LETTER

¹⁷O NMR evidence of free ionic clusters Mⁿ⁺ CO₃⁻ in silicate glasses: Precursors for carbonate-silicate liquids immiscibility

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ABSTRACT

Carbon dioxide is a ubiquitous component of low-silica melts such as kimberlites or melilitites. It is currently assumed that CO_2 molecules dissolving in low-silica melts as carbonate groups (CO_3^{2-}) induce a strong polymerization of the silicate network; however, the exact molecular configuration of this dissolution mechanism is still debated.

Using ¹⁷O MAS NMR spectroscopy, we have investigated the carbonate molecular environment in a series of synthesized low-silica (31-41 wt% SiO₂), CO₂-bearing (from 2.9 to 13.2 wt% CO₂) silicate glasses analogous to melilitites and kimberlites. With the selective {¹³C}-, {²⁷Al}-, and {²⁹Si}-¹⁷O J HMQC NMR method, we show that CO₂ dissolved in the studied low-silica glasses is totally disconnected from the silicate network, forming free ionic clusters (FIC) Mⁿ⁺ CO₂²⁻ with Mⁿ⁺, a charge compensating cation.

The M^{n+} CO²₃ FIC are considered as precursors to immiscibility in between carbonate and silicate liquids. Observed in all studied compositions, we suggest that this immiscibility can be produced from moderately to strongly depolymerized silicate melt compositions.

Keywords: ¹⁷O NMR spectroscopy, CO₂ dissolution mechanism, free ionic clusters, silicate glasses, immiscibility

INTRODUCTION

Providing constraints on the CO₂ dissolution mechanisms in depolymerized silicate melts contributes to our knowledge of kimberlite (Brooker et al. 2011; Russell et al. 2012), melilitite (Keller et al. 2006), and carbonatite genesis (Mitchell 2005), which are CO₂-enriched magmas. Carbonate–silicate liquid immiscibility is thought to be one possible genetic mechanism for these peculiar magmatic systems (Brooker and Kjarsgaard 2011; Guzmics et al. 2015); however, the exact modalities of this mechanism remain poorly constrained.

Early work on CO_2 dissolution in silicate melt (Mysen et al. 1976; Eggler 1978; Mysen and Virgo 1980) suggested that CO_2 plays the role of polymerizing agent of the silicate network structure according to the following reaction:

$$\operatorname{CO}_{2}^{\operatorname{fluid}} + 2Q^{n \operatorname{melt}} \leftrightarrow \operatorname{CO}_{3}^{2\operatorname{-melt}} + 2Q^{n+1 \operatorname{melt}}.$$
 (1)

In this reaction, a CO_2 molecule scavenges available oxygen from a Q^n (a SiO₄ tetrahedron unit with n bridging oxygen) unit to form a CO_3^{-2} group charge compensated by a network-modifying cation (e.g., Ca²⁺). Raman spectroscopic studies (Mysen et al. 2011; Mysen 2012; Moussallam et al. 2016) suggested that Equation 1 proceeds to the right upon CO₂ dissolution inducing a change in the proportion of the different oxygen species [i.e., non-bridging oxygen (NBO) and bridging oxygen (BO)]. However, the exact molecular configuration of the CO₃²⁻ groups has not been identified. Several dissolution mechanisms have been invoked for CO₂ molecules in silicate melts. It has been suggested that CO_2 can form network carbonates (T- CO_3^2 -T with T = Si or Al) and NBO- CO_3^{2-} where a CO_2 molecule connects to an available NBO of a tetrahedron (Brooker et al. 2001). An additional CO₂-dissolution mechanism has been proposed on the basis of molecular dynamic simulations (Xue and Kanzaki 2013; Vuilleumier et al. 2015) and also inferred from Raman spectroscopic studies (Mysen et al. 2011; Mysen 2012; Moussallam et al. 2016). In this mechanism the CO_3^{2-} molecular groups are be present in the silicate network as free ionic clusters (FIC) $M^{n+} CO_3^{2-}$ where M^{n+} is a charge balancing cation (i.e., alkali or alkaline-earth). Each type of CO2-dissolution mechanism is a strong function of the glass chemical composition (Brooker et al. 2001). For a given chemical composition, the melt physical, and chemical properties will be strongly affected by the type of CO₂-dissolution mechanism.

In the present work, we show direct proof of the Mⁿ⁺ CO₃² FIC existence in low-silica depolymerized melts. Based on ¹⁷O MAS NMR spectroscopy, we demonstrate that CO₃²⁻ molecular groups in low-silica melt are disconnected from the silicate network. Such a dissolution mechanism represents the precursor of the immiscibility process between a silicate melt and a carbonate melt.

EXPERIMENTAL METHODS

Several Fe-free glass compositions were investigated via ¹⁷O NMR spectroscopy. The studied compositions are depolymerized with SiO₂ content ranging from 30 to 40 wt% (Table 1) and a non-bridging oxygen concentration per tetrahedron

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(NBO/T) ratio of 1.2 to 3.2 calculated from the chemical composition obtained from electron probe microanalyses (EPMA, see Table 1 and Supplementary Material¹). Studied compositions are analogous to natural kimberlites (Kjarsgaard et al. 2009) and melilitites (Keller et al. 2006).

The starting material was weighed into Pt capsules, which were then sealed by arc welding. Experiments were performed in piston-cylinder apparatus using ³/₄ inch talc-Pyrex high-pressure assemblies between 0.5 and 1.5 GPa and at 1525 °C. Details of the experimental syntheses are provided in the Supplementary Material¹.

ANALYTICAL METHODS

Major elements and CO₂ concentrations: EPMA and Raman spectroscopy

We performed micro-Raman analyses 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 to determine the CO_2 content dissolved in silicate glasses using the protocol proposed by Morizet et al. (2013). A detailed description of the Raman analyses and the CO_2 determination from them is provided in Supplementary Material¹.

NMR spectroscopy

All solid-state ¹⁷O NMR were conducted on a Bruker 850 MHz Avance III Wide Bore spectrometer operating at a frequency of 115.3 MHz and referenced against liquid H₂O at 0 ppm. The ¹⁷O spectra were acquired using Full Hahn-echo and {²⁷Al, ¹³C, ²⁹Si} J-HMQC (heteronuclear multiple-quantum correlation) pulse sequences (Amoureux et al. 2007; Keeler 2010). The details of the analytical conditions are given in the Supplementary¹ Material. The J-HMQC experiment uses the so-called scalar coupling ("J") which arises from the electrons involved in the bond between two nuclei and allows the creation of Heteronuclear Multiple-Quantum Coherences. In an {X}-¹⁷O J-HMQC experiment where oxygen is the observed nuclei and X the indirect one, the resulting ¹⁷O spectrum displays only the oxygen environments that are chemically bound to X.

RESULTS AND DISCUSSION

The ¹⁷O MAS and {X}-¹⁷O J-HMQC NMR spectra are shown in Figure 1 for several samples: XE-2 (Fig. 1a), HK-1 (Fig. 1b), HK-M (Fig. 1c), and RB8E-12 (Fig. 1d). Several oxygen environments are witnessed in the ¹⁷O MAS NMR spectra: ~+50 ppm assigned to ¹⁷O nuclei in BO configuration associated with Si or Al tetrahedra; ~+100 ppm assigned to ¹⁷O nuclei in NBO configuration (Stebbins et al. 1999; Lee and Stebbins 2003; Kelsey et al. 2008) and ~+160 ppm assigned to ¹⁷O nuclei in CO_3^- environments (Morizet et al. 2017a). The peak at ~+100 ppm is less apparent in Mg-bearing compositions (HK and XE), whereas it is prominent in Mg-free Ca-rich RB8E composition consistent with the peak assignment to Ca²⁺ NBO (Thompson and Stebbins 2011). The presence of Mg²⁺ surrounded by oxygen atoms units is proposed at ~+50–70 ppm (Allwardt and Stebbins 2004) but not clearly visible here due to strong overlap with the BO-(Si,AI) signal at ~+50 ppm.

The selective heteronuclear $\{X\}^{-17}O$ J-HMQC NMR pulse sequence probes local environments of oxygen atoms bound to X atoms. Hence, it should be pointed out that chemical bonds involving nuclei other than the considered one (X) will not contribute to the ¹⁷O NMR signal in the $\{X\}$ -¹⁷O J-HMQC spectrum. Serendipitously, the {13C}-17O J-HMQC spectra show a single line located at ~+160 ppm confirming that this peak is associated with CO_3^{2-} molecular groups. More importantly, the absence of signal at ~+50 or +100 ppm indicates that the CO_3^{2-} is connected neither to an available NBO nor to a BO. This is also confirmed by the {²⁹Si}-¹⁷O J-HMQC spectra, which do not exhibit a signal at +160 ppm but only at +50 and +100 ppm; this is consistent with ¹⁷O atoms in BO and NBO configuration, respectively. The absence of common ¹⁷O signals in the {²⁹Si}-¹⁷O J-HMQC and {¹³C}-¹⁷O J-HMQC spectra shows that there is no oxygen atom simultaneously bound to silicon and carbon atoms (within the detection level of $\sim 5\%$) thereby precluding the existence of T-CO₃²⁻T and NBO-CO₃⁻ carbonate units. This CO₂-dissolution mechanism has been proposed on the basis of FTIR results (Brooker et al. 2001), inferred from Molecular Dynamic simulations (Vuilleumier et al. 2015) and indirectly suggested from the change in the network structure upon CO₂-dissolution (Mysen et al. 2011; Mysen 2012; Moussallam et al. 2016). Our results are consistent with the

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 TABLE 1.
 Experimental conditions and chemical compositions of the investigated synthetic Fe-free silicate glasses

			•						
Sample	HK-1	HK-2	HK-M	RB8E-7	RB8E-12	RB8E-13	XE-2	Kimberlite ^a	Melilitite ^a
P (GPa)	1.5	0.5	1.5	0.5	1.0	1.0	1.5		
			Glass chem	ical composit	ion in wt%				
SiO ₂	40.2	40.1	31.8	33.3	30.3	30.1	40.6	30.4	36.5
Al ₂ O ₃	4.3	4.4	3.5	8.7	8.1	8.6	14.8	2.3	7.7
MgO	21.9	21.3	21.9	0.0	0.1	0.2	12.6	29.7	11.8
CaO	22.0	22.3	22.0	41.8	39.8	36.0	17.8	9.6	14.2
Na ₂ O	4.5	4.5	3.5	5.7	4.8	5.0	4.8	0.1	4.3
CO ₂ ^b	7.1	2.9	13.2	6.5	12.6	7.7	4.2	6.40	0.52
H ₂ O ^c	0.8	1.0	1.3	0.7	1.5	1.3	1.0	7.10	1.06
NBO/T ^d	2.6	2.5	3.2	2.1	2.2	1.9	1.2	3.60	1.66
			NMR parame	ters in ppm: F	ree Ca ²⁺ CO ₃ ²⁻				
δ_{iso} / FWHM	154.2 / 42.0	157.3 / 41.3	155.7 / 44.2	164.9 / 34.7	164.6 / 30.7	166.0 / 33.6	157.8 / 45.3		
			NMR	parameters: E	BO-Si				
δ_{iso} / FWHM	54.4 / 24.4	57.4 / 29.3	55.2 / 24.3	61.0/23.3	51.6 / 24.3	53.4 / 22.3	48.7 / 25.5		
			NMR	parameters: B	IA-OI				
δ_{iso} / FWHM	42.5/25.8	42.5/25.8	42.5/25.8	47.8/25.6	45.5 / 25.7	47.5 / 25.5	42.5 / 25.8		
			NMR	oarameters: N	BO-Si				
δ_{iso} / FWHM	95.9/31.4	96.7 / 33.1	96.0 / 23.7	106.5/24.6	106.8 / 25.2	106.2 / 24.0	99.3 / 47.1		

^a Natural materials. The glass CO₂ content has been determined using Raman spectroscopy and the method described in Morizet et al. (2013). With the derived CO₃/HF ratio obtained from the deconvolution of the Raman spectra (see Supplementary Material¹), it is possible to determine the CO₂ content using the linear relationship wt% CO₂ = 13.5 × CO₃/HF. The typical error on the CO₂ content using Raman method is 10% in relative to the value.

^bThe H_2O content was determined by FTIR spectroscopy on a doubly polished glass plate. Contribution for OH⁻ and H_2O^{mal} vibrational peaks at 4500 and 5200 cm⁻¹ were summed to obtain the H_2O^{tot} . The error does not exceed ±0.2 wt% H_2O and corresponds to the standard deviation obtained on the replicated measurements. ^cThe NBO/T describing the average polymerization was calculated on a stoichiometric basis using the chemical composition measured by EPMA.

^d An average typical natural composition of kimberlite and melilitite were obtained from Kjarsgaard et al. (2009) and Keller et al. (2006), respectively. Additional oxides (TiO₂, FeO, and K₂O for the most important) have not been reported but are nominally present: ~0–4 wt% for TiO₂, ~10.0 wt% FeO, and ~2.0 for K₂O.



FIGURE 1. ¹⁷O MAS and {¹³C}-, {²⁷Al}-, and {²⁹Si}-¹⁷O J-HMQC NMR spectra of CO₂-bearing silicate glasses: XE-2 (**a**), HK-1 (**b**), HK-M (**c**), and RB8E-12 (**d**). Three oxygen environments are identified with MAS spectra: FIC $M^{n+}CO_3^{2-}$, Ca²⁺ NBO-Si, and BO-(Si,Al). The NMR spectra for the other synthesized glasses can be found in Supplementary Material¹. (Color online.)

MD results from Vuilleumier et al. (2015) suggesting that FIC represents 75% of the dissolved CO_3^{2-} molecular groups and 25% corresponding to network carbonate units (T- CO_3^{2-} T with T = Si or Al; Brooker et al. 2001). In the FIC Mⁿ⁺... CO_3^{2-} , Mⁿ⁺ is a charge-balancing cation that can be Mg²⁺, Ca²⁺, and Na⁺ to a lower extent (Na₂O is ~5 wt%) for the currently investigated compositions. Although, Morizet et al. (2017a) showed that CO_3^{2-} groups dissolve preferentially in the vicinity of Ca²⁺ cations, we do not exclude the possibility for Mg²⁺ CO₃²⁻ being formed considering that Mg²⁺ could play a role comparable to Ca²⁺ (Cormier and Cuello 2013).

At this point, we wish to raise the level of confidence in the above discussion. Indeed, one could argue that the 17O signal from Si-O-C linkages could be absent from the {29Si}-17O J-HMQC spectrum if the associated J(²⁹Si-¹⁷O) coupling value strongly differs from those occurring for ²⁹Si-¹⁷O(BO) or ²⁹Si-¹⁷O(NBO) linkages. A simple way to rule out this possibility is to show that the full ¹⁷O spectrum can be totally reconstructed as the sum of the three selective {X}-17O J-HMQC spectra. The reconstructions of the ${}^{17}OMASNMR$ spectra from the deconvolution of the ${X}-{}^{17}O$ J-HMQC spectra are shown in Figure 2 for three ¹⁷O MAS NMR spectra: Mg-free RB8E-12 (Fig. 2a) and Mg-bearing XE-2 and HK-1 (Figs. 2b and 2c). The deconvolution procedure was conducted as follows: each {X}-¹⁷O J-HMQC NMR spectrum was fitted with Gaussian lines; one line for the {13C}-17O J-HMQC, one line for the {²⁷Al}-¹⁷O J-HMQC and two lines for the {²⁹Si}-¹⁷O J-HMQC corresponding to the BO-Si and NBO-Si environments, respectively. The parameters obtained are reported in Table 1. Since the {27Al}-17O J-HMQC spectrum was not acquired for all the samples due to the requirement of very long acquisition times, we used the δ_{iso} and FWHM from the XE-2 deconvolution for HK spectra; and the average δ_{iso} and FWHM obtained from RB8E-12 and RB8E-13 for RB8E-7 spectrum. In Figure 2a, we show that the performed deconvolution adequately reproduces the 17O MAS NMR spectrum for the Mg-free RB8E-12 sample. The high carbon content of this sample excludes the possibility of a lack of ¹⁷O signal of significant intensity in the {29Si}-17O J-HMQC spectrum. For Mg-bearing compositions, the ¹⁷O MAS NMR spectra are not perfectly reproduced by the deconvolution. Regardless of the glass composition (XE-2 and HK), the residuals of the simulation exhibit a signal located at \sim +70 ppm not accounted for. Considering that this residual NMR signal is only observed in Mg-bearing glass composition, the signal could be attributed to oxygen atoms in MgO_x configuration. This assignment would be consistent with the results of Hung et al. (2016), which identified ¹⁷O resonance for MgO_x O atoms in Ca/Mg orthosilicate glasses at +60 ppm. Considering that the NMR signal of the CO_3^{2-} environments is reproduced adequately by a single line at $\sim +160$ ppm, the majority of the CO₃²⁻ groups are FIC in the investigated glass compositions.

IMPLICATIONS FOR CARBONATE-SILICATE LIQUID IMMISCIBILITY

Numerous implications arise from the present results; however we only focus on two of them: (1) the immiscibility between carbonate and silicate liquids and (2) the impact of free ionic clusters (FIC) on the carbonated melt transport properties. It is reasonable to consider that the $M^{n+} CO_3^2$ FIC constitutes a carbonate subnetwork intimately mixed within a silicate subnetwork. For instance, Kubicki and Stolper (1995) showed that the molecular energy involved for ion pairs complexes (similar to FIC $M^{n+}...CO_3^2$) is low as compared to any other type of carbonates dissolved in silicate melt. Therefore, the energy barrier to dissociate the carbonate subnetwork from the silicate subnetwork is lower in the case of FIC.

Network-modifying cations have varying coordination numbers in a silicate melt (e.g., 5 to 8 for Ca²⁺; Cormier and Cuello 2013). Upon CO₂ dissolution, the network-modifying cation will share less of its positive charges to the silicate network to compensate the negative charges of the CO_3^{2-} groups; resulting in a network-modifying cation that is less connected to the silicate network. In particular, Vuilleumier et al. (2014) showed that the Ca-O distance in molten CaCO₃ is on average 2.35 Å, suggesting that Ca²⁺ is more closely connected to the carbonate subnetwork than to the silicate subnetwork. Consequently, we believe that the presence of FIC Mⁿ⁺ CO₃²⁻ could be viewed as a possible precursor to immiscibility. For instance, removal of the carbonate network from the silicate network is a proposed mechanism to form calciocarbonatite from a melilitite parental melt (Guzmics et al. 2015).

We suggest that this immiscibility could also proceed from kimberlite owing to the fact that FIC groups are observed in the investigated HK composition analogous to kimberlite melt. However, the molecular configuration $M^{n+} CO_3^{-}$ FIC poses the problem of the way CO_2 degasses from depolymerized silicate melts. The CO_2 migration into the fluid phase imposes a molecular structure reconfiguration to dissociate the $M^{n+} CO_3^{-}$ groups and causes the network-modifying cation to remain in the silicate melt, thus depolymerizing the silicate network structure. This difficulty could explain the absence of degassing in kimberlitic melt upon decompression as witnessed by Moussallam et al. (2015).

Finally, it turns out that the identified CO₂-dissolution



mechanism can also affect the physical properties of carbonated melts (e.g., magma transport and electrical conductivity). Interconnection between FIC molecular groups could explain the high electrical conductivity observed in CO₂-bearing silicate melt (Sifré et al. 2014). There is an intimate mixture between a carbonate subnetwork having an extremely low viscosity and a silicate subnetwork with a higher viscosity (Morizet et al. 2017b). Through immiscibility, the carbonate liquid will migrate toward the surface due to its low viscosity and density (Vuilleumier et al. 2014), whereas the silicate liquid, which becomes enriched in SiO₂, is stalled at depth due to the increased viscosity (Giordano et al. 2008). Therefore, the direct proof of the existence of FIC gives legitimacy to the development and application of the immiscibility theory in a wide range of processes taking place in the Earth's interior.

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FIGURE 2. ¹⁷O MAS spectrum deconvolution obtained from Gaussian lines derived from {X}-¹⁷O J-HMQC spectra. The deconvolution of the ¹⁷O NMR spectra for the other synthesized glasses can be found in Supplementary Material¹. (Color online.)

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