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Carbon dioxide in silicate melts at upper mantle conditions: Insights from atomistic simulations

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ABSTRACT

The detail of the incorporation of carbon dioxide in silicate melts at upper mantle conditions is still badly known. To give some theoretical guidance, we have performed first-principle molecular dynamics simulations (FPMD) to quantify the speciation and the incorporation of carbon dioxide in two CO_2-rich silicate melts (~20 wt.% CO_2 at 2073 K and 12 GPa), a basaltic and a kimberlitic composition chosen in the CaO–MgO–Al_2O_3–SiO_2 system. In the basaltic composition, carbon dioxide is incorporated under the form of a minority population of CO_2 molecules and a prevailing population of carbonate ions (CO_3^{2-}). In contrast, the amount of CO_2 molecules is found to be very small in the kimberlitic melt. Moreover, a new (transient) species has been identified, the pyrocarbonate ion $C_2O_5^{2-}$ issued from the reaction between CO_2 and CO_3^{2-}. With regard to the structure of the CO_2-bearing melts, it is shown that the carbonate ions modify the silicate network by transforming some of the oxygen atoms into bridging carbonates, non-bridging carbonates, and free carbonates, with a distribution depending on the melt composition. In the basaltic melt a majority of carbonate ions are non-bridging or free, whereas in the kimberlitic melt, most of the carbonate ions are under the form of free carbonates linked to alkaline earth cations. Surprisingly, the addition of CO_2 only has a weak influence on the diffusion coefficients of the elements of the melt. The consequence is that the strong enhancement of the electrical conductivity reported recently for carbonated basalts (Sifré et al., 2014, Nature 509, 81), can be reproduced by simulation only if one assumes that the ionic charges assigned to the elements of the melt depend, in a non-trivial way, on the CO_2 content. Finally, a comparison of the FPMD calculations with classical molecular dynamics simulations using an empirical force field of the literature (Guillot and Sator, 2011, GCA 75, 1829) shows that the latter one needs some improvement.

1. Introduction

Evidence of CO_2-rich magmas in the upper mantle are well documented. For instance, the observation of extended volcanoclastic deposits at some ocean spreading centers suggests that an explosive subaqueous volcanism with magma disruption can be driven by CO_2-rich melts (Hékinian et al., 2000; Pineau et al., 2004; Sohn et al., 2008; Helo et al., 2011). Another example is given by kimberlite magmas which are volatile rich ($CO_2 + H_2O$) and ascend from deep in the mantle at high velocity, causing violent eruptions (Sparks et al., 2006; Brooker et al., 2011; Russell et al., 2012). Related to kimberlites, the carbonatites, although volumetrically insignificant on Earth, have seen their importance recently reevaluated (Woolley and Church, 2005; Woolley and Kjarsgaard, 2008). Carbonatites are found on all continents and a world distribution map shows that carbonatitic magmatism of explosive style is abundant from the late Archean to the Phanerozoic (Bailey and Kearns, 2012; Humphreys et al., 2012), their primary melts being formed from incipient melting of subducted oceanic crust in the mantle transition zone (Walter et al., 2008) or from the partial melting of plume material when they are associated with large igneous provinces (Bell and Simonetti, 2010; Ernst and Bell, 2010; Woolley and Bailey, 2012). Furthermore, magnetotelluric sounding reveals the presence of highly conductive phases in the asthenosphere (Lizzaralde et al., 1995; Baba et al., 2006, 2010) which could be carbonatitic melts (Gaillard et al. 2008, Yoshino et al., 2012; Dasgupta et al., 2013). Thus CO_2-rich melts seems to play a key role in the upper mantle for explaining the mobilization and the transport of CO_2 from a source region to the surface. However, in spite of a growing interest the physicochemical properties of CO_2-bearing silicate melts at mantle conditions are still poorly known.

During the last three decades many studies have been devoted to measuring the solubility of CO_2 in silicate melts of various compositions.

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But due to experimental difficulties these studies were generally restricted to low and moderate pressures (below ~2 GPa). IR spectroscopy studies (Mysen, 1975; Fine and Stolper, 1985a, 1985b; Stolper et al., 1987; Fogel and Rutherford, 1990; Pan et al., 1991; Brooker et al., 1999, 2001a,b; Morizet et al., 2002) have emphasized the importance of CO_2 speciation which may exist either as molecular CO_2 or as carbonate ion (CO_3^{2-}), the molecular form being favored in polymerized (silicic) melts while the carbonate ion is dominant in depolymerized (basic and ultrabasic) melts. However, it has been suggested (Morizet et al., 2001; Nowak et al., 2003; Spickenbom et al., 2010; Konschak and Keppler, 2014) that the CO_2 speciation observed in quenched glasses by IR spectroscopy may not be representative of that in silicate melts equilibrated at high temperature: in particular, the abundance of molecular CO_2 could be underestimated in the liquid at magmatic temperatures.

Recently, in introducing an empirical force field to describe the chemical reactivity of CO_2 in silicate liquids ($CO_2 + (O^{2-})_{melt} \leftrightarrow CO_3^{2-}$), it has been possible to evaluate by classical molecular dynamics (MD) simulation the solubility and speciation of CO_2 in silicate melts in various compositions (Guillot and Sator, 2011). The conclusions of these MD calculations are twofold: (i) The solubility of CO_2 increases markedly with the pressure and reaches value as high as ~20 wt.% in basaltic melts at 8 GPa, and (ii) the proportion of molecular CO_2 is found to be significant in CO_2-saturated basic and ultrabasic melts at superliquidus temperature and high pressures, a result at variance with post mortem analyses of basaltic glasses where only carbonate ions are detected. To check the consistency of the above MD calculations and to get some new insights we have performed first-principle molecular dynamics simulations (FPMD) of CO_2-rich basaltic and kimberlitic melts. The results of these FPMD simulations based on the explicit evaluation of the electronic structure are presented here. In particular, the effect of CO_2 on the structure, the diffusion of elements, and the electrical conductivity of basaltic and kimberlitic melts has been evaluated.

2. Computational details

The core of a classical MD calculation consists of solving iteratively the equations of motion of an assembly of atoms interacting via a force field. The latter one can be empirical (i.e. adjusted so as to reproduce some properties of the real material) or is obtained from a fit of a potential energy surface deduced from a quantum chemical calculation of a small part of the system under consideration (e.g. a monomer or a cluster of atoms). A more rigorous method, named FPMD, relies on the implementation of a molecular dynamics schema within an electronic structure calculation performed in the framework of the density functional theory (DFT). However, the computational cost of this method is very high and restricts its use to relatively small system sizes (a few hundred of atoms instead of several thousand or more with classical MD simulations) and short trajectories (10–100 ps instead of ~10 ns with classical MD).

In the present case, the FPMD simulations were performed within the DFT framework and the Born-Oppenheimer approximation using the freely available program package QUICKSTEP/CP2K (VandeVondele et al., 2005a). QUICKSTEP uses a hybrid Gaussian plane-wave (GPW) method (Lippert et al. 1997). We employed a triple-zeta valence doubly polarized (TZV2P) basis set for oxygen and carbon (VandeVondele et al. 2005b). For Ca, we used the double-zeta valence plus polarization (DZVP) basis set optimized for molecules (VandeVondele and Hutter, 2007). Core electrons were replaced by the Goedecker-Teter-Hutter (GTH) norm-conserving pseudo-potentials (Goedecker et al., 1996; Hartwigsen et al., 1998; Krack, 2005). The cutoff for the electronic density was set to 700 Ry and the gradient corrected exchange-correlation functional BLYP (Becke, 1988; Lee et al., 1988) was used in the DFT calculations. van der Waals interactions were taken into account using the schema DFT-D2 (Grimme, 2006). Constant temperature conditions were imposed by a Nosé-Hoover thermostat chain (Nosé, 1984a, b). The time step in the FPMD simulations was 0.5 fs, and the simulations were run for ~22 ps. The simulation cell was periodically replicated in three dimensions and contained 640 atoms for describing the CO_2-bearing silicate melts and about 460–470 atoms for the CO_2-free melts (see Table 1 for the investigated chemical compositions and the discussion below).

The results of FPMD simulations were compared to those generated by classical MD simulations and based upon the empirical force field developed by Guillot and Sator (2011) for the multi component system (CO_2–SiO_2–TiO_2–Al_2O_3–Fe_2O_3–FeO–MgO–CaO–Na_2O–K_2O). This force field (see Table 1 in Guillot and Sator, 2011) allows one to deal with the chemical reaction, $CO_2 + (O^{2-})_{melt} \leftrightarrow CO_3^{2-}$, where a CO_2 molecule reacts with an oxygen atom of the silicate melt to produce a carbonate ion (and vice versa). It was implemented into the DL_POLY 2.0 code for MD simulations (Smith and Forrester, 1996) in which the equations of motions for atoms were solved with the Verlet algorithm with a time step of 1 fs. The simulation box, composed of the same number of atoms as in FPMD calculations (see Table 1), was replicated in 3D and the long range coulombic interactions were evaluated by a Ewald sum. MD calculations were performed in the microcanonical ensemble (NVE) for evaluating dynamical properties, and in the canonical ensemble (NVT), or in the isothermal-isobaric ensemble (NPT), for determining the thermodynamic properties. The cost in computer time being much smaller than for FPMD calculations long simulation runs were performed for a better statistics (up to 10,000 ps or 10 ns).

Silicate melts from the CaO–MgO–Al_2O_3–SiO_2 (CMAS) system were chosen for our simulations because they have been used since long as realistic models for investigating the properties of natural magmas over a large composition range (Scarfe et al., 1983; Rivers and Carmichael, 1987; Rigden et al., 1988; Courtial and Dingwell, 1999; Shaw, 2004; Ai and Lange, 2008). Moreover, as these melts are iron-free their investigation avoids to deal with the iron redox, a difficult task when using FPMD calculations. The role of CO_2 on deep melting in the upper mantle has been enlightened thanks to partial melting experiments in the system CMAS–CO_2 (Wyllie and Huang, 1975; Eggler, 1976; Canil and Scarfe, 1990; Dalton and Presnall, 1998; Gudfinnsson and Presnall, 2005; Keshav and Gudfinnsson, 2010; Keshav et al., 2011). Gudfinnsson and Presnall (2005) have shown that the partial melting at 3–8 GPa of a silicate-carbonate phase assemblage involving garnet lherzolite in equilibrium with CO_2-bearing melts yields a continuous gradation in melt composition with temperature from carbonatitic to kimberlitic and basaltic. For instance at 7.6 GPa and 1973 K the melt in coexistence has a kimberlitic composition (35.8 wt.% SiO_2, 2.8 wt.% Al_2O_3, 36.6 wt.% MgO and 24.8 wt.% CaO in a CO_2-free basis) with 20.6 wt.% CO_2. We have chosen to investigate by FPMD simulation this kimberlitic composition with 20.6 wt.% CO_2, but at a slightly higher temperature (2073 K). Notice that the melt is likely undersaturated in CO_2 at the investigated thermodynamic conditions because there is no evidence of a vapor phase in the experimental data of Gudfinnsson and Presnall (2005). Furthermore, the evaluation by classical MD simulation of the solubility of CO_2 in this kimberlitic melt, in using the

Table 1
Chemical composition (in wt.%) of the simulated melts (with and without CO_2). The number of atoms of each species used in the simulations is also indicated.

	Basalt + CO_2	Basalt	Kimberlite + CO_2	Kimberlite
SiO_2	39.3	49.1	28.5	35.8
Al_2O_3	13.9	17.4	2.2	2.8
MgO	13.8	17.3	29.0	36.6
CaO	13.0	16.2	19.7	24.8
CO_2	20.0		20.6	
N_{Si}	81	81	60	60
N_{Al}	34	34	6	6
N_{Mg}	43	43	90	90
N_{Ca}	29	29	44	44
N_O	397	285	381	263
N_c	56		59	
(N_{Tot})	(640)	(472)	(640)	(463)