Earth and Planetary Science Letters 434 (2016) 129–140

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

The molecular structure of melts along the carbonatite–kimberlite–basalt compositional joint: CO_2 and polymerisation

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ARTICLE INFO

Article history:
Received 22 August 2015
Received in revised form 11 November 2015
Accepted 18 November 2015
Available online 4 December 2015
Editor: B. Marty

Keywords:
CO_2
polymerisation
speciation
transitional melt
kimberlite
glass

ABSTRACT

Transitional melts, intermediate in composition between silicate and carbonate melts, form by low degree partial melting of mantle peridotite and might be the most abundant type of melt in the asthenosphere. Their role in the transport of volatile elements and in metasomatic processes at the planetary scale might be significant yet they have remained largely unstudied. Their molecular structure has remained elusive in part because these melts are difficult to quench to glass. Here we use FTIR, Raman, ^{13}C and ^{29}Si NMR spectroscopy together with First Principle Molecular Dynamic (FPMD) simulations to investigate the molecular structure of transitional melts and in particular to assess the effect of CO_2 on their structure. We found that carbon in these glasses forms free ionic carbonate groups attracting cations away from their usual 'depolymerising' role in breaking up the covalent silicate network. Solution of CO_2 in these melts strongly modifies their structure resulting in a significant polymerisation of the aluminosilicate network with a decrease in NBO/Si of about 0.2 for every 5 mol% CO_2 dissolved.

This polymerisation effect is expected to influence the physical and transport properties of transitional melts. An increase in viscosity is expected with increasing CO_2 content, potentially leading to melt ponding at certain levels in the mantle such as at the lithosphere–asthenosphere boundary. Conversely an ascending and degassing transitional melt such as a kimberlite would become increasingly fluid during ascent hence potentially accelerate. Carbon-rich transitional melts are effectively composed of two sub-networks: a carbonate and a silicate one leading to peculiar physical and transport properties.

1. Introduction

Carbon dioxide (CO_2) is typically the second-most abundant volatile in terrestrial melts. In common silicate melts, found near the Earth's surface and in its crust, its concentration is typically greatly inferior to that of water and its influence on the melt physical properties secondary. In the Earth's upper mantle however, carbon-rich and typically silica-poor melts, generated by low degree partial melting of the mantle are probably widespread (e.g. Wyllie and Huang, 1976; Eggler, 1978; Dalton and Presnall, 1998; Gudfinnsson and Presnall, 2005; Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013; Massuyeau et al., in press). Very low degree partial melting of carbonated peridotite at ~250 km depth produces carbonatite liquid (e.g. Dasgupta and Hirschmann, 2006). With either increasing temperature, decreasing pressure or with

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http://dx.doi.org/10.1016/j.epsl.2015.11.025

Table 1
Starting oxide and natural rock powder mix compositions used for experiments (in wt%). The composition of a natural lamproite from Torre Alfina, Italy (Peccerillo et al., 1988), fused twice at 1400 °C and used to prepare the oxide-mix compositions is reported at the top of the table.

Name	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2	Total
TA	55.7	1.3	13.1	5.8	9.4	5.4	1.0	7.7	0.5	0.0	100
TA6	16.6	0.2	3.9	0.9	6.9	35.5	0.3	2.3	0.1	33.5	100
TA9	23.1	0.3	5.4	1.5	8.3	30.2	0.4	3.2	0.1	27.5	100
TA10	23.8	0.4	5.5	1.6	8.3	29.7	0.4	3.3	0.1	27.0	100
TA11	30.2	0.6	7.0	2.4	8.5	24.8	0.5	4.1	0.2	21.6	100
TA12	37.7	0.8	8.8	3.4	8.8	19.1	0.6	5.2	0.3	15.2	100

the addition of CO_2 or H_2O, the liquid produced by peridotite partial melting will become increasingly SiO_2-rich, forming kimberlite, melilitite and eventually basalt (e.g. Wyllie and Huang, 1976; Eggler, 1978; Wyllie, 1989). These melts – carbonatite, kimberlite and melilitite – transitional between pure carbonatite and silicate liquids ($\sim$10 to $\sim$40 wt% SiO_2), can contain up to several tens of weight percent of CO_2 (Brey and Green, 1976; Moussallam et al., 2014). Understanding the effect of CO_2 on the structure of these melts/glasses is therefore a cornerstone to predict their physical characteristics and transport properties.

The effect of CO_2 on melt polymerisation has remained unclear. Eggler (1978) suggested that the dissolution of CO_2 as carbonate ion (CO_3^{2-}) should result in melt polymerisation via the reaction:

$$CO_2 + 2Q^n(M^{m+}) \leftrightharpoons CO_3^{2-}(M^{m+}) + 2Q^{n+1} \qquad (1)$$

Where Q^n denotes a silica tetrahedron linked by bridging O atoms to n adjacent tetrahedra ($n = 0$ correspond to an isolated SiO_4 tetrahedron, $n = 4$ correspond to a fully connected tetrahedron with four bridging oxygen), M^{m+} denotes a metal cation in network modifying or charge balancing role. In Eq. (1), the increase in polymerisation is denoted by the building of Si–O–Si bonds.

This depiction has gained popularity, being referred to as a largely admitted concept in review articles (e.g. Mysen, 2013, 2012) and books (e.g. Frost and Frost, 2013; Mysen and Richet, 2005). Solid evidence of the effect of CO_2 dissolution on the aluminosilicate network structure however has been lacking. Mysen and Virgo (1980a, 1980b) found that CO_2 depolymerises albite and anortite melts while polymerising diopside and $NaCaAlSi_2O_7$ melts. Konschak (2008) investigated the albite – diopside joint and found no effect of CO_2 on polymerisation from $Ab_{50}Di_{50}$ to $Ab_{75}Di_{25}$ but found that a slight depolymerisation is associated with the addition of CO_2 to $Ab_{90}Di_{10}$. As noted by Ni and Keppler (2013) these evidence are all based on very subtle differences in Raman spectra, which interpretation can be controversial. All these studies have focused on the incorporation mechanisms of CO_2 and its impacts on the molecular structure of silicate melts. Here we look at CO_2 in transitional melts, typically produced by very low-degree partial mantle melting and with silica content being about half of that of basalts.

The principal question we target in this study is: Does carbon dioxide influence the degree of polymerisation of transitional melts? We present results from the first Infrared, Raman and Nuclear Magnetic Resonance (NMR) spectroscopy investigation of transitional glasses and compare them with results from Ab-initio First Principle Molecular Dynamic simulations applied to melt conditions. We explore a compositional range from $\sim$44 to 23 mol% SiO_2 (on a volatile-free basis) with 0 to 26 mol% CO_2. For all compositions investigated, we show that (1) CO_2 is present in the glass and in the melt dominantly as carbonate ion (2) the degree of polymerisation of the glass/melt increases with increasing CO_2 content. We conclude that the physical properties of transitional melts such as viscosity, electrical conductivity and sound velocity are expected to be greatly affected by their CO_2 content with implications regarding melt mobility in the upper mantle.

We note that polymerisation, in this manuscript is strictly defined as the process by which oxygen atoms are shared between silica (or alumina) tetrahedra and is expressed as the ratio of non-bridging oxygens to tetrahedral cations (NBO/T) or as the ratio of non-bridging oxygens per silicon (NBO/Si). We further note that the NBO/T ratio is only a calculated 'statistical average' and various combinations of Q species can give the same NBO/T. The NBO/T concept fails past NBO/T = 4 but Q units at greater values can still join up in isolated 'polymerised units'.

2. Methods

2.1. Experimental methodology

2.1.1. Starting material

Starting materials were produced by mixing powders from a natural lamproite from Torre Alfina, Italy (Peccerillo et al., 1988) with various amounts of synthetic powders of pure oxides (SiO_2, Al_2O_3, MgO, $CaCO_3$, Na_2CO_3, K_2CO_3) and natural dolomite. The strategy was to produce a series of progressively more silica and alumina poor compositions additionally low in iron in order for the final product to be analysable by NMR spectroscopy. The source of CO_2 in experiments was mainly $CaCO_3$. The Torre Alfina rock, was fused twice in air at 1400 °C and quenched to glass in order to ensure homogeneity and remove any volatile present. The composition of all mixtures used as starting materials is reported in Table 1.

2.1.2. HP-HT experiments

Experiments were performed in the pressure range 0.1 to 1500 MPa. High temperature experiments at 0.1 MPa were performed in a high-temperature furnace. The sample was contained in a Pt crucible and heated to 1500 °C for 30 min and then quenched to glass by complete immersion in cold water.

Experiments at high pressure were performed by Moussallam et al. (2014) in the pressure range 50 to 350 MPa at relatively constant temperature (1225 to 1270 °C) with no added water and under oxidised conditions ($\log fO_2 = FMQ + 3$). Experiments were performed in internally heated pressure vessels at the ISTO-CNRS laboratory in Orléans which can reach pressures of up to 400 MPa ($\pm$3 MPa) under controlled temperature up to 1300 °C ($\pm$5 °C) (see supplementary information).

Experiments at 1500 MPa and 1350 °C were performed in a piston-cylinder apparatus with in a 3/4 inch (1.9 cm) assemblies. Experimental charges consisted of natural anhydrous sample powder (30 mg) loaded in sealed gold–palladium (Au80Pd20) capsules (1 cm in length, 2.5 mm inner diameter and 2.9 mm outer diameter). The capsules were introduced in a talc–pyrex–graphite furnace assembly and surrounded by MgO. A B-type thermocouple was located at $\sim$1 mm atop of the capsule and the run temperature should be considered as a minimum value. Uncertainties are of 10% in relative for pressure and of 15 °C for temperature. We used a modified perforated anvil through which cold water was circulated in order to maximise quenching rate ($>$200 °C s^{-1}).

A pure carbonate glass of composition $K_2Mg(CO_3)_2$ was synthesised in internally heated pressure vessel at 803 °C and 1083