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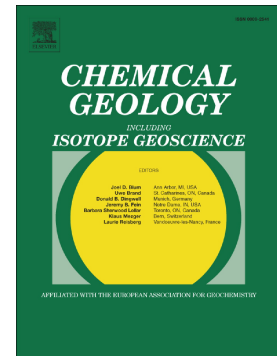
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Journal Pre-proof

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1. Introduction

There is a growing interest into the study of carbon dioxide (CO₂) in magmatic systems and capturing the dissolution mechanisms of CO₂ and how it affects the structure of silicate melts constitutes a prime milestone. The comment by Xue and this reply illustrate well the difficulties in addressing this fundamental quest. In the comment, Xue (2019) provides corrected NBO/T values using the ¹⁷O NMR data produced in Morizet et al. (2017c). The comment also shows that the quantitative relationship in between theoretical model for CO₂ dissolution in silicate melt structure and existing NMR data can be difficult to apprehend. Finally, the comment points out the lack of agreement in between the XCO₃²⁻ from ¹⁷O NMR and XCO₂ from Raman spectroscopy as reported in Morizet et al. (2017b). In the present reply, we propose a corrigendum to our work (Morizet et al., 2017c) and an addendum pointing towards the future scientific questions to be answered.

Since the seventies, many scientific questions arose concerning the CO₂ behaviour in magmatic systems: 1) the CO₂ solubility in silicate melts as a function of intensive conditions (P,T and *f*O₂) and compositions (e.g. silica content), 2) the way CO₂ molecules dissolve into the silicate melt structure (i.e. speciation) and 3) the influence CO₂ dissolution induces on the silicate melt physical properties (e.g. viscosity, density or electrical conductivity).

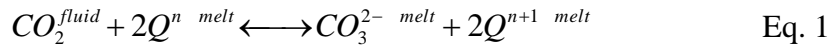
For the first two points, many scientific studies have produced large database for CO₂ solubility and subsequent thermodynamic modelling have been built to constrain CO₂ solubility (and degassing) in silicate melts and taking into account the CO₂ dissolution mechanisms (Newman and Lowenstern, 2002; Papale et al., 2006; Iacono-Marziano et al., 2012; Massuyeau et al., 2015). For the third point, the effect CO₂ induces on melt physical properties is still highly debated. Recent works addressed the effect of CO₂ onto silicate melt

density (Seifert et al., 2013) and silicate melt electrical conductivity (Sifré et al., 2014). For viscosity, the effect of CO₂ is unclear and requires further investigations to decipher the exact effect of CO₂ onto silicate melt viscosity. One way to address the effect CO₂ induces onto silicate melt viscosity is to investigate in detail the effect CO₂ dissolution induces onto the silicate melt structure which is considered as a proxy for melt physical properties and in particular viscosity. Our recent research has focused on this aspect and we believe to have reached a substantial answer to the effect of CO₂ onto silicate melt viscosity (Morizet et al., 2017c). The comment by Xue (2019) and our accompanying reply constitute a cornerstone on this hot scientific topic and emphasise that there is a need for future work in the subject.

2. Corrigendum to the evolution of the silicate melt degree of polymerization as a function of CO₂ content from ¹⁷O and ²⁹Si NMR

We have to admit that the accompanying comment by Xue (2019) is extremely well-conducted from the technical point of view and we recognize that we have not been cautious enough in the calculation of the NBO/T from the obtained ¹⁷O NMR spectra; as well as the apprehension of the theoretical equation for the polymerization of the silicate network upon CO₂ dissolution. In her comment Xue (2019) adequately recalculates the NBO/T values from the original ¹⁷O NMR data published in Morizet et al. (2017c).

In a recent paper (Morizet et al., 2014b), we conducted a similar work on a more polymerized melt composition (nephelinite with NBO/T ~ 1.3) than the one studied in Morizet et al. (2017c; NBO/T ~ 2). Using ²⁹Si NMR, we showed that CO₂ was polymerizing the aluminosilicate network; however, there was a glitch in the interpretation because mass balance calculation was not satisfied with respect to the initial reaction for CO₂ dissolution mechanism:



Hence, it was then suspected that a more complex mechanism occurred and that ^{29}Si NMR was not able to identify it. We concluded that ^{29}Si NMR was probably not the best appropriate method to determine the effect CO_2 induces on the aluminosilicate network. For instance, the distinction in between the effects of the topological changes (Q^n distribution) and geometrical changes (bond length and angles) (as defined in Massiot et al., 2013) appears difficult to determine with the sole use of ^{29}Si NMR. We suggested that CO_2 could induce unquantified topological changes and that the measured polymerization using ^{29}Si NMR did not reflect the true change in the degree of polymerization upon CO_2 solubility. Consequently, we changed our strategy and considered that it would be more appropriate to conduct ^{17}O NMR investigation (i.e. probing BO and NBO concentrations) in conjunction to ^{29}Si NMR (i.e. probing Q^n distribution). As such, the combined use of ^{17}O and ^{29}Si NMR spectroscopy would answer the initial problem as to whether or not the Q^n distribution measured by ^{29}Si NMR reflects the true change in the polymerization upon CO_2 dissolution.

From our work (Morizet et al., 2017c), we showed that both ^{17}O and ^{29}Si NMR results are totally consistent. However, the approach we employed to determine the NBO/T from the ^{17}O NMR results is not correct as shown by Xue (2019) who proposes the right method to calculate the NBO/T from the subsequent ^{17}O NMR deconvolution results. Anyhow, our results and interpretations supported the previous recent investigations on the effect of CO_2 onto silicate melt structure (Morizet et al., 2014b; Moussallam et al., 2016).

The second mistake pointed out by Xue (2019) is with regards to the theoretical equation (Eq. 1) for CO_2 dissolution. We lacked clear sighting in handling this theoretical equation. It has two consequences (see Figure 1): 1) the NMR results are in agreement with the theoretical

equation proposed in early work for CO₂ dissolution and corresponding to Eq. 1; and 2) CO₂ does not have a more polymerizing effect than the effect quantified with Eq. 1.

Consequently, we propose a corrigendum to the work in Morizet et al. (2017b), section 5.2

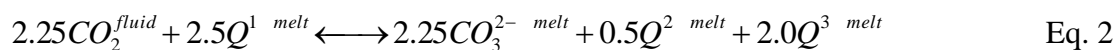
Fig. 3. We followed the description made by Xue (2019) and results are shown in Figure 1.

We choose to represent the data in a NBO/T vs XCO₂/T as it is more appropriate for

apprehending the change in the degree of polymerization as a function of CO₂ content:

different compositions (with different NBO/T) can be readily compared and the slope for CO₂ dissolution theoretical equation is -2.

For the RB8 sample, we report the NBO/T calculated from the ²⁹Si NMR data and corrected values of NBO/T from ¹⁷O NMR data; we also added the data for nephelinite (Morizet et al., 2014b) and haplokimberlite (Morizet et al., 2017a). From Figure 1, it can be observed that the whole dataset agrees and that CO₂ incorporation in the melt induces a decreasing in the NBO/T whatever the considered melt compositions. Using the correct calculation, the NBO/T derived from ¹⁷O NMR is in agreement with the ²⁹Si NMR results. Hence, the distribution of Qⁿ species as determined by ²⁹Si NMR can be used to constrain the change in the silicate glass degree of polymerization as a function of CO₂ content dissolved as Free Ionic Carbonate CO₃²⁻ molecular groups. Based on the Qⁿ distribution, we proposed the following equation for CO₂ dissolution mechanism in silica undersaturated melts:



We emphasise that ¹⁷O NMR results were only used in a qualitative manner in Morizet et al. (2017c) and the reaction for CO₂ dissolution was constrained by ²⁹Si NMR results. The Eq. 2 is a combination of several individual reactions such as the one reported in Eq. 1. We think that the use of this global reaction is more representative of the thermodynamic at stake: each individual reaction may not have the same equilibrium constant; the configuration entropy

(i.e. related to viscosity) is proportional to the sum of all Q^n species molar fraction. The Eq. 2 constitutes a real and unambiguous advance in our knowledge of the CO_2 dissolution in the silicate network structure for depolymerized silicate glass compositions.

The proposed Eq. 2 is equivalent to the theoretical Eq. 1. In Figure 1, we report the linear trends derived from Eq. 1 and for three different compositions (i.e. NBO/T = 1, 2 and 3). The change in the NBO/T as a function of CO_2 content from the theory and NMR data are in agreement; at least for RB8 (Morizet et al., 2017c) and HK (Morizet et al., 2017a) data. It suggests that the measured change in the glass polymerization degree strictly follows the theoretical change in the degree of polymerization imposed by Eq. 1. It seems that data obtained for nephelinite composition (^{29}Si NMR, Morizet et al., 2014b) departs from the theory imposed by Eq. 1; which is only valid if CO_2 dissolves as Free Ionic Carbonates that is the case for strongly depolymerized RB8 and HK compositions. The off-trend pattern for nephelinite data could be explained by a different CO_2 dissolution mechanism owing to the higher degree of polymerization for this glass composition (NBO/T ~ 1). For moderately depolymerized compositions, several CO_2 dissolution mechanisms can be evoked. We suspect that Free Ionic Carbonates are formed but accompanied by other types of CO_3^{2-} such as network carbonates and NBO carbonates (Brooker et al., 2001); however, these different types of CO_3^{2-} molecular groups do not necessarily involve an increase in the degree of polymerization and therefore cannot explain the steeper slope observed in Figure 1 for nephelinite ^{29}Si NMR data. One alternative explanation lies in the difficulty to interpret quantitatively the ^{29}Si NMR data: for example, we know that the δ_{iso} of each individual Q^n species is modified by the presence of surrounding Al atoms (Engelhardt et al., 1985; Hiet et al., 2009). As a result, if the question of the CO_2 effect onto the degree of polymerization is clearly sorted out for depolymerized glass composition and that reconciliation to the change in

physical properties has been proposed; we believe that the question still remains opened for glass compositions demonstrating several CO₂ dissolution mechanisms.

3. Quantification of CO₃²⁻ species with ¹⁷O NMR spectroscopy

In our recent work (Morizet et al., 2017b), using ¹⁷O NMR spectroscopy, we have shown that the peak intensity at ~+150 ppm was linearly correlated to the total CO₂ content determined by Raman spectroscopy (Morizet et al., 2013). The observed correlation helped us to assign the ¹⁷O NMR peak located at ~+150 ppm to carbonate environments in an unambiguous manner. We should point out that this was the first piece of evidence for CO₃²⁻ dissolved in silicate glasses by ¹⁷O NMR. The proposed assignment was later confirmed in our work (Morizet et al., 2017a) using {¹³C}-¹⁷O J-HMQC NMR technique. In this correlation (based on 7 data points), we determined a slope of 0.8. As reported in Morizet et al. (2017b) the XCO₃²⁻ ¹⁷O NMR cannot be straightforwardly related to XCO₂ Raman mainly because the quantitative calculations are dependent on too many parameters as pointed out by Xue (2019). We doubt that the CO₂ concentration determined by Raman can be put into question as most of the samples were also analysed using elemental analyser which is an absolute method (Moussallam et al., 2015). Instead, we believe that the quantification of CO₃²⁻ species using ¹⁷O NMR spectra acquired on a 500 MHz NMR spectrometer is inherently limited. Due to the broadening of the peak at ~+150 ppm and its relatively low intensity, the quantification of CO₃²⁻ species is certainly accompanied by a substantial error. The corollary problem is that it will induce an error in the derived oxygen species concentrations (NBO and BO); however, considering the large scatter observed in Figure 1 and the range of investigated CO₂, the quantitative error will have a limited impact. The reported trend in Morizet et al. (2017a)

using ^{17}O NMR can only be used in a qualitative manner and quantitative application will necessitate more thorough investigation.

4. Future work and perspectives

As pointed out in the introduction, obtaining a clear vision of the CO_2 dissolution mechanisms in silicate melt structure is a prerequisite for the understanding of the effect CO_2 dissolution induces on the silicate melt physical properties such as viscosity or electrical conductivity. It appears clear from the subsequent discussion, and the recent work we have published as well as the decades of knowledge on the CO_2 behaviour in silicate melts that there are still discoveries to be made. In particular, the work we accomplished (Morizet et al., 2017a, b, c) is only a small part of the iceberg as it focuses on particular melt compositions which are depolymerized (i.e. low silica content), CO_2 -rich and analogous to natural magmas which are very peculiar on Earth. As mentioned earlier, the question of the effect of CO_2 dissolution on the silicate melt structure for compositions having multiple CO_2 dissolution mechanisms (Free Ionic Carbonates, Network Carbonates and NBO Carbonates) is still to be determined.

Previous NMR studies (Kohn et al., 1991; Brooker et al., 1999; Morizet et al., 2014a, 2015) have commonly used ^{13}C NMR approach to investigate the CO_2 behaviour in silicate melt. Pioneer work by Kohn et al. (1991) used the ^{13}C NMR to investigate the CO_2 speciation in glasses when CO_2 is dissolved as both CO_2^{mol} and CO_3^{2-} groups. Considerable progresses were conducted with the work of Brooker et al. (1999, 2001) which stated that several types of carbonates groups are present in silicate glasses; with the type of CO_3^{2-} depending on the silicate glass composition. They clearly demonstrated that network carbonates (T-Carb.-T) are identified below +165 ppm in the ^{13}C NMR spectrum and the chemical shift being dependent on the nature of the cation (e.g. Si or Al) in the tetrahedral unit. This assignment was also later

confirmed for CO₂-bearing phonolitic glasses (Morizet et al., 2002). We proposed an assignment for ¹³C NMR signature above +165 ppm to NBO-Carb. Mⁿ⁺ or free carbonate groups (Morizet et al., 2014a). These carbonate groups were also suggested to be present in depolymerized composition from Brooker et al. (2001). However, the discrimination in between NBO-Carb Mⁿ⁺ and CO₃²⁻ Mⁿ⁺ was impossible using ¹³C NMR and we had to access this information by alternative means: {¹³C}-¹⁷O J-HMQC NMR technique (Morizet et al., 2017a). The recent work by Xue et al. (2017) combining ¹³C NMR and Ab-Initio calculations went further in identifying the different CO₃²⁻ species and investigated the change in the CO₃²⁻ molecular configuration for a wide range of glass compositions (i.e. from fully polymerized to strongly depolymerized).

We have conducted a simple approach which is to report the change in the peak centroid of the carbonate ¹³C NMR peak (Figure 2) as a function of composition expressed as wt.% Al₂O₃ + SiO₂ for simplicity. We considered ¹³C NMR spectra for compositions ranging from molten carbonates to depolymerized haplokimberlites (Moussallam et al., 2016) and to fully polymerized jadeite (Morizet et al., 2001), nepheline and albite (Brooker et al., 1999) having varying Al/Si ratio. We observe that the ¹³C peak centroid is slightly changing (~2 ppm) with increasing Al₂O₃ + SiO₂ content up to 60 wt.% Al₂O₃ + SiO₂. The slight decrease in the ¹³C ppm shift from 0 to 60 wt.% Al₂O₃ + SiO₂ is then followed by a brutal decrease in the ¹³C peak centre. This dichotomy might indicate the change in the CO₃²⁻ dissolution mechanisms from Free Ionic Carbonates (and possibly NBO-Carb. Mⁿ⁺) to Network Carbonates (T-Carb.-T). The brutal change in the ¹³C peak centre also seems to mark the limit between slightly depolymerized (NBO/T ~ 0.2 for phonolite, Morizet et al., 2002) to fully polymerized (NBO/T ~ 0 for jadeite, Morizet et al., 2001; 2007). In the Network carbonate region, Brooker et al. (1999) made the distinction in between the different types of carbonates for nepheline, jadeite and albite which have different Al/Si ratio. However, within the Free Ionic Carbonates

region in Figure 2 which represents the majority of natural magmatic systems in fact, a variation of ~ 2 ppm in the ^{13}C NMR spectrum (the assumed analytical error is on the order of ± 0.5 ppm) is subtle. Using in conjunction Ab-Initio calculations for NMR parameters and various NMR approaches (i.e. ^{17}O and ^{13}C) represents the ideal solution to investigate the CO_3^{2-} molecular environments and the recent works accomplished have demonstrated it (Morizet et al., 2017a,b,c; Xue et al., 2017).

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Figure caption:

Figure 1: Change in the NBO/T as a function of CO₂ content (expressed as the molar fraction of CO₂ dissolved in melt divided by the molar fraction of tetrahedral cations). The NBO/T is calculated either from ¹⁷O or ²⁹Si NMR. Data are from Morizet et al. (2014b) and Morizet et al. (2017a,b,c).

Figure 2: Change in the peak centroid position for carbonate molecular groups determined by ¹³C MAS NMR spectroscopy as a function of wt.% Al₂O₃ + SiO₂. Peak position in ppm has been determined for various melt compositions ranging from molten carbonates to silica-rich jadeite and albite.

Figure 1

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Figure 2

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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