Chemical Geology 418 (2015) 89–103

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

# A NMR and molecular dynamics study of $CO_2$-bearing basaltic melts and glasses

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ARTICLE INFO

*Article history:*
Accepted 23 March 2015
Available online 2 April 2015

*Keywords:*
$CO_2$ speciation
Aluminosilicate network speciation
High temperature melt *versus* glass
MAS NMR
First-principles molecular dynamics simulations

ABSTRACT

The presence of volatile, especially carbon dioxide ($CO_2$), in silicate liquids is considered as a key parameter to magmatic degassing and eruptive processes. Unfortunately, due to experimental difficulties, our current knowledge on the $CO_2$ effect on silicate melt structure is weak and relies on the observation of *ex-situ* recovered $CO_2$-bearing glasses.

In the present work, we confront the results obtained from NMR spectroscopic observations of glass synthesised at pressure between 0.5 and 3.0 GPa and theoretical investigations from first-principles molecular dynamics (FPMD) simulations conducted at 5.0 and 8.0 GPa on high temperature melt for a simplified basaltic composition. The results obtained on the aluminosilicate framework (molar fraction of silicon species and Al average coordination number) suggest that both *ex-situ* and *in-situ* results compare adequately. The results are in agreement with our current knowledge on the change in aluminosilicate melt/glass structure with changing intensive conditions. Increasing pressure from 0.5 to 8.0 GPa induces 1) an increase in the average Al coordination number from 4.1 to almost 5.0 and 2) an increase in the degree of polymerisation with NBO/Si changing from 1.30 to 0.80. The presence of $CO_2$ does not seem to induce a dramatic change on both the average Al coordination number and the NBO/Si. FPMD simulations performed with 0 and 20 wt.% $CO_2$ at 8.0 GPa result in a change from 4.84 to 4.96 for the average Al coordination number and in a change from 0.87 to 0.80 for the NBO/Si value, respectively.

On the contrary, there is a lack of consistency in between the $CO_2$ speciation obtained from NMR spectroscopy and from FPMD simulations. Whereas the analysis of glasses does not reveal the presence of $CO_2^{mol}$ species, the FPMD simulation results suggests the existence of a small proportion of $CO_2^{mol}$. Further work with *in-situ* experimental approach is therefore required to explain the observed lack of consistency between the $CO_2$ speciation in glass and in high temperature melt with basaltic composition.

## 1. Introduction

Fluids and melt are ubiquitous materials within the Earth deep interiors. After water, carbon dioxide ($CO_2$) is the second most important volatile involved in magmatic systems (Gerlach and Graeber, 1985; Jambon, 1994; Symonds et al., 1994; Morizet et al., 2002, 2010) and in some volcanic systems $CO_2$ becomes the dominant one (Holloway, 1981; Giggenbach, 1997; Andersen and Neumann, 2001; Massuyeau et al., submitted for publication, in this issue). Its impact on magmatic processes is now well-recognized (Eggler, 1974; Brey and Green, 1975, 1976; Wallace and Green, 1988; Falloon and Green, 1989; Draper and Green, 1997). Owing to the large amount of experimental investigations since decades, $CO_2$ solubility and speciation are currently well-constrained as a function of composition (Fine and Stolper, 1986; Pan et al., 1991; Dixon, 1997; Papale, 1999; Botcharnikov et al., 2005, 2006; Iacono-Marziano et al., 2008; Shishkina et al., 2010; Iacono-Marziano et al., 2012; Morizet et al., 2014a) and intensive parameters (Blank and Brooker, 1994; Dixon et al., 1995; Morizet et al., 2002; Newman and Lowenstern, 2002; Behrens et al., 2009; Lesne et al., 2011; Iacono-Marziano et al., 2012).

However, one of the major deficiencies of our current knowledge of $CO_2$ behaviour in aluminosilicate compositions is that most of the available information on $CO_2$ speciation is based on the study of *ex-situ* recovered samples quenched to glasses. It appears problematic because recent investigations showed that the $CO_2$ speciation recorded in glasses cannot unambiguously be applied to a corresponding high temperature melt condition (Morizet et al., 2001; Nowak et al., 2003; Spickenbom et al., 2010). The $CO_2$ speciation is suggested to be decoupled from the aluminosilicate network speciation. At temperature

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http://dx.doi.org/10.1016/j.chemgeo.2015.03.021

below the glass transition, the silicate network speciation is fixed but $CO_2$ speciation still evolves. The results from Nowak et al. (2003) conducted on dacite and albite compositions (Fig. 1A) suggest that at high temperature in the melt, part of the $CO_2$ speciation is represented by $CO_2^{mol}$ species formed through the following interconversion reaction governed by an equilibrium constant (K) between a carbonate group ($CO_3^{2-}$) and a $CO_2$ molecule ($CO_2^{mol}$):

$$CO_c^{mol} + O^{2-} \overset{K}{\leftrightarrow} CO_3^{2-}. \tag{1}$$

The interconversion reaction in Eq. (1) is probably oversimplified. The nature of the involved oxygen from the melt ($O^{2-}$ in Eq. (1)) is currently unknown, (*i.e.* the negative charge distribution around the oxygen atom is not asserted and the surrounding cation is variable in nature). Those pioneer works (Morizet et al., 2001; Nowak et al., 2003) have focussed on simple compositions in which both C species ($CO_2^{mol}$ and $CO_3^{2-}$) are present initially in the glasses.

For basalt-like composition in which $CO_2$ is dissolved solely as $CO_3^{2-}$ groups, we currently do not have solid evidence of such an interconversion mechanism at high temperature in the melt. However, recent molecular modelling conducted by Guillot and Sator (2011) on simple haplo-basaltic composition (MORB) invoked a similar mechanism. As shown in Fig. 1B molecular dynamics simulation results on MORB under high temperature melt conditions conducted at 2273 K show that the proportion of $CO_2^{mol}$ is gradually increasing with decreasing pressure (up to 70% $CO_2^{mol}$ in relative to the total C species at 2.0 GPa). Guillot and Sator (2011) also showed that the proportion of $CO_2^{mol}$ is strongly temperature dependent: 70% and 37% $CO_2^{mol}$ at 2273 and 1473 K, respectively. Those results are in agreement with our current view of the interconversion between $CO_2^{mol}$ and $CO_3^{2-}$ groups observed in more acidic compositions (Morizet et al., 2001; Nowak et al., 2003). Nevertheless, it has never been witnessed experimentally for basaltic compositions in which the $CO_2$ speciation is only represented by $CO_3^{2-}$ groups (*e.g.* Fine and Stolper, 1986; Pan et al., 1991; Pawley et al., 1992; Dixon et al., 1995; Morizet et al., 2010).

The molecular structure of aluminosilicate glass/melt can be approximated by a combination of several individual structural units, called Q-species (*e.g.* Grimmer et al., 1984; Brandiss and Stebbins, 1988; Merzbacher et al., 1990; Stebbins, 1995; Mysen and Richet, 2005) where Q represents a $SiO_4$ tetrahedron and is considered as a network forming unit. The notation $Q^n$ is often employed where n represents the number of bridging oxygen (BO) per tetrahedron.

In complex aluminosilicate melts, $Al^{3+}$ is also considered as a network forming cation ($AlO_4$ tetrahedra) whereas other cations (for example, $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) are either network modifiers or charge balancing cations (*e.g.* Neuville and Mysen, 1996; Lee and Stebbins, 2000).

The way the different $Q^n$ species combines within a silicate glass/melt has been extensively addressed. Early work by Mysen and co-workers based on micro-Raman spectroscopy (Mysen and Virgo, 1980; Mysen et al., 1980; Mysen and Frantz, 1994; Mysen, 1997) clearly established that several $Q^n$ species are in equilibrium in the glass such as:

$$2Q^n \leftrightarrow Q^{n+1} + Q^{n-1} \quad n = 1,\ 2 \text{ or } 3. \tag{2}$$

Similar conclusion was also drawn from NMR investigations (Maekawa et al., 1991; Maekawa and Yokokawa, 1997; Zhang et al., 1997; Schneider et al., 2003; Xue and Kanzaki, 2004; Malfait et al., 2007a; Davis et al., 2011; Morizet et al., 2014b) for various types of compositions from simple binary $M_nO–SiO_2$ systems but also for more complex Al-bearing systems. This reaction implies that for a given chemical composition three Q-species are in equilibrium in glasses. The equilibrium in Eq. (2)provides also a view of the degree of polymerisation of a silicate glass/melt. This degree of polymerisation obtained by the Q-species distribution is dependent on the chemical composition and is commonly expressed by the NBO/T parameter which corresponds to the ratio between the non-bridging oxygen and the tetrahedra (Mysen, 1988, 1990). The NBO/T can be readily calculated from the concentrations of oxides. It is commonly assumed that for a $0.1 < NBO/T < 1$ calculated from the chemical composition, the reaction given in Eq. (2) involves $Q^4$, $Q^3$ and $Q^2$ such as:

$$2Q^3 \leftrightarrow Q^4 + Q^2. \tag{3}$$

This situation is of particular interest in the present study as the NBO/T is very close to one for the investigated composition (see Section 2).

From a general stand point, the molecular structure ($Q^n$ distribution) of a high temperature melt is different from the one of the corresponding glass (Stebbins and Xue, 2014). The glass transition temperature (Tg) (Moynihan et al., 1976) separates the glassy state, with a frozen-in molecular structure, from the liquid state in which molecular

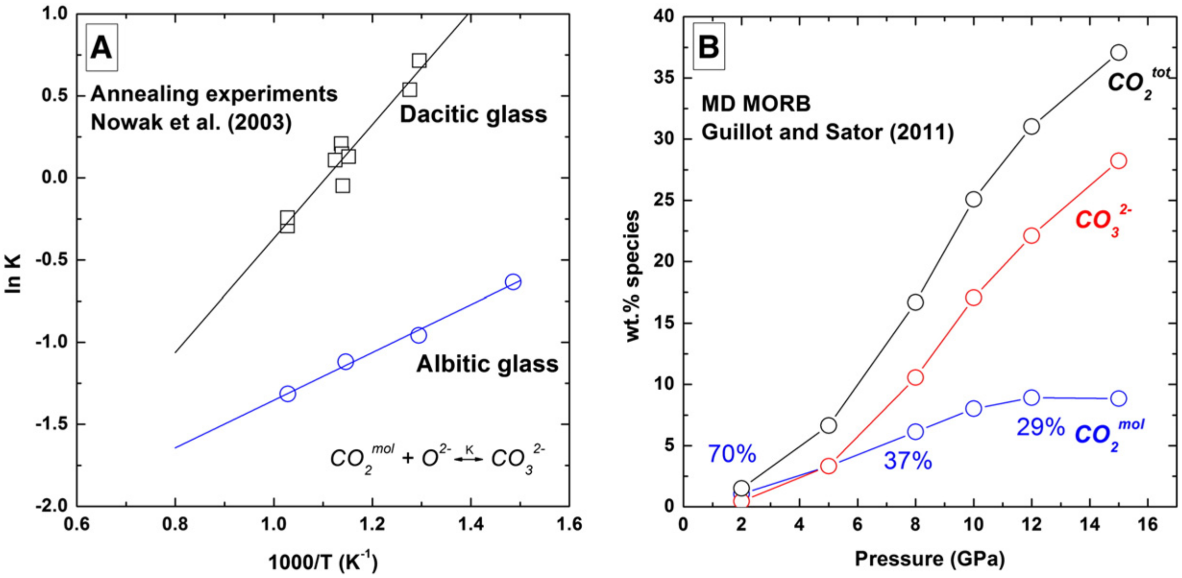

**Fig. 1.** A) Evolution of the equilibrium constant (K) for the interconversion reaction between $CO_3^{2-}$ and $CO_2^{mol}$ from annealing experiments of Nowak et al. (2003) on albitic and dacitic compositions. B) $CO_2$ solubility ($CO_2^{tot}$) and speciation ($CO_2^{mol}$ and $CO_3^{2-}$ groups) in MORB as a function of pressure (up to 15 GPa) derived from classical molecular dynamics simulations from Guillot and Sator (2011). Both studies imply the existence of a non-negligible abundance of $CO_2^{mol}$ at high temperature in the melt.