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1 TOWARDS THE RECONCILIATION OF VISCOSITY CHANGE AND CO₂-INDUCED
2 POLYMERIZATION IN SILICATE MELTS

3

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29

30 **Abstract:**

31 Deep mantle melts contain massive amounts of CO₂ but three critical issues related to the
32 effect of CO₂ on molecular structure and physical properties of magmatic melts remain poorly
33 constrained: 1) there is no exact picture of CO₂ dissolution mechanism in silicate melt, 2) the
34 silicate melt polymerization upon CO₂ dissolution has not been reliably quantified and 3) the
35 effect of CO₂ on silicate melt viscosity has never been measured adequately.

36 We synthesized a series of ¹⁷O and ²⁹Si-enriched CO₂-bearing melilitite (SiO₂ ~ 35 wt.%)
37 silicate glasses at high temperature and pressure. Using NMR spectroscopy, we have
38 interrogated both anionic and cationic networks for quantifying the change in the degree of
39 polymerization associated to CO₂ incorporation in the melt. Increasing CO₂ content induces a
40 strong increase in the degree of polymerization. CO₂ dissolution follows a complex
41 mechanism involving the formation of Free Ionic Carbonate (FIC) Ca²⁺..CO₃²⁻ species. This
42 carbonate subnetwork is the precursor to the immiscibility process between a carbonate liquid
43 and a silicate liquid.

44 Glass transition temperature (T_g) measurements show that increasing CO₂ content induces a
45 decrease in T_g implying a decrease in viscosity for the studied low silica melt composition.
46 This result appears in complete contradiction with the melt polymerization induced by CO₂ as
47 quantified by NMR. We propose a model that reconciles both aspects. CO₂ induces silicate
48 subnetwork polymerization resulting in a viscosity increase but it also induces a competing
49 effect by forming a carbonate subnetwork having a low viscosity. The overall result appears
50 dominated by the carbonate subnetwork resulting in a slight decrease in melt viscosity in
51 agreement with existing studies.

52 *Number of word: 265*

53

54 Keywords: CO₂ dissolution mechanism, low silica melt polymerization, CO₂ effect on silicate

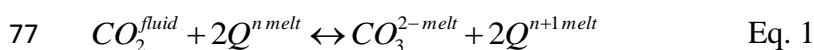
55 melt viscosity.

56

57 **1. Introduction:**

58 Carbon dioxide (CO₂) is a ubiquitous component of the Earth's mantle and it is known to play
59 a major role in the mantle melting (Wyllie and Huang, 1976; Taylor and Green, 1988;
60 Wallace and Green, 1988; Dasgupta and Hirschmann, 2006; Dasgupta, 2013). Melts with low
61 silica content (< 40 wt.%) and high CO₂ content are broadly produced by low degree partial
62 melting (Massuyeau et al., 2015) over a great depth interval and are possibly affecting large
63 scale geophysical observations such as electrical conductivity as shown by Sifré et al. (2014).
64 A key question related to their physical properties (i.e. viscosity) is: how fast such buoyant
65 melts move through the surrounding mantle? Silicate melts and carbonate melts at mantle
66 conditions have been well studied while the intermediate CO₂-rich silicate (e.g. melilitites and
67 nephelinites), which are prevailing in the mantle (Mitchell, 2005) have poorly defined
68 physical properties. To circumvent the experimental difficulties in measuring viscosity in
69 CO₂-bearing silicate melt, one method often quoted is to scrutinize the change in the silicate
70 melt molecular structure upon CO₂ dissolution to gain access to the melt viscosity (Stebbins,
71 2016).

72 Pioneer works (Eggler, 1978; Mysen and Virgo, 1980a) on CO₂ dissolution in silicate melt
73 conjectured that CO₂ acts as a polymerizing agent hence increasing melt viscosity. The
74 suspected CO₂ dissolution involves the polymerization (i.e. increasing connectivity of the
75 oxygen atoms) of the structural units (Mysen and Virgo, 1980b; Qⁿ species where Q is a
76 tetrahedral unit with n bridging oxygens) with the following reaction:



78 Where a CO₂ molecule scavenges an available oxygen of a Qⁿ unit to form a free Mⁿ⁺..CO₃²⁻
79 group in which Mⁿ⁺ is a charge balancing or network modifying cation (e.g. Ca²⁺). As Eq. 1
80 proceeds to the right, there is a change in the proportion of the different oxygen species: a

81 Non-Bridging Oxygen (NBO) is consumed by the CO₂ molecule and a Bridging Oxygen (BO)
82 is produced. The proportion of both oxygen species defines the degree of polymerization.
83 Although this mechanism appears intuitively acceptable, it has never been reliably determined
84 experimentally. Recent work using ²⁹Si MAS NMR spectroscopy (Morizet et al., 2014b;
85 Moussallam et al., 2016) attempted to quantitatively measure the change in polymerization
86 upon CO₂ dissolution and corroborated the polymerizing effect of CO₂. However, simple
87 mass balance calculations using Eq. 1 do not match the calculations made from ²⁹Si NMR
88 spectra: the increase in polymerization is too large for the amount of CO₂ dissolved. This lack
89 of internal consistency shows the difficulty of the ²⁹Si NMR method and suggests that a more
90 complex structural mechanism is at stake for CO₂ dissolution in silicate melts . This
91 mechanism could involve changes: 1) in the distribution of the structural units (Qⁿ species),
92 and 2) in the distribution of bond length and angles within the structural units (Lee, 2004,
93 2005; Massiot et al., 2012).

94 As a result, a reliable quantification of the silicate degree of polymerization upon CO₂
95 dissolution with spectroscopic methods needs to be carefully conducted. One problem arises
96 from the fact that the measurement of the degree of polymerization in the melt has been
97 always approached from the cationic view side (²⁹Si MAS NMR mainly) which is easily
98 accessible from the experimental point of view. However, the determination of the degree of
99 polymerization is hindered by the strong influence of the silicate melt chemical composition
100 on the ²⁹Si peak position and the strong overlapping in between individual spectral lines
101 (Engelhardt et al., 1985; Schmidt et al., 2000; Hiet et al., 2009).

102 Although ¹⁷O MAS NMR is less accessible and the available data on silicate glasses are rare,
103 it is recognized as a powerful tool for determining the degree of polymerization in silicate
104 glasses (Farnan et al., 1992; Stebbins et al., 2001; Alwardt and Stebbins, 2004; Lee and
105 Stebbins, 2009) by probing the different oxygen species. The reason being that the spectral

106 distribution of the different kind of oxygens, Bridging (BO) and Non-Bridging Oxygen
107 (NBO), in a silicate glasses is directly distinguished and consequently the degree of
108 polymerization expressed as the NBO/T (number of NBO per Tetrahedron) is readily
109 determined.

110 In the present work, we have investigated the change in the degree of polymerization as a
111 function of CO₂ content in a silicate glass composition close to melilitite composition using
112 ¹⁷O and ²⁹Si NMR spectroscopy. Both results obtained by ¹⁷O and ²⁹Si NMR spectroscopy are
113 compared and point towards an increase in the degree of polymerization of the silicate
114 network structure. We clarify the CO₂ dissolution mechanism in the studied silica
115 undersaturated glass composition. Calorimetric measurements of the glass transition
116 temperatures (T_g) suggest a decrease in viscosity with increasing CO₂ content. The
117 inconsistency between spectroscopy and calorimetry is discussed and we propose
118 reconciliation to both aspects. We conclude with a first order model for silicate melt viscosity
119 as a function of CO₂ content.

120

121 **2. Experimental method:**

122 We synthesized at high pressure (between 0.5 and 1.5 GPa) a series of silicate glasses with
123 composition analogous to melilitite melt (Brooker et al., 2001; Bosshardt-Stadlin et al., 2014)
124 in the Na₂O-CaO-Al₂O₃-SiO₂ system: ~35 wt.% SiO₂ and NBO/T = 2 calculated from the
125 stoichiometric chemical composition corresponding to a highly depolymerized composition
126 (see Table 1). The composition was prepared from a mixture of oxides (Al₂O₃ and SiO₂) and
127 carbonate (Na₂CO₃ and CaCO₃). For NMR acquisition, we used ¹⁷O and ²⁹Si isotopically
128 enriched oxides: ²⁹SiO₂, Si¹⁷O₂ and Al₂¹⁷O₃; the resulting starting composition was enriched
129 at ~10 and ~40 mol.% in ¹⁷O and ²⁹Si, respectively.

130 The CaCO_3 and the Na_2CO_3 are the source of CO_2 during the experiments. Except for RB8E-
131 13 (see Table 1) in which we aimed at equilibrating the melt composition with a CO_2 fluid in
132 undersaturated conditions (initial CO_2 content = 8.8 wt.%), all the glass samples were
133 synthesized under supersaturated conditions (initial CO_2 content > 30 wt.%).

134 The high-pressure experiments were performed in an end-loaded piston-cylinder apparatus in
135 the 0.5 to 1.5 GPa pressure range. The temperature was set 1525°C to insure supraliquidus
136 conditions. The temperatures were monitored by a $\text{WRe}_3\text{-WRe}_{25}$ thermocouple in all
137 experiments. The capsule was surrounded by an alumina sleeve to avoid contact with the
138 graphite furnace.

139 A 19 mm talc-Pyrex assembly was used with a tapered graphite furnace to reduce the
140 temperature gradient along the capsule (less than 20°C along the 12 mm Pt capsule). A
141 pressure correction of 5% was applied for the talc pyrex assemblies consistent with the
142 suggested friction correction (McDade et al., 2002) for talc-pyrex assemblies. Run durations
143 were at least 1 hour to ensure equilibrium.

144 We used a special $\frac{3}{4}$ inch pressure plate with a special design in which holes have been drilled
145 to improve the experimental quench rate (more than 200°C/s). Isobaric quenching ensured
146 that quench (decompression) bubbles were not formed. Most of the recovered glasses are
147 clear and crystal free; although in some samples, a small fraction of corundum (on the order
148 of a few %) was identified in the ^{27}Al NMR spectrum. This corundum signal was also
149 observed on a clear glass and we think the corundum signal arises from an external pollution
150 coming from the outer alumina sleeve.

151

152 **3. Analytical techniques:**

153 *3.1 Electron Probe Micro-Analysis*

154 The major element compositions of glasses were determined using Electron Probe Micro-
155 Analyses (EPMA) on a Cameca SXFive©. The analytical conditions were 15kV and 10 nA
156 for voltage and current, respectively; and a 10 s peak counting time was used for each
157 element. Albite ($\text{NaAlSi}_3\text{O}_8$), alumina (Al_2O_3) and garnet ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) were used as
158 standards for Na, Si, Al and Ca, respectively. Na was analyzed first. Analyses were conducted
159 in defocused mode (20 μm beam diameter) in order to reduce any elemental loss (Di Carlo et
160 al., 2006). The average major elements concentrations for the synthesized glasses were
161 obtained from more than 15 analyses. The determined glass composition is reported in Table
162 1 in wt.%. The standard deviation for each oxide does not exceed ± 1 wt.%. From the major
163 element concentrations, it was then possible to calculate the degree of polymerization
164 expressed as the NBO/T and calculated on a stoichiometric basis (Mysen, 1988; see Table 1
165 and 2).

166

167 *3.2 Micro-Raman spectroscopy*

168 Micro-Raman spectra were acquired on a Jobin-Yvon Labram 300 spectrometer equipped
169 with an Innova 300-5W Argon ion laser from Coherent© operating at a wavelength of 514 nm
170 and on a Jobin-Yvon Labram HR800 equipped with a solid-state diode laser operating at 532
171 nm. The Labram 300 spectrometer is equipped with a 2400 grooves/mm grating allowing a
172 spectral resolution on the order of 1 cm^{-1} ; Labram HR800 spectrometer is equipped with a
173 1800 grooves/mm grating allowing a spectral resolution on the order of 0.4 cm^{-1} . Analyses
174 were performed in confocal mode, using x50 Olympus objectives. The spectral range covered
175 was between 200 and 1250 cm^{-1} . The spectral frequency position was calibrated using the
176 emission lines of Ne- and Hg-lamps. On both spectrometers, the output power was set to 125

177 mW. Several spectra are collected on each sample. For each spectrum, we performed 10 scans
178 on a given sample with an acquisition time of 5 to 10 s each on the Labram HR800 and 15 to
179 60 s on the Labram 300.

180 The CO₂ content in the recovered glass was determined by Raman spectroscopy using the
181 deconvolution method proposed by Morizet et al. (2013) (details on the method are provided
182 in the Supplementary material 1). For clarity, we provide the simulation of the Raman spectra
183 in the Supplementary material 1 and the entire set of simulation results in Supplementary
184 material 2. The determined CO₃/HF ratio corresponding to the ratio between the areas of the
185 ν_1 CO₃²⁻ peak at ~1080 cm⁻¹ and the areas of the silicate network high frequency envelop
186 between 800 and 1050 cm⁻¹ is reported in Table 1 and ranges from 0.45 and 1.33. It
187 corresponds to a CO₂ solubility ranging from 6.0 to 18.0 wt.% for glass synthesized in
188 between 0.5 and 1.5 GPa. Using the major element concentrations determined by EPMA
189 provided in Table 1; we have calculated the corresponding CO₂ on a molar basis and
190 expressed as the CO₂ molar fraction (XCO₂, see Table 1 and 2). For 6.0 to 18.0 wt.% CO₂, the
191 XCO₂ varies between 0.086 to 0.234.

192

193 *3.3 Micro-Fourier Transform Infra-Red spectroscopy*

194 Micro-FTIR analyses were carried out on doubly-polished glass chips to determine the H₂O
195 content. Analyses were conducted on a ThermoFisher FTIR5700 equipped with a Continuum
196 microscope. The spectrometer configuration was CaF₂ beamsplitter, and MCT-B detector and
197 IR light to cover the 4000-6000 cm⁻¹ spectral range. The concentration of OH⁻ (4500 cm⁻¹)
198 and H₂O^{mol} (5200 cm⁻¹) was determined with the Beer-Lambert law (Ohlhorst et al., 2001).
199 We used density values calculated from the chemical composition with the model of Lange
200 and Carmichael (1990) which includes the change in oxides partial molar volume as a

201 function of pressure and temperature. Although this density model calculation is applied for
202 liquid; recent work (Guillot and Sator, 2007) showed that the change in density in between
203 liquid and glass is small (~10% in relative) towards an increase in density from the liquid to
204 the glass. Therefore, the derived H₂O content with Beer-Lambert law will represent a
205 maximum. As the OH⁻ and H₂O^{mol} extinction coefficient values are a strong function of the
206 glass chemical composition, it was not possible to use an appropriate extinction coefficient
207 value for the presently synthesized silicate glasses. We used the linear extinction coefficient
208 applied to Alban Hill phonotephritic glass provided by Behrens et al. (2009): $\sigma_{\text{OH}} = 0.62$
209 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $\sigma_{\text{H}_2\text{O}^{\text{mol}}} = 1.02 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. We choose those extinction coefficients as
210 they were applied to glass compositions which are close to the ones studied here. The H₂O^{tot}
211 is the sum of the OH and H₂O^{mol} concentrations. The H₂O^{tot} ranges from 0.5 to 2.8 wt.% with
212 a typical error better than 0.2 wt.%. Except for RB8E-8 loaded with 6.9 wt.% H₂O, the
213 presence of water is due to adsorption of atmospheric H₂O onto the starting material prior
214 capsule preparation and sealing. Considering the high CO₂ solubility, the presence of H₂O
215 does not play a crucial role on the measured CO₂ solubility in such depolymerized
216 compositions (Xue and Kanzaki, 2004; Moussallam et al., 2016).

217

218 *3.4 ¹⁷O and ²⁹Si MAS NMR spectroscopy*

219 We have measured the change in the degree of polymerization as a function of CO₂ content
220 using ²⁹Si and ¹⁷O MAS NMR spectroscopies (see Table 2). Solid State ¹⁷O and ²⁹Si MAS
221 NMR were performed with a Bruker Avance III 500 MHz spectrometer. The ¹⁷O and ²⁹Si
222 spectra were referenced against liquid H₂O at 0 ppm and TMS (Tetramethylsilane) at 0 ppm,
223 respectively.

224 The ^{17}O MAS NMR spectra were acquired with a 2.5 mm CP/MAS probe and a MAS
225 frequency of 30 kHz. We used a full shifted echo acquisition ($\pi/12$ - τ - $\pi/6$ -acq) sequence with a
226 pulse length of 1 μs for the $\pi/12$ pulse. The delay τ was set to 1.13 ms (rotor-synchronized). A
227 recycle delay between scans of 2 s was determined to be sufficient to insure complete
228 relaxation of the ^{17}O spins. ^{29}Si -MAS NMR spectra were acquired with single $\pi/2$ excitation
229 of 4 μs at a MAS frequency of 10 kHz. ^{29}Si -species can have long spin lattice relaxation time
230 T1 in silicate glasses (Maekawa et al., 1991). A recycle delay of 120 s was shown to be
231 sufficient for quantitative purpose. The spectra deconvolution was conducted with the
232 DMFit2015 software (Massiot et al., 2002).

233

234 *3.5 Differential Scanning Calorimetry*

235 An indirect measurement of the melt viscosity in the CO_2 -bearing glass was achieved by
236 determining the glass transition temperature using Differential Scanning Calorimetry (DSC).
237 One definition of the glass transition temperature is the temperature at which the $\log \eta = 12$
238 (Moynihan, 1995; Dingwell, 1995). The DSC measurements were conducted conjointly with
239 thermogravimetric analyzer (ATG) in order to monitor weight loss during heating.

240 The glass samples were crushed to avoid sample fragmentation during the DSC experiment.
241 The crushed glass was placed in one of the crucibles and its heat flow was measured. All
242 measurements were performed with the same two crucibles under a constant flow of Ar gas of
243 $20 \text{ ml}\cdot\text{min}^{-1}$. Each sample was heated from 40°C across the glass transition at a rate of 20
244 K/min. An effective viscosity of $10^{12} \text{ Pa}\cdot\text{s}$ is usually achieved with a heating rate of 5 K/min
245 (Webb and Knoche, 1996; Russell and Giordano, 2005). Using a faster heating rate (20 K/min)
246 will lead to higher temperature for the definition of the onset peak and hence a corresponding
247 lower viscosity than $10^{12} \text{ Pa}\cdot\text{s}$. However, we used the same heating rate for all the analyzed

248 samples and the derived Tg could be compared in relative. We used Differential Scanning
249 Calorimeter (DSC SETSYS EVO 2400) equipped with a thermogravimetric analyser (TGA)
250 to determine the glass transition temperature (Tg) for four recovered glass samples (RB8-1, -2
251 and RB8E-3, -6). The DSC measurements determined the variation of heat flow (in mW) with
252 increasing temperature. The calibration of the DSC was achieved by measuring the heat flow
253 from two identical empty Pt-Rh crucibles (6 mm in diameter). The temperature calibration of
254 the DSC apparatus was conducted by measuring the enthalpy of fusion of metal standards
255 (gold, silver, aluminium and nickel). The baseline from the apparatus was subtracted from the
256 standard and sample measurements. The DSC was then calibrated by measuring the enthalpy
257 of fusion of metal standards (gold, silver, aluminium and nickel) and the sensitivity is better
258 than 0.5% in relative with respect to the temperature measurement. Additional TGA
259 measurements were also conducted conjointly to DSC measurements in order to determine the
260 possible volatile loss during the heating. For RB8E-6, the TGA measurement was not
261 conducted.

262

263 **4. Results:**

264 *4.1 ¹⁷O and ²⁹Si NMR spectra as a function of CO₂ content:*

265 ²⁹Si and ¹⁷O MAS NMR spectra are shown in Figure 1. We conducted ²⁹Si MAS NMR
266 spectra deconvolutions using three Gaussian lines (Figure 1A). Interpretation and assignment
267 of the ²⁹Si spectrum simulation is complicated by the fact that there is only a single
268 asymmetric peak resulting from the overlapping of several individual structural units (Qⁿ).
269 However, it is commonly assumed that there is a structural equilibrium in between Qⁿ species
270 (Stebbins, 1987; Maekawa et al., 1991; Mysen, 1999; Malfait et al., 2007a); such as:

271 $2Q^n \leftrightarrow Q^{n+1} + Q^{n-1}$ Eq. 2

272 The n values depend on the stoichiometric NBO/T of the melt. Here n = 2 for the glass
273 composition with NBO/T ~ 2. Hence, there is equilibrium in between Q², Q³ and Q¹. The
274 derived peak positions (-76.3, -81.9 and -88.3 ppm for Q¹, Q² and Q³, respectively) are
275 consistent with previous work (Engelhardt et al., 1985; Murdoch et al., 1985; Maekawa et al.,
276 1991; Zhang et al., 1997). The apparent NBO/T can then be calculated from the molar
277 fraction of the different Qⁿ species. The present simulation model is simplified as there is no
278 distinction between the Si environments surrounded by various Al atoms (Qⁿm(Al) where m
279 represents the number of Al atoms surrounding the Qⁿ species; Hiet et al., 2009; Morizet et
280 al., 2014b) and those species are distributed in the single Gaussian line corresponding to a Qⁿ
281 species. As a result, the shown deconvolution in Figure 1A induces inevitably a systematic
282 bias on the NBO/T subsequent determination.

283 The difficulty of interpretation inherent to the overlapping contributions in ²⁹Si NMR spectra
284 is not present in the ¹⁷O NMR spectra and the degree of polymerization is readily extracted
285 from the ¹⁷O NMR spectra decomposition. ¹⁷O MAS NMR spectrum line shape consists in
286 two main lines close to Gaussian shape due to the limited effect of second order quadrupolar
287 contribution (Kelsey et al., 2008). In agreement with Stebbins et al. (1997), each line at ~+100
288 ppm and ~+40 ppm in chemical shift is attributed to oxygen environments in NBO
289 configuration in the vicinity of Ca atoms (Ca-NBO) and to oxygen environments in BO
290 configuration (i.e. Si-O^{BO}-T with T = Si or Al), respectively. Two additional contributions are
291 also observed at ~-25 and +150 ppm and are attributed to the ¹⁷O signature in oxygen
292 triclusters (O^{III}) and CO₃²⁻ environments (Morizet et al., *subm.*). The existence of O^{III}
293 (threefold coordinated O atom) is postulated in silicate glasses (Stebbins et al., 2001; Toplis et
294 al., 1997; Benoit et al., 2005; Iuga et al., 2005; Thompson et al., 2011) at ¹⁷O chemical shift

295 close to the BO ^{17}O chemical shift. We did not identify possible contribution from free
296 oxygens which have been inferred in silicate melt from previous studies (Nesbitt et al., 2015;
297 Sawyer et al., 2015). The exact position of this contribution in the ^{17}O NMR spectrum is not
298 clear and would overlap with oxygen signal in NBO configuration (Nasikas et al., 2012).
299 Furthermore, in the present investigated silicate melt composition ($\text{SiO}_2 > 50$ mol.%), the
300 abundance of free O^{2-} anions is expected to be extremely low (<4% of the total oxygen;
301 Nesbitt et al., 2015).

302

303 *4.2 Glass transition temperature determination*

304 We show in Figure 2 the change in the heat flow as a function of the temperature; except for
305 RB8E-6 the thermogravimetric changes (ATG) are also reported in mg as a function of
306 temperature. There is a constant decrease in the heat flow followed by an increase above
307 600°C . This abrupt change in the heat flow curve shape with increasing temperature may be
308 attributed to crystallization of the sample. The increase in the heat flow is also accompanied
309 by a brutal change in the ATG curve indicating a substantial loss in the sample mass. This
310 important loss might be attributed probable CO_2 diffusion out of the sample. Recovered
311 samples exhibit large bubbled aspect suggesting an efficient CO_2 degassing. Anyhow, this
312 process occurs well-above the glass transition temperature. The comparison of the heat flow
313 and ATG curves in the vicinity of T_g does not indicate mass loss; hence the determined T_g
314 reflects the effective glass transition temperature for the CO_2 -bearing glass sample.

315 In DSC measurements, the T_g determination is done by the in-built DSC software (Setsoft
316 2000) using the three points definition. Two tangents with identical slope are fitted prior and
317 after the supposed glass transition region. A third tangent is then fitted in the glass transition
318 region and T_g is defined as the mid-point of the third tangent in between the two parallel

319 tangents (Morizet et al., 2015a). DSC measurements result in a typical error on the order of
320 ± 10 K for the Tg determination (Morizet et al., 2015a); however, some studies reported a
321 lower error ± 2.5 K (Giordano et al., 2005; Morizet et al., 2007). Considering an error of ± 10
322 K does not induce any change in the outcome of the present work. For the four measured
323 samples, we observe a change in Tg from 475 to 571°C for RB8-1 and RB8E-6, respectively.
324 Hence, the observed variation in Tg is far above the potential error. Meanwhile, it should be
325 pointed out that for two samples (RB8-1 and RB8E-3) having similar 1) CO₂ content (~ 17
326 wt.% CO₂), 2) similar degree of polymerization (1.9 and 2.1, respectively), we observe a
327 difference of 38°C in Tg value. Such a difference can be due to slight change in the glass
328 chemical composition inducing a change in Tg value.

329

330 **5. Discussion:**

331 *5.1 Change in silicate glass polymerization as a function of CO₂ content from ¹⁷O and ²⁹Si*

332 *NMR*

333 In the present work, we investigated the change in the degree of polymerization for CO₂-
334 bearing silicate glasses using both ²⁹Si and ¹⁷O NMR results with the subsequent simulations
335 (²⁹Si and ¹⁷O) shown in Figure 1. We consider the deviation in the degree of polymerization
336 (DDP) which corresponds to the ratio between the NBO/T determined from ¹⁷O and ²⁹Si
337 NMR spectroscopy and the NBO/T calculated from the stoichiometric chemical composition
338 determined by EPMA (see Table 1). Using the DDP instead of the NBO/T has the advantage
339 to average out any potential major element composition heterogeneities (see Table 1).
340 However, we also provide in the Supplementary material plots showing the non-normalized
341 change in the NBO/T as determined from ²⁹Si and ¹⁷O NMR spectroscopy as a function of
342 XCO₂. We show in Figure 3 the DDP as a function of XCO₂ for 1) the CO₂ dissolution model

343 of Eq. 1, 2) the decomposition of ^{29}Si NMR spectra and 3) the decomposition of ^{17}O NMR
344 spectra. We observe that the change in the DDP from ^{29}Si and ^{17}O NMR spectra is linearly
345 correlated to the CO_2 content. Both results show that increasing XCO_2 induces a strong
346 increase in the degree of polymerization (i.e. decreasing DDP with increasing XCO_2)
347 confirming the recent work (Morizet et al., 2014b; Moussallam et al., 2016) for strongly
348 silica-undersaturated melt compositions and therefore extending the observation to a large
349 variety of silicate melt chemical composition.

350 This result has a major implication as it tends to endorse the chemical model of Eq. 1 for CO_2
351 dissolution. Consequently, in accordance to Eq. 1, CO_2 molecules mainly dissolve in silicate
352 melt structure as Free Ionic Carbonate $\text{M}^{n+} \cdot \text{CO}_3^{2-}$ groups (FIC) as proposed by recent works
353 (Moussallam et al., 2016; Morizet et al., 2015b). For the studied composition, the FIC are
354 mainly $\text{Ca}^{2+} \cdot \text{CO}_3^{2-}$. The presence of FIC also indicates that a carbonate subnetwork is
355 coexisting with a silicate subnetwork. Both are intimately linked; however, as suggested in
356 recent study (Morizet et al., 2014a) for alkali-rich melt composition, the FIC represents the
357 precursor of the two liquids immiscibility (carbonate liquid and silicate liquid) process often
358 invoked to explain the coexistence of CO_2 -rich silicate rocks and carbonatites (Mitchell, 2005;
359 Brooker and Kjarsgaard, 2011; Sharygin et al., 2012; Russell et al., 2012).

360 Although we do not have data points for $\text{XCO}_2 < 0.086$, for both ^{29}Si and ^{17}O NMR, we
361 expect that CO_2 does not influence the degree of polymerization possibly because of another
362 unidentified CO_2 dissolution mechanism. This would also be consistent with the recent results
363 of Sifré et al. (2014) showing that the silicate melt electrical conductivity is not affected up to
364 6 wt.% CO_2 . Until we fulfil this lack of data, it seems that the trend at $\text{XCO}_2 = 0$ could extend
365 at NBO/T ratio > 1 suggesting an excess in NBOs concentration. The excess in NBOs has
366 been identified in polymerized $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ silicate glasses (Benoit et al., 2005; Stebbins
367 and Xu, 1997) but never reported for more depolymerized compositions.

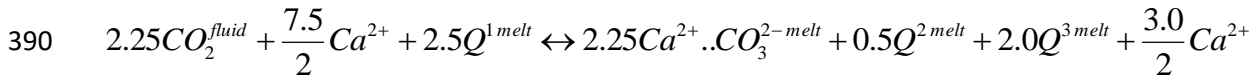
368 We observe a slight mismatch (10% difference) in between the ^{29}Si and ^{17}O NMR results: the
369 ^{29}Si NMR results show a lower DDP than in ^{17}O NMR results. Although the ^{29}Si simulation
370 approach is simplified, it appears that both ^{17}O and ^{29}Si NMR results are consistent. Hence,
371 the ^{29}Si NMR results can be used to quantify the effect CO_2 produces on the degree of silicate
372 melt polymerization. Furthermore, it can be used to establish a clear CO_2 dissolution
373 mechanism reaction for the studied composition.

374

375 *5.2 CO_2 dissolution mechanism reaction in silicate undersaturated glass composition*

376 The DDP as a function of CO_2 content obtained by NMR strongly deviates from the chemical
377 model of Eq. 1 (*red line* in Figure 3) suggesting that there is a much more important change in
378 NBO/T than the suggested change by Eq. 1. This implies that CO_2 has a much stronger effect
379 on the silicate melt degree of polymerization than suggested. Serendipitously, we interpret
380 this discrepancy by the fact that the CO_2 dissolution mechanism does not strictly follow the
381 mole-to-mole basis changes of Eq. 1. A more complex mechanism is possible where network
382 modifying cations (mostly Ca^{2+} in here) in silicate melt/glass share their positive charges with
383 several oxygen negative charges (Allwardt and Stebbins, 2004; Benoit et al., 2005; Mountjoy,
384 2007) and consequently throughout multiple weak bonding in the silicate network.

385 Considering that ^{29}Si and ^{17}O NMR results in Figure 3 show a comparable evolution; the Q^n
386 species distribution as a function of CO_2 content can be extracted from ^{29}Si NMR results. We
387 used ^{29}Si NMR results to propose the CO_2 dissolution mechanism represented by Eq. 3. This
388 mechanism reproduces adequately the change in Q^n speciation shown in Figure 4 and the
389 increase in the degree of polymerization (Figure 3) for the currently investigated composition:



391 Eq. 3

392 In this equation, Q^1 species transform into Q^2 species in agreement with Eq. 1 but it also
 393 transforms into Q^3 species. The stoichiometric coefficients in front of each Q^n species
 394 correspond to the slope of the linear regressions determined in Figure 4 for the evolution of
 395 each Q^n species: -2.5, +0.5 and +2.0 for Q^1 , Q^2 and Q^3 , respectively. The number of involved
 396 Ca^{2+} is fixed by the total negative charge carried by the Q^1 species: $2.5 \times 3 = 7.5$. The same
 397 applies on the right hand side of the chemical reaction: $2.0 \times 1 + 0.5 \times 2 = 3.0$. Hence, the
 398 excess Ca^{2+} ($7.5/2 - 3.0/2 = 4.5/2$) is compensated by CO_3^{2-} to form FIC $Ca^{2+}..CO_3^{2-}$ in the
 399 melt structure. Hence, the number of FIC $Ca^{2+}..CO_3^{2-}$ formed fixes the number of CO_2
 400 molecules incorporated from the fluid phase into the melt structure.

401

402 *5.3 Implication on the effect of CO₂ on silicate melt viscosity: A preliminary model*

403 The conventional view of the relationship in between the melt structure and the corresponding
 404 melt physical properties is to consider that an increase in melt polymerization induces an
 405 increase in melt viscosity (Mysen, 1998; Giordano et al., 2008; Moussallam et al., 2016;
 406 Stebbins, 2016). Hence, the presented NMR results in Figure 3 are by extension in favor for
 407 this increase in melt viscosity with increasing CO_2 content.

408 For several glass samples (6.0 and 17.1 wt.% CO_2), we have determined the glass transition
 409 temperature (T_g), which represents a proxy of the melt viscosity ($\log \eta = 12$; Moynihan,
 410 1995; Dingwell, 1995; Webb and Knoche, 1996). T_g was measured at 571 and $475 \pm 5^\circ C$ for
 411 6.2 and 17.1 wt.% CO_2 glass samples, respectively. As shown in Figure 5, compositions with
 412 the more polymerization (i.e. lower CO_2 content) have lower value of T_g . This result is in

413 stark contrast with our current knowledge on the link between the silicate melt molecular
414 structure and the corresponding silicate melt physical properties. As indicated in Figure 5, the
415 increase in polymerization is accompanied by a decrease in melt viscosity which is
416 counterintuitive and in opposition to what is currently accepted.

417 The discrepancy between spectroscopic observations and physical measurements observed in
418 Figure 5 has a major implication. Indeed, we show in the present work that quantification in
419 the silicate network changes upon CO₂ dissolution using spectroscopic methods cannot be
420 straightforwardly related to a corresponding change in melt physical properties since an
421 increase in silicate network polymerization implies an increase in viscosity. This contrasts
422 with studies on H₂O dissolution in silicate melt showing that both the silicate melt structure
423 and the physical properties are strongly correlated (Richet, 1984; Dingwell et al., 1996; Richet
424 et al., 1996; Giordano et al., 2008). Mantle melts, particularly rich in CO₂ such as melilitites
425 and kimberlites, therefore seem more complex than the conventional silicate melts in their
426 structure-properties relationships.

427 We propose a possible reconciliation of the spectroscopic results and physical measurements.
428 We have shown in Eq. 3 that CO₂ dissolves in silicate melt structure by forming FIC groups
429 (i.e. Ca²⁺..CO₃²⁻). Our proposition is that FIC clusters forming an individual carbonate
430 subnetwork along a silicate melt subnetwork behave in a similar way to a carbonate liquid
431 (Kono et al., 2014; Vuilleumier et al., 2015). Therefore upon CO₂ dissolution, the molten
432 system is an intimate mixture (i.e. two interacting liquids) of a silicate melt and a carbonate
433 melt. With increasing CO₂ dissolution, the silicate melt is progressively diluted by a carbonate
434 melt having an extremely low viscosity as demonstrated by Kono et al. (2014). The viscosity
435 of the silicate melt subnetwork increases due to the fact that CO₂ induces a polymerization of
436 the Qⁿ species (see Eq. 3 and Figure 3) but this increase in viscosity is counterbalanced by the
437 progressive increase in the carbonate melt subnetwork of extremely low viscosity. Hence, the

438 progressive CO₂ dissolution in a silicate melt induces a decrease in melt viscosity therefore
 439 explaining the extremely low viscosity of CO₂-rich deep mantle magmatic liquids such as
 440 kimberlites.

441 We propose a model for silicate melt viscosity change as a function of CO₂ content. We
 442 should emphasize that the proposed scenario is preliminary and needs to be confirmed in the
 443 future by experimental investigations. To establish this model we started with the following
 444 hypothesis: in presence of CO₂, the system is an intimate mixture between a silicate melt and
 445 a carbonate melt with each melt having its own viscosity properties. Hence, the entire system
 446 viscosity can be approximated by a linear combination of viscosity as suggested by chemical
 447 science studies (Mialkowski et al., 2002; Chagnes et al., 2004; Ye et al., 2016) such as:

$$448 \quad \eta_{SL+CL} = X_{SL}\eta_{SL} + X_{CL}\eta_{CL} \quad \text{Eq. 4}$$

449 Where η_{SL} , η_{CL} and η_{SL+CL} correspond to the viscosity of the silicate liquid, carbonate liquid
 450 and the mixture of both liquids, respectively. X_{SL} and X_{CL} correspond to the molar fraction of
 451 the silicate and carbonate liquid, respectively. We considered a constant viscosity value for
 452 the carbonate liquid given by Kono et al. (2014): $\log \eta_{CL} = -2.21$ Pa.s. This value is
 453 independent of pressure and has been determined at 1750 K by Kono et al. (2014). The X_{CL} is
 454 given by the molar fraction of the dissolved CO₂ (X_{CO_2} in Table 1). Hence, the silicate melt
 455 molar fraction can be calculated such as $X_{SL} = 1 - X_{CL}$.

456 In order to calculate the η_{SL} we considered that when CO₂ molecule dissolves in the system, it
 457 withdraws one Ca²⁺ cation and one O²⁻ anion to form FIC Ca²⁺..CO₃²⁻. Hence, the silicate
 458 liquid composition changes at each XCO₂ due to the withdrawing of the Ca²⁺ cation. The
 459 silicate liquid composition is therefore recalculated at each XCO₂ such as:

$$460 \quad X_{SL}^{CaO} = X_{SL}^{CaO\ Init.} - X_{CO_2} \quad \text{Eq. 5}$$

461 In Eq. 5, $X_{SL}^{CaO\ Init.}$ represents the initial CaO molar fraction in the silicate melt composition
462 and is 0.531 calculated from the volatile-free theoretical composition reported in Table 1. We
463 used the viscosity model proposed by Giordano and Russell (2007) to calculate the silicate
464 liquid viscosity. Calculation was conducted at 1750 K so as to match the carbonate liquid
465 viscosity value proposed by Kono et al. (2014). We did not take into account the effect of
466 pressure on the viscosity of the silicate liquid as in the interval 0.5-1.5 GPa the change in
467 silicate melt viscosity is likely to be negligible (Allwardt et al., 2007). Under these conditions,
468 the $\log \eta_{SL\ Init.} = -0.32$ Pa.s for the RB8 theoretical composition reported in Table 1.

469 The calculation results are shown in Figure 6; the corresponding calculations are provided in
470 the Supplementary material 2 as a spreadsheet. We have reported the calculation in three
471 different cases. The η_{SL} represents the change in viscosity of the silicate liquid determined
472 with the model of Giordano and Russel (2007) and taking into account the changes in silicate
473 liquid composition (i.e. Eq. 5). The $X_{SL}\eta_{SL\ Init.} + X_{CL}\eta_{CL}$ represents the change in viscosity of
474 the two liquid mixtures considering a constant viscosity for the silicate liquid at $\log \eta_{SL\ Init.} = -$
475 0.32 Pa.s and calculated for the theoretical composition using the model of Giordano and
476 Russell (2007). The proportion of each liquid is progressively changed with increasing X_{CO_2} .
477 The third curve $X_{SL}\eta_{SL} + X_{CL}\eta_{CL}$ corresponds to the change in viscosity of the two liquid
478 mixtures as proposed in Eq. 4. The calculation includes the effect of the progressive
479 enrichment in the carbonate liquid and the progressive Ca depletion in the silicate liquid.

480 As shown in Figure 6, the viscosity of the silicate liquid increases with CO_2 content due to the
481 progressive Ca depletion (i.e. SiO_2 increase). For a constant silicate liquid viscosity, the
482 increase in carbonate liquid proportion induces a linear decrease in the viscosity of the two
483 liquid mixtures. The combination of the different effects show that the viscosity of the two
484 liquid mixtures is almost not affected or only slightly decreasing; in other words, the presence
485 of CO_2 does not induce a dramatic effect on the viscosity of the two liquid mixtures. The

486 calculations conducted at 1600 K produce similar results with only a slight decrease in
487 viscosity of the two liquid mixtures (see Supplementary material 2). For fully polymerized
488 compositions, Brearley and Montana (1989) and White and Montana (1990) suggested a
489 decreasing effect of CO₂ on silicate melt viscosity. Bourgue and Richet (2001) proposed a
490 decrease in silicate melt viscosity with increasing CO₂ content. Morizet et al. (2007) pointed
491 out the absence of effect of CO₂ on viscosity for phonolitic and jadeitic silicate melt
492 compositions. The model calculation results suggest that the addition of CO₂ to a silicate melt
493 induces negligible effect on the viscosity or a slight decrease in melt viscosity. Although there
494 is a strong increase in silicate melt polymerization, the interplay between a carbonate liquid
495 and a silicate liquid counterbalances the increase in the silicate melt viscosity and the
496 viscosity of the two liquid mixtures is slightly decreasing with increasing CO₂ content.

497 In an immiscible process between a silicate liquid and a carbonate liquid, the exsolution of the
498 carbonate liquid would provoke the silicate liquid to be stalled in depth due to its high
499 viscosity.

500

501 **6. Summary:**

502 For silica undersaturated melt composition equivalent to melilitite lava composition, using
503 ¹⁷O and ²⁹Si NMR spectroscopy, we have shown that increasing CO₂ content induces the
504 polymerization of the silicate network structure. This polymerization involves the formation
505 of Free Ionic Carbonate such as Ca²⁺..CO₃²⁻ which constitutes a carbonate subnetwork linked
506 to the silicate subnetwork. However, such dissolution mechanism does not proceed on a mole-
507 to-mole basis and a more complex mechanism is to be considered. We used the Qⁿ
508 distribution determined by ²⁹Si NMR to constrain the CO₂ dissolution mechanism and showed
509 that the polymerization is much stronger than proposed by chemical models. We derived a

510 chemical reaction for the CO₂ dissolution which could be applied to a large variety of low
511 silica melt such as kimberlites.

512 If the increasing polymerization with increasing CO₂ content points towards an increase in
513 melt viscosity, glass transition temperature changes negatively with increasing CO₂ content
514 suggesting a negative effect of CO₂ on melt viscosity. This inconsistency can be reconciled
515 considering that the silicate subnetwork (high viscosity) is progressively diluted by a
516 carbonate subnetwork having an extremely low viscosity. Hence, the viscosity of the two
517 liquid mixtures is not increasing but decreasing instead. This mechanism would explain the
518 fast ascent rate of CO₂-rich kimberlitic melt. The strong buoyancy and rapid ascent of the
519 kimberlitic melt will be ensured by the existence of a CO₂-rich fluid phase created upon
520 decompression through the ascent but also because the viscosity is kept low in the two liquid
521 mixtures configuration.

522

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529

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738

739 **Figure caption:**

740 Figure 1: A, CO₂-bearing glass ²⁹Si NMR spectra simulated with three individual Gaussian
741 lines: Q¹, Q² and Q³ at -76.3, -81.9 and -88.3 ppm, respectively. The CO₂ content calculated
742 as a molar fraction (XCO₂) is reported next to each spectrum. B, CO₂-bearing glass ¹⁷O NMR
743 spectra simulated with four individual Gaussian lines: oxygen triclusters (O^{III}) at ~-27 ppm,
744 bridging oxygens ((Si,Al)-BO) at ~+40 ppm, non-bridging oxygens (Ca-NBO) at ~+101 ppm
745 and carbonate groups (CO₃²⁻) at ~+149 ppm.

746 Figure 2: Differential Scanning Calorimetric curves measuring the Heat Flow (mW) as a
747 function of the temperature for different glass samples. Thermo-Gravimetric Analysis (TGA)
748 as a function of temperature measuring the weight loss in mg during heating. The glass
749 transition temperature is determined using the three point definition and double tangent
750 method (Morizet et al., 2015a). Weight loss occurs above T_g suggesting that the determined
751 T_g corresponds to the T_g at the measured volatile content.

752 Figure 3: Deviation in the degree of polymerization (DDP) as a function of CO₂ content. The
753 deviation is calculated as the ratio in between the NBO/T determined from ¹⁷O (*filled symbol*)
754 and ²⁹Si (*open symbol*) NMR results and the NBO/T determined from EPMA analyses (see
755 Table 1). Theoretical line corresponds to a constant degree of polymerization; Dissolution line
756 (*red line*) corresponds to the deviation in the degree of polymerization following the
757 dissolution mechanism reported in Eq. 1.

758 Figure 4: Evolution of the Qⁿ species as a function of XCO₂. The data points represent the Qⁿ
759 molar fraction determined by ²⁹Si NMR spectral deconvolution shown in Figure 1. The
760 straight lines represent linear regression for the change in Qⁿ species. The slope coefficients
761 have then been used to establish the chemical reaction of Eq. 3.

762 Figure 5: Change in glass transition temperature (T_g) as a function of the DDP measured by
763 ^{29}Si NMR. The X_{CO_2} is reported for each data point. The assumed error is 10% in relative for
764 the DDP and $\pm 10^\circ\text{C}$ for T_g . This figure highlights the inconsistency between molecular
765 structure and physical properties changes since decreasing DDP is consistent with increasing
766 polymerization whereas decreasing T_g is consistent with decreasing viscosity.

767 Figure 6: CO_2 -bearing silicate melt viscosity as a function of CO_2 content. The model
768 calculation is conducted at 1750K. The X_{CO_2} is calculated from the EPMA results in Table 1.
769 Three different calculations are performed: constant silicate melt viscosity and increasing
770 carbonate proportion in the liquid mixture ($X_{\text{SL}}\eta_{\text{SL}}^{\text{init.}} + X_{\text{CL}}\eta_{\text{CL}}$); increasing silicate melt
771 viscosity calculated from the model of Giordano and Russell (2007) due to the progressive
772 depletion in Ca (η_{SL}); combined effect, increasing silicate melt viscosity and decreasing
773 silicate melt fraction with increasing carbonate liquid fraction at constant viscosity obtained
774 from Kono et al. (2014) ($X_{\text{SL}}\eta_{\text{SL}} + X_{\text{CL}}\eta_{\text{CL}}$).

775

776 **Table caption:**

777 Table 1: Experimental pressure; major element concentrations determined by EPMA; volatile
778 content determined from Raman spectroscopy.

779 Table 2: Degree of polymerization expressed as the NBO/T from EPMA and ^{29}Si and ^{17}O
780 NMR spectroscopy. Glass transition temperature obtained by Differential Scanning
781 Calorimetric measurements.

782

1 Table 1:

Sample	Pressure (GPa)	Wt.% SiO ₂	Wt.% Al ₂ O ₃	Wt.% CaO	Wt.% Na ₂ O	Total wt.%	NBO/T ^b	Wt.% H ₂ O ^c	CO ₃ /HF Raman ^e	Wt.% CO ₂ Raman ^d	XCO ₂ ^e
<i>RB8</i>											
<i>Theoretical^a</i>		37.5	10.6	46.2	5.7		1.96				
RB8E-6	0.5	32.1 (0.3)	9.8 (0.2)	42.9 (0.3)	5.9 (0.2)	90.8	2.12	0.6 (0.2)	0.46 ±0.02	6.2 ±0.3	0.086
RB8E-7	0.5	33.3 (0.4)	8.7 (0.2)	41.8 (0.3)	2.7 (0.3)	89.5	2.08	0.7 (0.1)	0.48 ±0.01	6.5 ±0.1	0.091
RB8-2	0.5	33.2 (0.3)	9.8 (0.2)	40.4 (0.2)	4.9 (0.1)	88.3	1.92	0.5 (0.1)	0.45 ±0.02	6.0 ±0.3	0.086
RB8E-13	1.0	30.1 (0.4)	8.6 (0.2)	36.0 (0.4)	5.0 (0.2)	79.6	1.92	1.3 (0.1)	0.57 ±0.10	7.7 ±1.4	0.118
RB8E-12	1.0	30.3 (0.6)	8.1 (0.2)	39.8 (0.3)	4.8 (0.1)	83.0	2.14	1.5 (0.1)	0.94 ±0.04	12.6 ±0.5	0.173
RB8E-3	1.5	30.1 (0.2)	8.7 (0.2)	39.4 (0.2)	5.5 (0.3)	83.8	2.11	0.6 (0.1)	1.27 ±0.01	17.2 ±0.1	0.220
RB8-1	1.5	31.3 (0.5)	9.3 (0.2)	37.9 (0.5)	4.4 (0.2)	82.9	1.88	0.6 (0.2)	1.27 ±0.01	17.1 ±0.1	0.221
RB8E-8	1.5	30.1 (0.3)	9.3 (0.2)	36.8 (0.3)	4.9 (0.3)	81.1	1.89	2.8 (0.1)	1.23 ±0.02	16.6 ±0.3	0.221
RB8E-11	1.5	29.7 (0.5)	8.0 (0.1)	38.6 (0.3)	4.6 (0.1)	80.8	2.11	0.9 (0.1)	1.33 ±0.01	18.0 ±0.1	0.234

2 ^a The RB8 theoretical composition is similar to the one studied in Brooker et al. (2001).

3 ^b The NBO/T corresponds to the concentration of Non-Bridging Oxygen per Tetrahedron and is calculated from the chemical composition given in the Table 1. The NBO concentration corresponds to the excess
4 negative charges brought by the oxygen in each oxide. This excess negative charge is subsequently divided by the positive charges on tetrahedra which is represented by the molar concentration of Si⁴⁺ and Al³⁺.

5 ^c The H₂O content was determined by FTIR, summing the contribution of the OH⁻ and H₂O^{mol} vibrational peaks at 4500 and 5200 cm⁻¹, respectively. The error does not exceed ±0.2 wt.% H₂O and corresponds to the
6 standard deviation obtained on the replicated measurements.

7 ^d The CO₂ solubility has been determined using the method of Morizet et al. (2013) and using the derived CO₃/HF value obtained from the deconvolution of the Raman spectra shown in Figure S3 and subsequent
8 parameters in the Supplementary material 2. The linear relationship has been re-evaluated and is wt.% CO₂ = 13.5 x CO₃/HF. The actual reported error corresponds to the standard deviation of the CO₃/HF ratio obtained
9 from the replicated spectra and shows the global homogeneity of the glass samples. As discussed in the text and mentioned in Table 1, the assumed typical error on the CO₂ solubility using Raman method is 10% in
10 relative to the value.

11 ^e The XCO₂ has been calculated from the wt.% CO₂ determined by Raman spectroscopy and from the major element concentrations (in wt.%). We used the same error as for the wt.% CO₂ content (10% in relative to the
12 value).

Table 2:

Sample	XCO ₂	NBO/T from EPMA ^a	Q ¹	Q ²	Q ³	NBO/T from ²⁹ Si ^b	(Si,Al)-BO	Ca-NBO	O ^{III}	CO ₃ ²⁻	NBO/T from ¹⁷ O ^c	DDP ²⁹ Si NMR/EPMA	DDP ¹⁷ O NMR/EPMA	Tg (°C) ^f
RB8E6	0.086	2.12	0.677	0.334	-0.011	1.98						0.93		571
RB82	0.086	1.92	0.414	0.444	0.141	1.69						0.88		526
RB8E7	0.091	2.08					0.379	0.479	0.038	0.104	2.14		1.03	
RB8E13 ^d	0.118	1.92	0.388	0.542	0.070	1.73	0.419	0.450	0.054	0.076	1.95	0.90	1.02	
RB8E12	0.173	2.14	0.222	0.493	0.285	1.47	0.429	0.384	0.040	0.146	1.80	0.69	0.84	
RB8E3	0.220	2.11	0.228	0.617	0.156	1.55						0.73		513
RB81	0.221	1.88	0.188	0.425	0.387	1.33						0.71		475
RB8E8 ^e	0.221	1.89	0.214	0.393	0.394	1.33						0.70		
RB8E11	0.234	2.11	0.133	0.503	0.364	1.34	0.447	0.344	0.033	0.176	1.67	0.64	0.79	

^a The NBO/T from EPMA has been calculated from the major element concentrations on a stoichiometric basis.

^b The NBO/T from ²⁹Si NMR is calculated from the Qⁿ species concentration. We used the following relation $NBO/Si = 3XQ^1 + 2XQ^2 + XQ^3$; the NBO/T is calculated from the NBO/Si and considering the XAl determined by EPMA. In the calculation Al atoms are considered to be fourfold coordinated.

^c The NBO/T from ¹⁷O NMR is calculated using the following equation: $NBO/T = 4 X(Ca-NBO) / (X(Ca-NBO) + X((Si,Al)-BO) + X(O^{III}))$. The CO₃²⁻ is not included in the calculation considering that CO₂ dissolves as Ca²⁺..CO₃²⁻.

^d Sample RB8E13 has been synthesized at 1.0 GPa with undersaturated conditions. The initial CO₂ content loaded was 8.8 wt.%.

^e Sample RB8E8 has been synthesized in a mixed H₂O-CO₂ fluid phase composition. 6.9 wt.% H₂O was loaded into the capsule prior to the experiment. Micro-FTIR measurements lead to 2.8 wt.% H₂O in the recovered glass.

^f The glass transition temperature was determined by DSC measurement using the double tangent definition (see Supplementary material 1). Tg is a proxy to melt viscosity and represents a temperature of equal relaxation times.

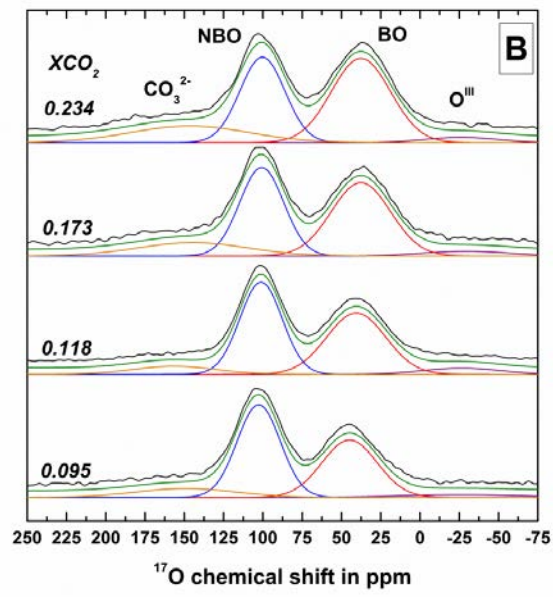
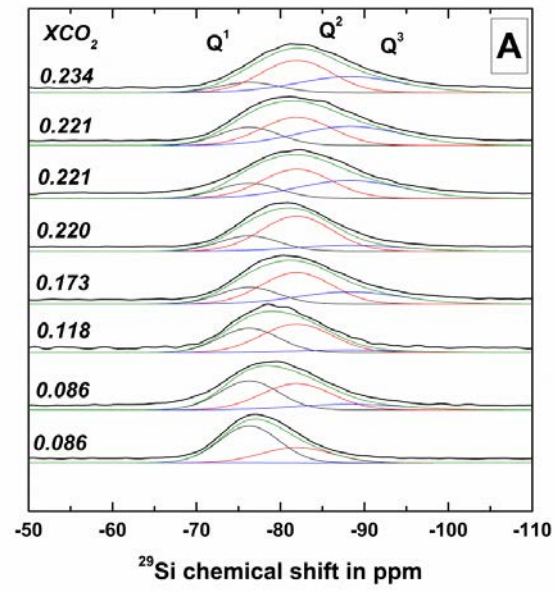


Figure 1

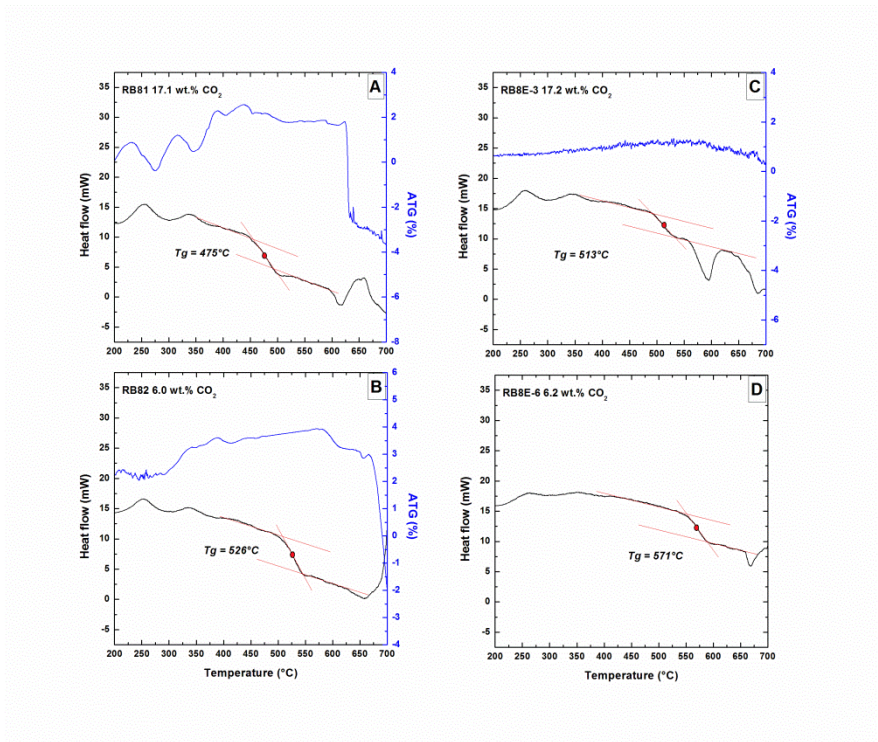


Figure 2

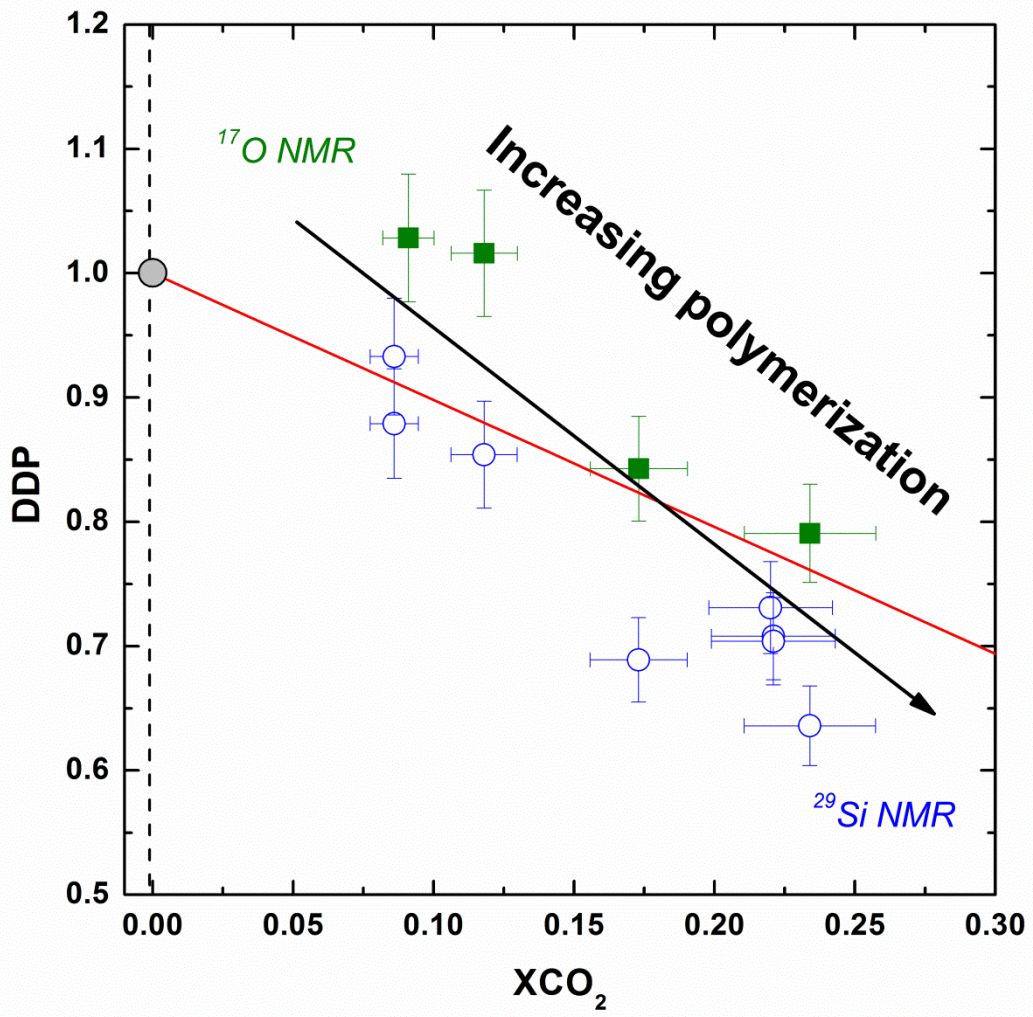


Figure 3

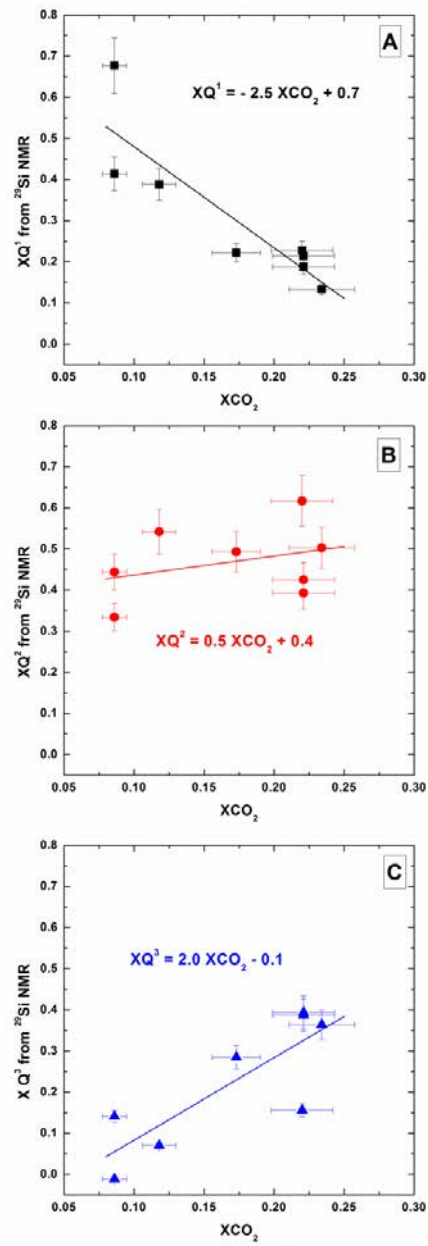


Figure 4

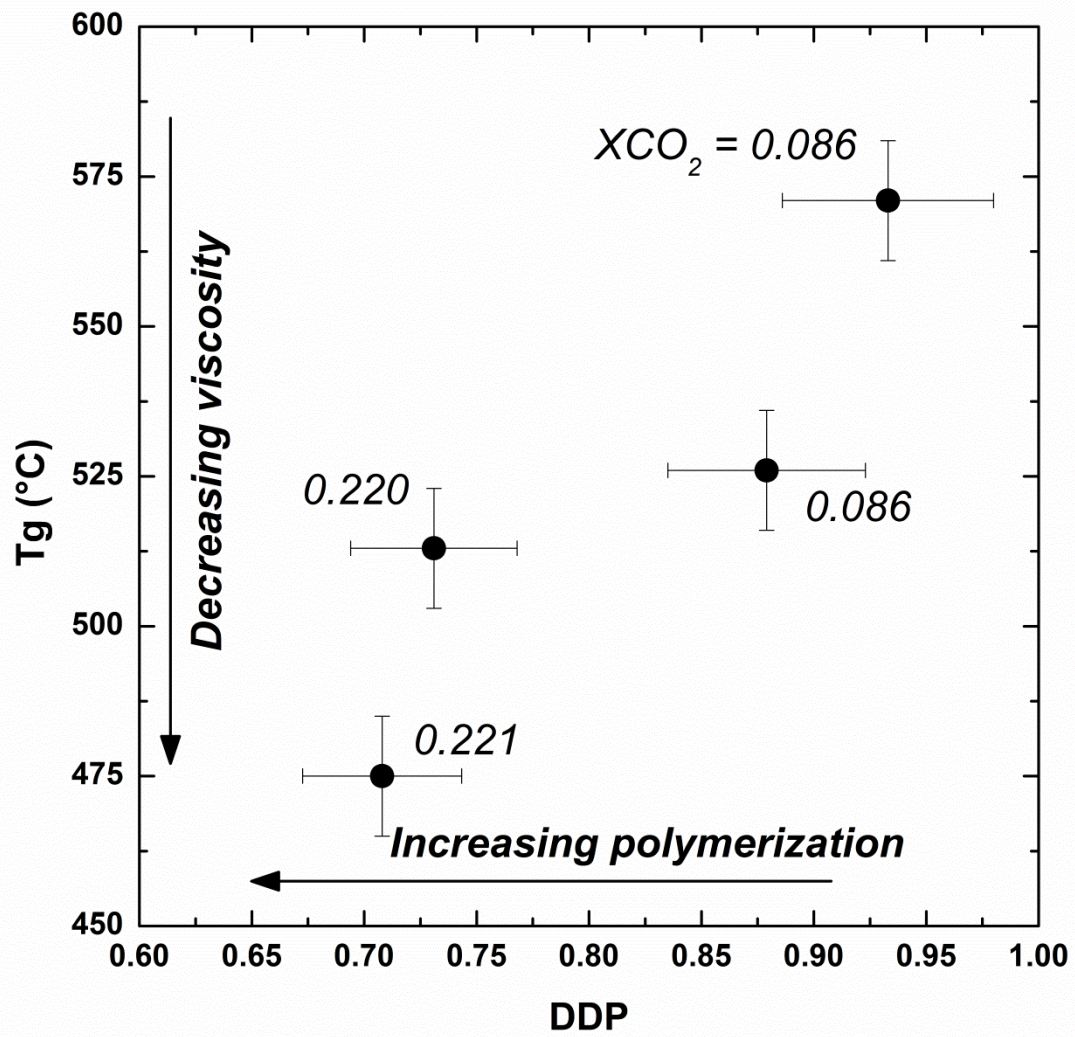


Figure 5

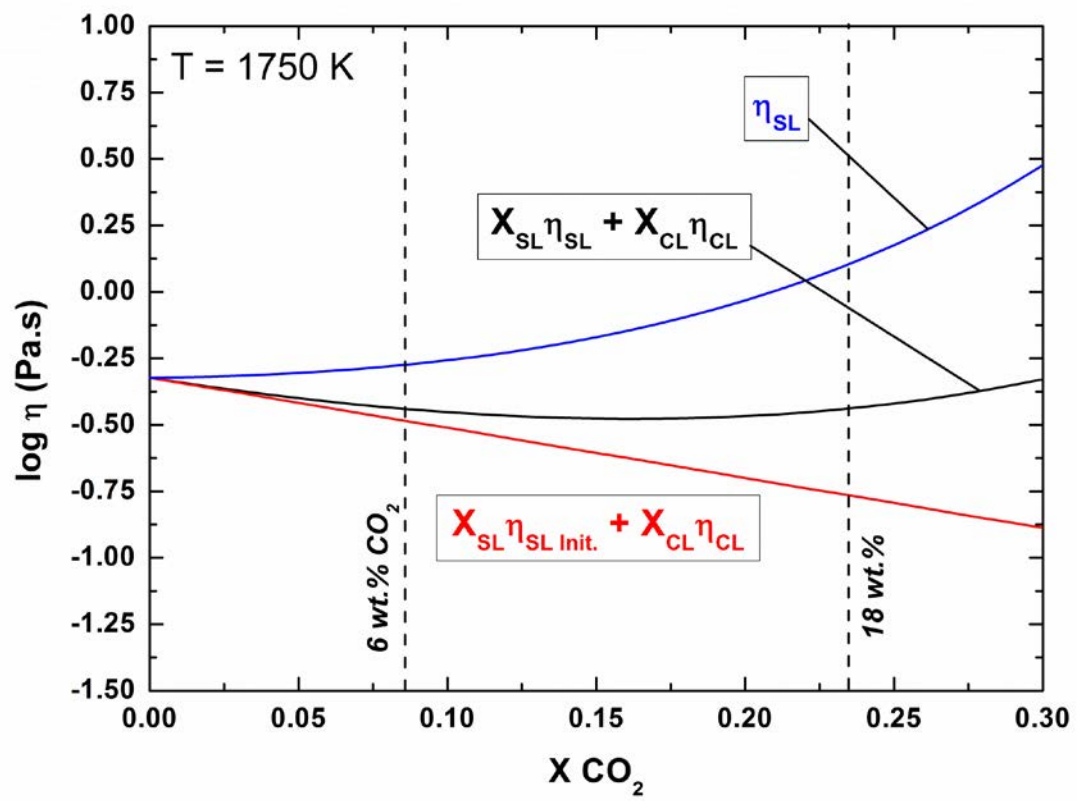


Figure 6