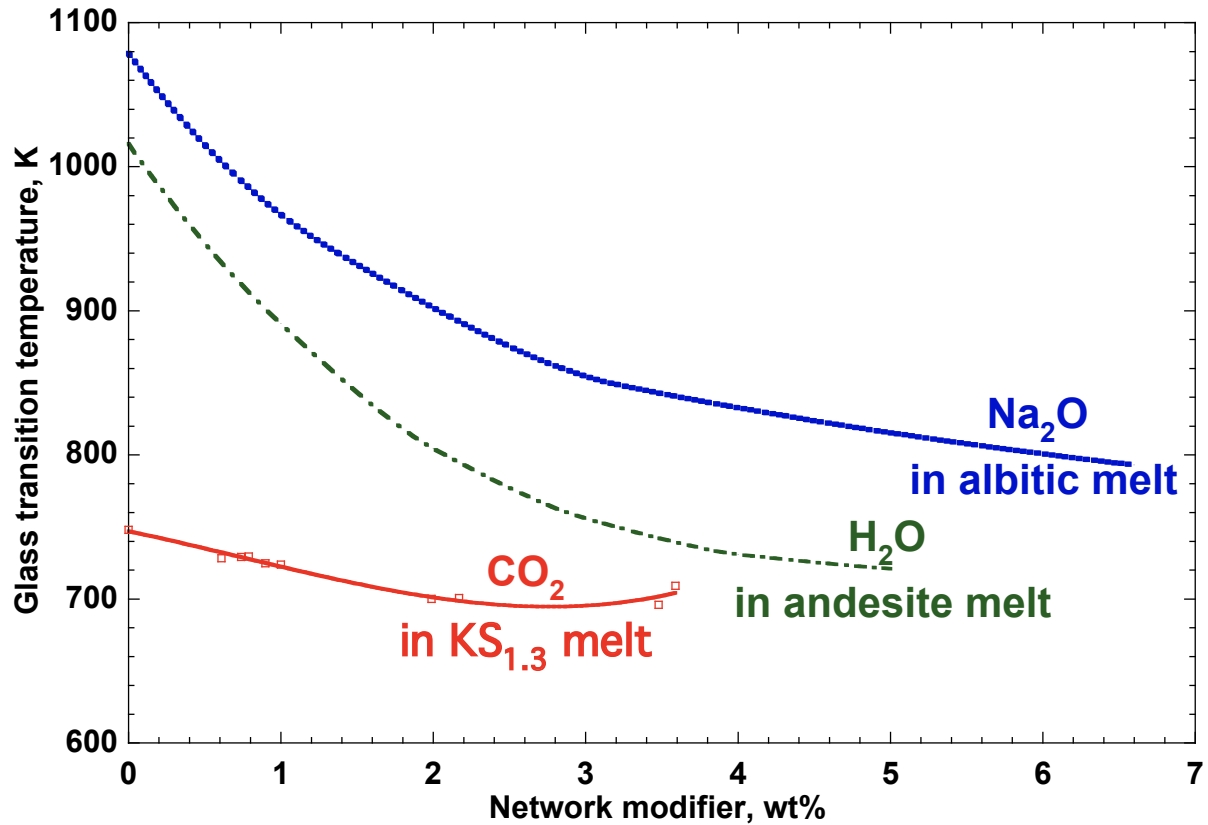
1913 Zoom on the low-pressure side of Fig. 8, showing measured values for mafic compositions, and our
1914 simulation curves, as well as other data from Pan et al. (1991), Matthey (1991), Stanley et al.
1915 (2011) and Shishkina et al. (2010; except two points < 0.2 GPa). Some data between 0 and <0.2
1916 GPa are impossible to show here (e.g., Stolper and Holloway (1988), Pawley et al. (1992), Dixon et
1917 al. (1995), Jendrzewski et al. (1997), Botcharnikov et al. (2005). Are also shown the straight line
1918 corresponding to the Henry's law of Dixon et al. (1995) and the recent thermodynamic model of
1919 Eguchi and Dasgupta (2018) for MORB (higher curve) and haplo-basaltic compositions (lower
1920 curve).

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4.3. Influence of melt composition

Relation to melt properties and solvation structure.



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Figure S8: Influence of CO₂ dissolution on the glass transition temperature of K₂OSiO₂ melt, compared to dissolution of H₂O in andesite melt and of Na₂O in albite melt. Data from Bourgue and Richet (2001) for CO₂ in KS; Vetere et al. (2006) for H₂O in andesite; Le Losq et al. (2014) for Na₂O in albite melt.

