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

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Abstract:

Deep mantle melts contain massive amounts of CO$_2$ but three critical issues related to the effect of CO$_2$ on molecular structure and physical properties of magmatic melts remain poorly constrained: 1) there is no exact picture of CO$_2$ dissolution mechanism in silicate melt, 2) the silicate melt polymerization upon CO$_2$ dissolution has not been reliably quantified and 3) the effect of CO$_2$ on silicate melt viscosity has never been measured adequately.

We synthesized a series of $^{17}$O and $^{29}$Si-enriched CO$_2$-bearing melilitite (SiO$_2$ ~ 35 wt.%) silicate glasses at high temperature and pressure. Using NMR spectroscopy, we have interrogated both anionic and cationic networks for quantifying the change in the degree of polymerization associated to CO$_2$ incorporation in the melt. Increasing CO$_2$ content induces a strong increase in the degree of polymerization. CO$_2$ dissolution follows a complex mechanism involving the formation of Free Ionic Carbonate (FIC) $\text{Ca}^{2+}..\text{CO}_3^{2-}$ species. This carbonate subnetwork is the precursor to the immiscibility process between a carbonate liquid and a silicate liquid.

Glass transition temperature (Tg) measurements show that increasing CO$_2$ content induces a decrease in Tg implying a decrease in viscosity for the studied low silica melt composition. This result appears in complete contradiction with the melt polymerization induced by CO$_2$ as quantified by NMR. We propose a model that reconciles both aspects. CO$_2$ induces silicate subnetwork polymerization resulting in a viscosity increase but it also induces a competing effect by forming a carbonate subnetwork having a low viscosity. The overall result appears dominated by the carbonate subnetwork resulting in a slight decrease in melt viscosity in agreement with existing studies.

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Keywords: CO$_2$ dissolution mechanism, low silica melt polymerization, CO$_2$ effect on silicate melt viscosity.
1. **Introduction:**

Carbon dioxide (CO$_2$) is a ubiquitous component of the Earth’s mantle and it is known to play a major role in the mantle melting (Wyllie and Huang, 1976; Taylor and Green, 1988; Wallace and Green, 1988; Dasgupta and Hirschmann, 2006; Dasgupta, 2013). Melts with low silica content (< 40 wt.%) and high CO$_2$ content are broadly produced by low degree partial melting (Massuyèau et al., 2015) over a great depth interval and are possibly affecting large scale geophysical observations such as electrical conductivity as shown by Sifré et al. (2014). A key question related to their physical properties (i.e. viscosity) is: how fast such buoyant melts move through the surrounding mantle? Silicate melts and carbonate melts at mantle conditions have been well studied while the intermediate CO$_2$-rich silicate (e.g. melilitites and nephelinites), which are prevailing in the mantle (Mitchell, 2005) have poorly defined physical properties. To circumvent the experimental difficulties in measuring viscosity in CO$_2$-bearing silicate melt, one method often quoted is to scrutinize the change in the silicate melt molecular structure upon CO$_2$ dissolution to gain access to the melt viscosity (Stebbins, 2016).

Pioneer works (Eggler, 1978; Mysen and Virgo, 1980a) on CO$_2$ dissolution in silicate melt conjectured that CO$_2$ acts as a polymerizing agent hence increasing melt viscosity. The suspected CO$_2$ dissolution involves the polymerization (i.e. increasing connectivity of the oxygen atoms) of the structural units (Mysen and Virgo, 1980b; $Q^n$ species where $Q$ is a tetrahedral unit with $n$ bridging oxygens) with the following reaction:

\[
\text{CO}_2^{\text{fluid}} + 2Q^{n\text{melt}} \leftrightarrow CO_3^{2-n\text{melt}} + 2Q^{n+1\text{melt}} \quad \text{Eq. 1}
\]

Where a CO$_2$ molecule scavenges an available oxygen of a $Q^n$ unit to form a free M$^{n+}$..CO$_3^{2-}$ group in which M$^{n+}$ is a charge balancing or network modifying cation (e.g. Ca$^{2+}$). As Eq. 1 proceeds to the right, there is a change in the proportion of the different oxygen species: a
Non-Bridging Oxygen (NBO) is consumed by the CO$_2$ molecule and a Bridging Oxygen (BO) is produced. The proportion of both oxygen species defines the degree of polymerization. Although this mechanism appears intuitively acceptable, it has never been reliably determined experimentally. Recent work using $^{29}$Si MAS NMR spectroscopy (Morizet et al., 2014b; Moussallam et al., 2016) attempted to quantitatively measure the change in polymerization upon CO$_2$ dissolution and corroborated the polymerizing effect of CO$_2$. However, simple mass balance calculations using Eq. 1 do not match the calculations made from $^{29}$Si NMR spectra: the increase in polymerization is too large for the amount of CO$_2$ dissolved. This lack of internal consistency shows the difficulty of the $^{29}$Si NMR method and suggests that a more complex structural mechanism is at stake for CO$_2$ dissolution in silicate melts. This mechanism could involve changes: 1) in the distribution of the structural units ($Q^s$ species), and 2) in the distribution of bond length and angles within the structural units (Lee, 2004, 2005; Massiot et al., 2012).

As a result, a reliable quantification of the silicate degree of polymerization upon CO$_2$ dissolution with spectroscopic methods needs to be carefully conducted. One problem arises from the fact that the measurement of the degree of polymerization in the melt has been always approached from the cationic view side ($^{29}$Si MAS NMR mainly) which is easily accessible from the experimental point of view. However, the determination of the degree of polymerization is hindered by the strong influence of the silicate melt chemical composition on the $^{29}$Si peak position and the strong overlapping in between individual spectral lines (Engelhardt et al., 1985; Schmidt et al., 2000; Hiet et al., 2009).

Although $^{17}$O MAS NMR is less accessible and the available data on silicate glasses are rare, it is recognized as a powerful tool for determining the degree of polymerization in silicate glasses (Farnan et al., 1992; Stebbins et al., 2001; Alwardt and Stebbins, 2004; Lee and Stebbins, 2009) by probing the different oxygen species. The reason being that the spectral
distribution of the different kind of oxygens, Bridging (BO) and Non-Bridging Oxygen (NBO), in a silicate glasses is directly distinguished and consequently the degree of polymerization expressed as the NBO/T (number of NBO per Tetrahedron) is readily determined.

In the present work, we have investigated the change in the degree of polymerization as a function of CO$_2$ content in a silicate glass composition close to melilitite composition using $^{17}$O and $^{29}$Si NMR spectroscopy. Both results obtained by $^{17}$O and $^{29}$Si NMR spectroscopy are compared and point towards an increase in the degree of polymerization of the silicate network structure. We clarify the CO$_2$ dissolution mechanism in the studied silica undersaturated glass composition. Calorimetric measurements of the glass transition temperatures (Tg) suggest a decrease in viscosity with increasing CO$_2$ content. The inconsistency between spectroscopy and calorimetry is discussed and we propose reconciliation to both aspects. We conclude with a first order model for silicate melt viscosity as a function of CO$_2$ content.

2. **Experimental method:**

We synthesized at high pressure (between 0.5 and 1.5 GPa) a series of silicate glasses with composition analogous to melilitite melt (Brooker et al., 2001; Bosshardt-Stadlin et al., 2014) in the Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ system: ~35 wt.% SiO$_2$ and NBO/T = 2 calculated from the stoichiometric chemical composition corresponding to a highly depolymerized composition (see Table 1). The composition was prepared from a mixture of oxides (Al$_2$O$_3$ and SiO$_2$) and carbonate (Na$_2$CO$_3$ and CaCO$_3$). For NMR acquisition, we used $^{17}$O and $^{29}$Si isotopically enriched oxides: $^{29}$SiO$_2$, Si$^{17}$O$_2$ and Al$_2^{17}$O$_3$; the resulting starting composition was enriched at ~10 and ~40 mol.% in $^{17}$O and $^{29}$Si, respectively.
The CaCO$_3$ and the Na$_2$CO$_3$ are the source of CO$_2$ during the experiments. Except for RB8E-13 (see Table 1) in which we aimed at equilibrating the melt composition with a CO$_2$ fluid in undersaturated conditions (initial CO$_2$ content = 8.8 wt.%), all the glass samples were synthesized under supersaturated conditions (initial CO$_2$ content > 30 wt.%).

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

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

We used a special ¾ inch pressure plate with a special design in which holes have been drilled to improve the experimental quench rate (more than 200°C/s). Isobaric quenching ensured that quench (decompression) bubbles were not formed. Most of the recovered glasses are clear and crystal free; although in some samples, a small fraction of corundum (on the order of a few %) was identified in the $^{27}$Al NMR spectrum. This corundum signal was also observed on a clear glass and we think the corundum signal arises from an external pollution coming from the outer alumina sleeve.

3. **Analytical techniques:**
3.1 Electron Probe Micro-Analysis

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

3.2 Micro-Raman spectroscopy

Micro-Raman spectra were acquired on a Jobin-Yvon Labram 300 spectrometer equipped with an Innova 300-5W Argon ion laser from Coherent© operating at a wavelength of 514 nm and on a Jobin-Yvon Labram HR800 equipped with a solid-state diode laser operating at 532 nm. The Labram 300 spectrometer is equipped with a 2400 grooves/mm grating allowing a spectral resolution on the order of 1 cm$^{-1}$; Labram HR800 spectrometer is equipped with a 1800 grooves/mm grating allowing a spectral resolution on the order of 0.4 cm$^{-1}$. Analyses were performed in confocal mode, using x50 Olympus objectives. The spectral range covered was between 200 and 1250 cm$^{-1}$. The spectral frequency position was calibrated using the emission lines of Ne- and Hg-lamps. On both spectrometers, the output power was set to 125
mW. Several spectra are collected on each sample. For each spectrum, we performed 10 scans on a given sample with an acquisition time of 5 to 10 s each on the Labram HR800 and 15 to 60 s on the Labram 300.

The CO$_2$ content in the recovered glass was determined by Raman spectroscopy using the deconvolution method proposed by Morizet et al. (2013) (details on the method are provided in the Supplementary material 1). For clarity, we provide the simulation of the Raman spectra in the Supplementary material 1 and the entire set of simulation results in Supplementary material 2. The determined CO$_3$/HF ratio corresponding to the ratio between the areas of the $\nu_1$ CO$_3^-$ peak at ~1080 cm$^{-1}$ and the areas of the silicate network high frequency envelop between 800 and 1050 cm$^{-1}$ is reported in Table 1 and ranges from 0.45 and 1.33. It corresponds to a CO$_2$ solubility ranging from 6.0 to 18.0 wt.% for glass synthesized in between 0.5 and 1.5 GPa. Using the major element concentrations determined by EPMA provided in Table 1; we have calculated the corresponding CO$_2$ on a molar basis and expressed as the CO$_2$ molar fraction ($X_{CO_2}$, see Table 1 and 2). For 6.0 to 18.0 wt.% CO$_2$, the $X_{CO_2}$ varies between 0.086 to 0.234.

### 3.3 Micro-Fourier Transfrom Infra-Red spectroscopy

Micro-FTIR analyses were carried out on doubly-polished glass chips to determine the H$_2$O content. Analyses were conducted on a ThermoFisher FTIR5700 equipped with a Continuum microscope. The spectrometer configuration was CaF$_2$ beamsplitter, and MCT-B detector and IR light to cover the 4000-6000 cm$^{-1}$ spectral range. The concentration of OH$^-$ (4500 cm$^{-1}$) and H$_2$O$_{mol}$ (5200 cm$^{-1}$) was determined with the Beer-Lambert law (Ohlhorst et al., 2001). We used density values calculated from the chemical composition with the model of Lange and Carmichael (1990) which includes the change in oxides partial molar volume as a
function of pressure and temperature. Although this density model calculation is applied for liquid; recent work (Guillot and Sator, 2007) showed that the change in density in between liquid and glass is small (~10% in relative) towards an increase in density from the liquid to the glass. Therefore, the derived H$_2$O content with Beer-Lambert law will represent a maximum. As the OH$^-$ and H$_2$O$^{mol}$ extinction coefficient values are a strong function of the glass chemical composition, it was not possible to use an appropriate extinction coefficient value for the presently synthesized silicate glasses. We used the linear extinction coefficient applied to Alban Hill phonotephritic glass provided by Behrens et al. (2009): $\sigma_{OH} = 0.62$ L.mol$^{-1}$.cm$^{-1}$ and $\sigma_{H_2O^{mol}} = 1.02$ L.mol$^{-1}$.cm$^{-1}$. We choose those extinction coefficients as they were applied to glass compositions which are close to the ones studied here. The H$_2$O$^{tot}$ is the sum of the OH and H$_2$O$^{mol}$ concentrations. The H$_2$O$^{tot}$ ranges from 0.5 to 2.8 wt.% with a typical error better than 0.2 wt.% Except for RB8E-8 loaded with 6.9 wt.% H$_2$O, the presence of water is due to adsorption of atmospheric H$_2$O onto the starting material prior capsule preparation and sealing. Considering the high CO$_2$ solubility, the presence of H$_2$O does not play a crucial role on the measured CO$_2$ solubility in such depolymerized compositions (Xue and Kanzaki, 2004; Moussallam et al., 2016).

3.4 $^{17}$O and $^{29}$Si MAS NMR spectroscopy

We have measured the change in the degree of polymerization as a function of CO$_2$ content using $^{29}$Si and $^{17}$O MAS NMR spectroscopies (see Table 2). Solid State $^{17}$O and $^{29}$Si MAS NMR were performed with a Bruker Avance III 500 MHz spectrometer. The $^{17}$O and $^{29}$Si spectra were referenced against liquid H$_2$O at 0 ppm and TMS (Tetramethylsilane) at 0 ppm, respectively.
The $^{17}$O MAS NMR spectra were acquired with a 2.5 mm CP/MAS probe and a MAS frequency of 30 kHz. We used a full shifted echo acquisition ($\pi/12$-\(\tau\)-\(\pi/6\)-acq) sequence with a pulse length of 1 $\mu$s for the $\pi/12$ pulse. The delay $\tau$ was set to 1.13 ms (rotor-synchronized). A recycle delay between scans of 2 s was determined to be sufficient to insure complete relaxation of the $^{17}$O spins. $^{29}$Si-MAS NMR spectra were acquired with single $\pi/2$ excitation of 4 $\mu$s at a MAS frequency of 10 kHz. $^{29}$Si-species can have long spin lattice relaxation time $T_1$ in silicate glasses (Maekawa et al., 1991). A recycle delay of 120 s was shown to be sufficient for quantitative purpose. The spectra deconvolution was conducted with the DMFit2015 software (Massiot et al., 2002).

3.5 Differential Scanning Calorimetry

An indirect measurement of the melt viscosity in the CO$_2$-bearing glass was achieved by determining the glass transition temperature using Differential Scanning Calorimetry (DSC). One definition of the glass transition temperature is the temperature at which the $\log \eta = 12$ (Moynihan, 1995; Dingwell, 1995). The DSC measurements were conducted conjointly with thermogravimetric analyzer (ATG) in order to monitor weight loss during heating.

The glass samples were crushed to avoid sample fragmentation during the DSC experiment. The crushed glass was placed in one of the crucibles and its heat flow was measured. All measurements were performed with the same two crucibles under a constant flow of Ar gas of 20 ml.min$^{-1}$. Each sample was heated from 40°C across the glass transition at a rate of 20 K/min. An effective viscosity of 10$^{12}$ Pa.s is usually achieved with a heating rate of 5 K/min (Webb and Knoche, 1996; Russell and Giordano, 2005). Using a faster heating rate (20 K/min) will lead to higher temperature for the definition of the onset peak and hence a corresponding lower viscosity than 10$^{12}$ Pa.s. However, we used the same heating rate for all the analyzed
samples and the derived Tg could be compared in relative. We used Differential Scanning Calorimeter (DSC SETSYS EVO 2400) equipped with a thermogravimetric analyser (TGA) to determine the glass transition temperature (Tg) for four recovered glass samples (RB8-1, -2 and RB8E-3, -6). The DSC measurements determined the variation of heat flow (in mW) with increasing temperature. The calibration of the DSC was achieved by measuring the heat flow from two identical empty Pt-Rh crucibles (6 mm in diameter). The temperature calibration of the DSC apparatus was conducted by measuring the enthalpy of fusion of metal standards (gold, silver, aluminium and nickel). The baseline from the apparatus was subtracted from the standard and sample measurements. The DSC was then calibrated by measuring the enthalpy of fusion of metal standards (gold, silver, aluminium and nickel) and the sensitivity is better than 0.5% in relative with respect to the temperature measurement. Additional TGA measurements were also conducted conjointly to DSC measurements in order to determine the possible volatile loss during the heating. For RB8E-6, the TGA measurement was not conducted.

4. Results:

4.1 $^{17}$O and $^{29}$Si NMR spectra as a function of CO$_2$ content:

$^{29}$Si and $^{17}$O MAS NMR spectra are shown in Figure 1. We conducted $^{29}$Si MAS NMR spectra deconvolutions using three Gaussian lines (Figure 1A). Interpretation and assignment of the $^{29}$Si spectrum simulation is complicated by the fact that there is only a single asymmetric peak resulting from the overlapping of several individual structural units (Q$^n$). However, it is commonly assumed that there is a structural equilibrium in between Q$^n$ species (Stebbins, 1987; Maekawa et al., 1991; Mysen, 1999; Malfait et al., 2007a); such as:
The n values depend on the stoichiometric NBO/T of the melt. Here n = 2 for the glass composition with NBO/T ~ 2. Hence, there is equilibrium in between Q^2, Q^3 and Q^1. The derived peak positions (-76.3, -81.9 and -88.3 ppm for Q^1, Q^2 and Q^3, respectively) are consistent with previous work (Engelhardt et al., 1985; Murdoch et al., 1985; Maekawa et al., 1991; Zhang et al., 1997). The apparent NBO/T can then be calculated from the molar fraction of the different Q^n species. The present simulation model is simplified as there is no distinction between the Si environments surrounded by various Al atoms (Q^n\text{m(Al)} where m represents the number of Al atoms surrounding the Q^n species; Hiet et al., 2009; Morizet et al., 2014b) and those species are distributed in the single Gaussian line corresponding to a Q^n species. As a result, the shown deconvolution in Figure 1A induces inevitably a systematic bias on the NBO/T subsequent determination.

The difficulty of interpretation inherent to the overlapping contributions in $^{29}$Si NMR spectra is not present in the $^{17}$O NMR spectra and the degree of polymerization is readily extracted from the $^{17}$O NMR spectra decomposition. $^{17}$O MAS NMR spectrum line shape consists in two main lines close to Gaussian shape due to the limited effect of second order quadrupolar contribution (Kelsey et al., 2008). In agreement with Stebbins et al. (1997), each line at ~+100 ppm and ~+40 ppm in chemical shift is attributed to oxygen environments in NBO configuration in the vicinity of Ca atoms (Ca-NBO) and to oxygen environments in BO configuration (i.e. Si-O^{BO}-T with T = Si or Al), respectively. Two additional contributions are also observed at ~-25 and +150 ppm and are attributed to the $^{17}$O signature in oxygen triclusters (O^{III}) and CO$_3^{2-}$ environments (Morizet et al., subm.). The existence of O^{III} (threefold coordinated O atom) is postulated in silicate glasses (Stebbins et al., 2001; Toplis et al., 1997; Benoit et al., 2005; Iuga et al., 2005; Thompson et al., 2011) at $^{17}$O chemical shift.
close to the BO $^{17}$O chemical shift. We did not identify possible contribution from free oxygens which have been inferred in silicate melt from previous studies (Nesbitt et al., 2015; Sawyer et al., 2015). The exact position of this contribution in the $^{17}$O NMR spectrum is not clear and would overlap with oxygen signal in NBO configuration (Nasikas et al., 2012). Furthermore, in the present investigated silicate melt composition (SiO$_2$ > 50 mol.%), the abundance of free O$^{2-}$ anions is expected to be extremely low (<4% of the total oxygen; Nesbitt et al., 2015).

4.2 Glass transition temperature determination

We show in Figure 2 the change in the heat flow as a function of the temperature; except for RB8E-6 the thermogravimetric changes (ATG) are also reported in mg as a function of temperature. There is a constant decrease in the heat flow followed by an increase above 600°C. This abrupt change in the heat flow curve shape with increasing temperature may be attributed to crystallization of the sample. The increase in the heat flow is also accompanied by a brutal change in the ATG curve indicating a substantial loss in the sample mass. This important loss might be attributed probable CO$_2$ diffusion out of the sample. Recovered samples exhibit large bubbled aspect suggesting an efficient CO$_2$ degassing. Anyhow, this process occurs well-above the glass transition temperature. The comparison of the heat flow and ATG curves in the vicinity of Tg does not indicate mass loss; hence the determined Tg reflects the effective glass transition temperature for the CO$_2$-bearing glass sample.

In DSC measurements, the Tg determination is done by the in-built DSC software (Setsoft 2000) using the three points definition. Two tangents with identical slope are fitted prior and after the supposed glass transition region. A third tangent is then fitted in the glass transition region and Tg is defined as the mid-point of the third tangent in between the two parallel
tangents (Morizet et al., 2015a). DSC measurements result in a typical error on the order of ±10 K for the Tg determination (Morizet et al., 2015a); however, some studies reported a lower error ±2.5 K (Giordano et al., 2005; Morizet et al., 2007). Considering an error of ±10 K does not induce any change in the outcome of the present work. For the four measured samples, we observe a change in Tg from 475 to 571°C for RB8-1 and RB8E-6, respectively. Hence, the observed variation in Tg is far above the potential error. Meanwhile, it should be pointed out that for two samples (RB8-1 and RB8E-3) having similar 1) CO₂ content (~17 wt.%) 2) similar degree of polymerization (1.9 and 2.1, respectively), we observe a difference of 38°C in Tg value. Such a difference can be due to slight change in the glass chemical composition inducing a change in Tg value.

5. Discussion:

5.1 Change in silicate glass polymerization as a function of CO₂ content from \(^{17}\)O and \(^{29}\)Si NMR

In the present work, we investigated the change in the degree of polymerization for CO₂-bearing silicate glasses using both \(^{29}\)Si and \(^{17}\)O NMR results with the subsequent simulations (\(^{29}\)Si and \(^{17}\)O) shown in Figure 1. We consider the deviation in the degree of polymerization (DDP) which corresponds to the ratio between the NBO/T determined from \(^{17}\)O and \(^{29}\)Si NMR spectroscopy and the NBO/T calculated from the stoichiometric chemical composition determined by EPMA (see Table 1). Using the DDP instead of the NBO/T has the advantage to average out any potential major element composition heterogeneities (see Table 1). However, we also provide in the Supplementary material plots showing the non-normalized change in the NBO/T as determined from \(^{29}\)Si and \(^{17}\)O NMR spectroscopy as a function of XCO₂. We show in Figure 3 the DDP as a function of XCO₂ for 1) the CO₂ dissolution model
of Eq. 1, 2) the decomposition of $^{29}\text{Si}$ NMR spectra and 3) the decomposition of $^{17}\text{O}$ NMR spectra. We observe that the change in the DDP from $^{29}\text{Si}$ and $^{17}\text{O}$ NMR spectra is linearly correlated to the CO$_2$ content. Both results show that increasing XCO$_2$ induces a strong increase in the degree of polymerization (i.e. decreasing DDP with increasing XCO$_2$) confirming the recent work (Morizet et al., 2014b; Moussallam et al., 2016) for strongly silica-undersaturated melt compositions and therefore extending the observation to a large variety of silicate melt chemical composition.

This result has a major implication as it tends to endorse the chemical model of Eq. 1 for CO$_2$ dissolution. Consequently, in accordance to Eq. 1, CO$_2$ molecules mainly dissolve in silicate melt structure as Free Ionic Carbonate M$^{n+}$.CO$_3^{2-}$ groups (FIC) as proposed by recent works (Moussallam et al., 2016; Morizet et al., 2015b). For the studied composition, the FIC are mainly Ca$^{2+}$.CO$_3^{2-}$. The presence of FIC also indicates that a carbonate subnetwork is coexisting with a silicate subnetwork. Both are intimately linked; however, as suggested in recent study (Morizet et al., 2014a) for alkali-rich melt composition, the FIC represents the precursor of the two liquids immiscibility (carbonate liquid and silicate liquid) process often invoked to explain the coexistence of CO$_2$-rich silicate rocks and carbonatites (Mitchell, 2005; Brooker and Kjarsgaard, 2011; Sharygin et al., 2012; Russell et al., 2012).

Although we do not have data points for XCO$_2$ < 0.086, for both $^{29}\text{Si}$ and $^{17}\text{O}$ NMR, we expect that CO$_2$ does not influence the degree of polymerization possibly because of another unidentified CO$_2$ dissolution mechanism. This would also be consistent with the recent results of Sifré et al. (2014) showing that the silicate melt electrical conductivity is not affected up to 6 wt.% CO$_2$. Until we fulfil this lack of data, it seems that the trend at XCO$_2$ = 0 could extend at NBO/T ratio > 1 suggesting an excess in NBOs concentration. The excess in NBOs has been identified in polymerized CaO-Al$_2$O$_3$-SiO$_2$ silicate glasses (Benoit et al., 2005; Stebbins and Xu, 1997) but never reported for more depolymerized compositions.
We observe a slight mismatch (10% difference) in between the $^{29}$Si and $^{17}$O NMR results: the $^{29}$Si NMR results show a lower DDP than in $^{17}$O NMR results. Although the $^{29}$Si simulation approach is simplified, it appears that both $^{17}$O and $^{29}$Si NMR results are consistent. Hence, the $^{29}$Si NMR results can be used to quantify the effect CO$_2$ produces on the degree of silicate melt polymerization. Furthermore, it can be used to establish a clear CO$_2$ dissolution mechanism reaction for the studied composition.

5.2 CO$_2$ dissolution mechanism reaction in silicate undersaturated glass composition

The DDP as a function of CO$_2$ content obtained by NMR strongly deviates from the chemical model of Eq. 1 (red line in Figure 3) suggesting that there is a much more important change in NBO/T than the suggested change by Eq. 1. This implies that CO$_2$ has a much stronger effect on the silicate melt degree of polymerization than suggested. Serendipitously, we interpret this discrepancy by the fact that the CO$_2$ dissolution mechanism does not strictly follow the mole-to-mole basis changes of Eq. 1. A more complex mechanism is possible where network modifying cations (mostly Ca$^{2+}$ in here) in silicate melt/glass share their positive charges with several oxygen negative charges (Allwardt and Stebbins, 2004; Benoit et al., 2005; Mountjoy, 2007) and consequently throughout multiple weak bonding in the silicate network.

Considering that $^{29}$Si and $^{17}$O NMR results in Figure 3 show a comparable evolution; the $Q^n$ species distribution as a function of CO$_2$ content can be extracted from $^{29}$Si NMR results. We used $^{29}$Si NMR results to propose the CO$_2$ dissolution mechanism represented by Eq. 3. This mechanism reproduces adequately the change in $Q^n$ speciation shown in Figure 4 and the increase in the degree of polymerization (Figure 3) for the currently investigated composition:
In this equation, $Q^1$ species transform into $Q^2$ species in agreement with Eq. 1 but it also transforms into $Q^3$ species. The stoichiometric coefficients in front of each $Q^n$ species correspond to the slope of the linear regressions determined in Figure 4 for the evolution of each $Q^n$ species: -2.5, +0.5 and +2.0 for $Q^1$, $Q^2$ and $Q^3$, respectively. The number of involved $Ca^{2+}$ is fixed by the total negative charge carried by the $Q^1$ species: 2.5 x 3 = 7.5. The same applies on the right hand side of the chemical reaction: 2.0 x 1 + 0.5 x 2 = 3.0. Hence, the 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 melt structure. Hence, the number of FIC $Ca^{2+}..CO_3^{2-}$ formed fixes the number of $CO_2$ molecules incorporated from the fluid phase into the melt structure.

5.3 Implication on the effect of $CO_2$ on silicate melt viscosity: A preliminary model

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

For several glass samples (6.0 and 17.1 wt.% $CO_2$), we have determined the glass transition temperature (Tg), which represents a proxy of the melt viscosity (log $\eta$ = 12; Moynihan, 1995; Dingwell, 1995; Webb and Knoche, 1996). Tg was measured at 571 and 475 ±5°C for 6.2 and 17.1 wt.% $CO_2$ glass samples, respectively. As shown in Figure 5, compositions with the more polymerization (i.e. lower $CO_2$ content) have lower value of Tg. This result is in
stark contrast with our current knowledge on the link between the silicate melt molecular structure and the corresponding silicate melt physical properties. As indicated in Figure 5, the increase in polymerization is accompanied by a decrease in melt viscosity which is counterintuitive and in opposition to what is currently accepted.

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

We propose a possible reconciliation of the spectroscopic results and physical measurements. We have shown in Eq. 3 that CO₂ dissolves in silicate melt structure by forming FIC groups (i.e. Ca²⁺..CO₃²⁻). Our proposition is that FIC clusters forming an individual carbonate subnetwork along a silicate melt subnetwork behave in a similar way to a carbonate liquid (Kono et al., 2014; Vuilleumier et al., 2015). Therefore upon CO₂ dissolution, the molten system is an intimate mixture (i.e. two interacting liquids) of a silicate melt and a carbonate melt. With increasing CO₂ dissolution, the silicate melt is progressively diluted by a carbonate melt having an extremely low viscosity as demonstrated by Kono et al. (2014). The viscosity of the silicate melt subnetwork increases due to the fact that CO₂ induces a polymerization of the Q⁸ species (see Eq. 3 and Figure 3) but this increase in viscosity is counterbalanced by the progressive increase in the carbonate melt subnetwork of extremely low viscosity. Hence, the
progressive CO\textsubscript{2} dissolution in a silicate melt induces a decrease in melt viscosity therefore explaining the extremely low viscosity of CO\textsubscript{2}-rich deep mantle magmatic liquids such as kimberlites.

We propose a model for silicate melt viscosity change as a function of CO\textsubscript{2} content. We should emphasize that the proposed scenario is preliminary and needs to be confirmed in the future by experimental investigations. To establish this model we started with the following hypothesis: in presence of CO\textsubscript{2}, the system is an intimate mixture between a silicate melt and a carbonate melt with each melt having its own viscosity properties. Hence, the entire system viscosity can be approximated by a linear combination of viscosity as suggested by chemical science studies (Mialkowski et al., 2002; Chagnes et al., 2004; Ye et al., 2016) such as:

\[ \eta_{SL+CL} = X_{SL}\eta_{SL} + X_{CL}\eta_{CL} \quad \text{Eq. 4} \]

Where \( \eta_{SL} \), \( \eta_{CL} \) and \( \eta_{SL+CL} \) correspond to the viscosity of the silicate liquid, carbonate liquid and the mixture of both liquids, respectively. \( X_{SL} \) and \( X_{CL} \) correspond to the molar fraction of the silicate and carbonate liquid, respectively. We considered a constant viscosity value for the carbonate liquid given by Kono et al. (2014): \( \log \eta_{CL} = -2.21 \) Pa.s. This value is independent of pressure and has been determined at 1750 K by Kono et al. (2014). The \( X_{CL} \) is given by the molar fraction of the dissolved CO\textsubscript{2} (XCO\textsubscript{2} in Table 1). Hence, the silicate melt molar fraction can be calculated such as \( X_{SL} = 1 - X_{CL} \).

In order to calculate the \( \eta_{SL} \) we considered that when CO\textsubscript{2} molecule dissolves in the system, it withdraws one Ca\textsuperscript{2+} cation and one O\textsuperscript{2-} anion to form FIC Ca\textsuperscript{2+}.CO\textsubscript{3}\textsuperscript{2-}. Hence, the silicate liquid composition changes at each XCO\textsubscript{2} due to the withdrawing of the Ca\textsuperscript{2+} cation. The silicate liquid composition is therefore recalculated at each XCO\textsubscript{2} such as:

\[ X_{SL}^{\text{CaO}} = X_{SL}^{\text{CaO Init}} - X_{CO_2} \quad \text{Eq. 5} \]
In Eq. 5, $X_{SL}^{CaO \text{ Init.}}$ represents the initial CaO molar fraction in the silicate melt composition and is 0.531 calculated from the volatile-free theoretical composition reported in Table 1. We used the viscosity model proposed by Giordano and Russell (2007) to calculate the silicate liquid viscosity. Calculation was conducted at 1750 K so as to match the carbonate liquid viscosity value proposed by Kono et al. (2014). We did not take into account the effect of pressure on the viscosity of the silicate liquid as in the interval 0.5-1.5 GPa the change in silicate melt viscosity is likely to be negligible (Allwardt et al., 2007). Under these conditions, the log $\eta_{SL \text{ Init.}} = -0.32$ Pa.s for the RB8 theoretical composition reported in Table 1.

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

As shown in Figure 6, the viscosity of the silicate liquid increases with CO$_2$ content due to the progressive Ca depletion (i.e. SiO$_2$ increase). For a constant silicate liquid viscosity, the increase in carbonate liquid proportion induces a linear decrease in the viscosity of the two liquid mixtures. The combination of the different effects show that the viscosity of the two liquid mixtures is almost not affected or only slightly decreasing; in other words, the presence of CO$_2$ does not induce a dramatic effect on the viscosity of the two liquid mixtures. The...
calculations conducted at 1600 K produce similar results with only a slight decrease in viscosity of the two liquid mixtures (see Supplementary material 2). For fully polymerized compositions, Brearley and Montana (1989) and White and Montana (1990) suggested a decreasing effect of CO_{2} on silicate melt viscosity. Bourgue and Richet (2001) proposed a decrease in silicate melt viscosity with increasing CO_{2} content. Morizet et al. (2007) pointed out the absence of effect of CO_{2} on viscosity for phonolitic and jadeitic silicate melt compositions. The model calculation results suggest that the addition of CO_{2} to a silicate melt induces negligible effect on the viscosity or a slight decrease in melt viscosity. Although there is a strong increase in silicate melt polymerization, the interplay between a carbonate liquid and a silicate liquid counterbalances the increase in the silicate melt viscosity and the viscosity of the two liquid mixtures is slightly decreasing with increasing CO_{2} content. In an immiscible process between a silicate liquid and a carbonate liquid, the exsolution of the carbonate liquid would provoke the silicate liquid to be stalled in depth due to its high viscosity.

6. **Summary:**

For silica undersaturated melt composition equivalent to melilitite lava composition, using {^{17}O and} {^{29}Si NMR spectroscopy, we have shown that increasing CO_{2} content induces the polymerization of the silicate network structure. This polymerization involves the formation of Free Ionic Carbonate such as Ca^{2+}..CO_{3}^{2-} which constitutes a carbonate subnetwork linked to the silicate subnetwork. However, such dissolution mechanism does not proceed on a mole-to-mole basis and a more complex mechanism is to be considered. We used the Q^n distribution determined by {^{29}Si NMR to constrain the CO_{2} dissolution mechanism and showed that the polymerization is much stronger than proposed by chemical models. We derived a
chemical reaction for the CO$_2$ dissolution which could be applied to a large variety of low silica melt such as kimberlites.

If the increasing polymerization with increasing CO$_2$ content points towards an increase in melt viscosity, glass transition temperature changes negatively with increasing CO$_2$ content suggesting a negative effect of CO$_2$ on melt viscosity. This inconsistency can be reconciled considering that the silicate subnetwork (high viscosity) is progressively diluted by a carbonate subnetwork having an extremely low viscosity. Hence, the viscosity of the two liquid mixtures is not increasing but decreasing instead. This mechanism would explain the fast ascent rate of CO$_2$-rich kimberlitic melt. The strong buoyancy and rapid ascent of the kimberlitic melt will be ensured by the existence of a CO$_2$-rich fluid phase created upon decompression through the ascent but also because the viscosity is kept low in the two liquid mixtures configuration.

**Acknowledgements**

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Mysen, B.O., Virgo, D., 1980b. The solubility behavior of CO$_2$ in melts on the join NaAlSi$_3$O$_8$–CaAl$_2$Si$_2$O$_8$–CO$_2$ at high pressures and temperatures; a Raman spectroscopic study. Am. Mineral. 65, 1166–1175.


Figure caption:

Figure 1: A, CO$_2$-bearing glass $^{29}$Si NMR spectra simulated with three individual Gaussian lines: Q$^1$, Q$^2$ and Q$^3$ at -76.3, -81.9 and -88.3 ppm, respectively. The CO$_2$ content calculated as a molar fraction (XCO$_2$) is reported next to each spectrum. B, CO$_2$-bearing glass $^{17}$O NMR spectra simulated with four individual Gaussian lines: oxygen triclusters (O$^{III}$) at ~-27 ppm, bridging oxygens ((Si,Al)-BO) at ~+40 ppm, non-bridging oxygens (Ca-NBO) at ~+101 ppm and carbonate groups (CO$_3^{2-}$) at ~+149 ppm.

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

Figure 3: Deviation in the degree of polymerization (DDP) as a function of CO$_2$ content. The deviation is calculated as the ratio in between the NBO/T determined from $^{17}$O (filled symbol) and $^{29}$Si (open symbol) NMR results and the NBO/T determined from EPMA analyses (see Table 1). Theoretical line corresponds to a constant degree of polymerization; Dissolution line (red line) corresponds to the deviation in the degree of polymerization following the dissolution mechanism reported in Eq. 1.

Figure 4: Evolution of the Q$^n$ species as a function of XCO$_2$. The data points represent the Q$^n$ molar fraction determined by $^{29}$Si NMR spectral deconvolution shown in Figure 1. The straight lines represent linear regression for the change in Q$^n$ species. The slope coefficients have then been used to establish the chemical reaction of Eq. 3.
Figure 5: Change in glass transition temperature (Tg) as a function of the DDP measured by $^{29}\text{Si}$ NMR. The XCO$_2$ is reported for each data point. The assumed error is 10% in relative for the DDP and ±10°C for Tg. This figure highlights the inconsistency between molecular structure and physical properties changes since decreasing DDP is consistent with increasing polymerization whereas decreasing Tg is consistent with decreasing viscosity.

Figure 6: CO$_2$-bearing silicate melt viscosity as a function of CO$_2$ content. The model calculation is conducted at 1750K. The XCO$_2$ is calculated from the EPMA results in Table 1. Three different calculations are performed: constant silicate melt viscosity and increasing carbonate proportion in the liquid mixture ($X_{\text{SL}}\eta_{\text{SL Init}} + X_{\text{CL}}\eta_{\text{CL}}$); increasing silicate melt viscosity calculated from the model of Giordano and Russell (2007) due to the progressive depletion in Ca ($\eta_{\text{SL}}$); combined effect, increasing silicate melt viscosity and decreasing silicate melt fraction with increasing carbonate liquid fraction at constant viscosity obtained from Kono et al. (2014) ($X_{\text{SL}}\eta_{\text{SL}} + X_{\text{CL}}\eta_{\text{CL}}$).

Table caption:

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

Table 2: Degree of polymerization expressed as the NBO/T from EPMA and $^{29}\text{Si}$ and $^{17}\text{O}$ NMR spectroscopy. Glass transition temperature obtained by Differential Scanning Calorimetric measurements.
## Table 1:

<table>
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<th>Sample</th>
<th>Pressure (GPa)</th>
<th>Wt.% SiO$_2$</th>
<th>Wt.% Al$_2$O$_3$</th>
<th>Wt.% CaO</th>
<th>Wt.% Na$_2$O</th>
<th>Total wt.%</th>
<th>NBO/T$^b$</th>
<th>Wt.% H$_2$O$^c$ Raman$^d$</th>
<th>CO$_3$/HF Raman$^e$</th>
<th>Wt.% CO$_2$</th>
<th>XCO$_2$</th>
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<td>8.7 (0.2)</td>
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$^a$ The RB8 theoretical composition is similar to the one studied in Brooker et al. (2001).

$^b$ 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 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 Si$^{4+}$ and Al$^{3+}$.

$^c$ The H$_2$O content was determined by FTIR, summing the contribution of the OH$^-$ and H$_2$O$^{\text{mol}}$ vibrational peaks at 4500 and 5200 cm$^{-1}$, respectively. The error does not exceed ±0.2 wt.% H$_2$O and corresponds to the standard deviation obtained on the replicated measurements.

$^d$ The CO$_2$ solubility has been determined using the method of Morizet et al. (2013) and using the derived CO$_3$/HF value obtained from the deconvolution of the Raman spectra shown in Figure S3 and subsequent parameters in the Supplementary material 2. The linear relationship has been re-evaluated and is wt.% CO$_2$ = 13.5 x CO$_3$/HF. The actual reported error corresponds to the standard deviation of the CO$_3$/HF ratio obtained 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 CO$_2$ solubility using Raman method is 10% in relative to the value.

$^e$ The XCO$_2$ has been calculated from the wt.% CO$_2$ determined by Raman spectroscopy and from the major element concentrations (in wt.%). We used the same error as for the wt.% CO$_2$ content (10% in relative to the value).
Table 2:

<table>
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<th>NBO/T from EPMA</th>
<th>Q₁</th>
<th>Q₂</th>
<th>Q₃</th>
<th>NBO/T from ²⁹Si</th>
<th>(Si,Al)-BO</th>
<th>Ca-NBO</th>
<th>O=</th>
<th>CO₃⁻</th>
<th>NBO/T from ¹⁷O</th>
<th>DDP ²⁹Si NMR/EPMA</th>
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</table>

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

* The NBO/T from ²⁹Si NMR is calculated from the Qⁿ species concentration. We used the following relation NBO/Si = 3XQ₁ + 2XQ₂ + XQ₃; 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.

* 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 CO₃⁻ is not included in the calculation considering that CO₂ dissolves as Ca^{2+}.CO₂⁻.

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

* 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.

* 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

A

$XQ^* = 2.5 XCO_2 + 0.7$

B

$XQ^* = 0.5 XCO_2 + 0.4$

C

$XQ^* = 2.6 XCO_2 - 0.1$
Figure 5
Figure 6