TOWARDS THE RECONCILIATION OF VISCOSITY CHANGE AND CO$_2$-INDUCED POLYMERIZATION IN SILICATE MELTS

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1. CO$_2$ content determination

We used the method described by Morizet et al. (2013) to determine the CO$_2$ content via Raman spectroscopy. This Raman calibration for CO$_2$ content is a linear calibration function such as wt.% CO$_2$ = 15.17 x CO$_3$/HF relating the CO$_2$ content to the ratio between the area of the CO$_3^{2-}$ peak and the high frequency envelop of the silicate glass vibrational signature.
(CO$_3$/HF). The calibration was established from a database on CO$_2$-bearing silicate glasses (65 data points) with CO$_2$ up to ~16 wt.% CO$_2$. We extended this Raman calibration to additional CO$_2$ content data (89 data points) with higher CO$_2$ content (up to 23 wt.% CO$_2$) determined using bulk analyzer (Figure S1). The entire dataset for this calibration is provided in the Supplementary material 2 as a spreadsheet. The calibration function has been modified according to this new database and the linear relationship is wt.% CO$_2$ = 13.5 x CO$_3$/HF; where HF stands for the high-frequency of the symmetric stretch of the aluminosilicate network. Using this method, the typical error on the CO$_2$ content is 10% in relative to the value. We made an analysis of the typical error with the updated database. In Figure S1, we added the error dispersion lines as reported by the fit. The standard deviation on the CO$_3$/HF ratio is 0.125 and the $r^2$ parameter is 0.969. As a result, for a CO$_3$/HF = 1.25, the error is 10% in relative to the value; it will be lower than 10% at higher CO$_3$/HF and higher than 10% at lower CO$_3$/HF. Considering the dispersion of the data points in Figure S1, we definitely think this cannot be the truth: we observe that the scattering of the data point at low CO$_3$/HF ratio is small and on the contrary is more important at high CO$_3$/HF ratio. In order to be on the safe side, we consider a 10% error in relative to the value for the whole range of CO$_3$/HF ratio determination.

We show in Figure S2 a comparison of the CO$_2$ content determination using Raman spectroscopy and EPMA shortfall. This latter approach has been commonly used to estimate CO$_2$ content dissolved in silicate glasses (Dasgupta et al., 2007; Moussallam et al., 2015); however, the accuracy in the determination of the CO$_2$ content is low (error above 20% in relative to the value as reported by Dasgupta et al., 2007). The corresponding data are provided in Table 1. In Figure S2, the wt.% CO$_2$ by EPMA is calculated using the difference to 100% from the major element analyses and corrected by the H$_2$O content determined by FTIR spectroscopy. We observe in Figure S2 that the data points except for RB8E-13 are
aligned along the 1:1 line suggesting that the Raman calibration method is accurate enough to
determine the CO\textsubscript{2} solubility in the present investigated glasses.

The typical deconvolution of the Raman spectra for the CO\textsubscript{2}-bearing glasses is shown in
Figure S3. We report the deconvolution for several samples with CO\textsubscript{2} ranging from 6.2
(RB8E-6) to 18.0 wt.% (RB8E-11). On each spectrum, we added the derived CO\textsubscript{3}/HF ratio
from the area of the peaks as well as the calculated CO\textsubscript{2} content using the calibration factor of
13.5 mentioned earlier. We should emphasize that such approach is only one possible
solution; however, there is a clear definition of the \( v_1 \) CO\textsubscript{3}\textsuperscript{2-} peak at 1075 cm\textsuperscript{-1}, hence any
variation in the deconvolution would not induce strong variation in the CO\textsubscript{3}/HF ratio and
therefore in the derived CO\textsubscript{2} content. The entire set of simulation parameters is provided in
Supplementary material 2.

2. **Change in \( ^{17}\text{O} \) species as a function of CO\textsubscript{2} content**

We present in Figure S4 the change in the O species abundances as a function of XCO\textsubscript{2} as
determined from Raman spectroscopy (see Table 1). The O species concentrations were
determined from the \( ^{17}\text{O} \) NMR spectra simulations shown in Figure 1B. We clearly observe as
the XCO\textsubscript{2} increases that there is a gradual increase in the abundance of bridging oxygens
species (BO), whereas in the same time the concentration of non-bridging oxygens (NBO)
decreases. These opposite trends are consistent with the identified effect of CO\textsubscript{2} towards an
increase in the degree of polymerization of the silicate melt structure.

The concentration of the oxygen triclusters (O\textsuperscript{III}) does not seem to change as a function of
CO\textsubscript{2} content, however, due to the low abundance of the O\textsuperscript{III} identifying any fluctuation would
be unwise. The peak identified at ~+150 ppm in the \( ^{17}\text{O} \) NMR spectra has been attributed to
the signature of $^{17}\text{O}$ nuclei in $\text{CO}_2^2$- dissolved within the glass structure. This peak appears to increase with increasing $\text{CO}_2$ content with an increasing factor very close to 1. Similar chemical shift is also mentioned in early work (Klemperer, 1978) which reports a $^{17}\text{O}$ chemical shift ranging from +100 to +180 ppm for carbonate groups in organic compounds.

3. Change in NBO/T as a function of $\text{CO}_2$ content

In the main text (see Figure 2), we report the deviation in the NBO/T ($\Delta\text{NBO/T}$) as a function of $\text{CO}_2$ content calculated as the molar fraction ($X_{\text{CO}_2}$). In Figure S5, we show the actual change in the NBO/T measured by $^{17}\text{O}$ and $^{29}\text{Si}$ NMR spectroscopy as a function of the $X_{\text{CO}_2}$. As expected, the observed change in the NBO/T from $^{17}\text{O}$ and $^{29}\text{Si}$ NMR corroborates the drawn conclusions in the main text: 1) the measured NBO/T from $^{17}\text{O}$ and $^{29}\text{Si}$ NMR is higher than the one obtained from stoichiometric calculation indicating an excess NBOs concentration ($\text{NBO/T} > 2$ at $X_{\text{CO}_2} = 0$); 2) CO$_2$ induces a polymerization of the silicate melt structure; 3) the induced polymerization is much more important than the predicted polymerization from the theoretical dissolution mechanism (see Eq. 1). For this latter point, we derived in Figure S5A and B a slope of -3.1 and -3.2 for $^{17}\text{O}$ and $^{29}\text{Si}$ NMR results, respectively; in comparison to the slope of -2 following the dissolution mechanism of Eq. 1.

References Supplementary material 1:

Figure S1: Calibration for CO₂ content in silicate glasses using Raman spectroscopy. This calibration represents an updated version of the one proposed by Morizet et al. (2013) based on 65 data points and for CO₂ content up to 16 wt.%. The new calibration is based on 89 data points and for CO₂ content up to 23 wt.% in silicate glasses (see Supplementary material 2 for the entire dataset). The dashed lines represent the 95% confidence interval. The $r^2$ of the linear regression is 0.969.
Figure S2: wt.% CO$_2$ determined by Raman versus wt.% CO$_2$ estimated from the EPMA shortfall. The EPMA shortfall represents the difference to 100% in the major element concentration (see Table 1). The EPMA shortfall is corrected by the H$_2$O content determined by FTIR to extract the CO$_2$ content. No error is reported for the CO$_2$ content determined by EPMA as this method leads to high uncertainty (see the outlier at 20 wt.% CO$_2$ from EPMA and 8 wt.% CO$_2$ from Raman).
Figure S3: Glass sample Raman spectra simulated with five Gaussian lines corresponding to the symmetric stretch of the CO$_3^{2-}$ group ($\nu_1$ CO$_3^{2-}$) and silicate network ($\nu_1$ Q$^0$). The simulation is reported for RB8 and RB8E samples. The ratio CO$_3$/HF is reported next to each simulation and is used to calculate the CO$_2$ content from the linear correlation (see text for detailed discussion).
Figure S4: Distribution of $^{17}$O species as a function of XCO$_2$. The XCO$_2$ was determined from the Raman simulation results given in Table 1 and using the major element concentrations obtained from EPMA analyses. The molar fraction of the $^{17}$O species was obtained from the simulation of the $^{17}$O NMR spectra shown in Figure 1B of the manuscript main text.
Figure S5: Change in the degree of polymerization (NBO/T) determined from $^{17}$O (A) and $^{29}$Si (B) NMR as a function of XCO$_2$ (see Table 2). Line corresponding to the theoretical degree of polymerization (1.96, see Table 1) is shown. Line corresponding to the change in the degree of polymerization following the Eq. 1 dissolution mechanism is reported. On each plot, we added the linear regression for $^{29}$Si and $^{17}$O NMR data points.