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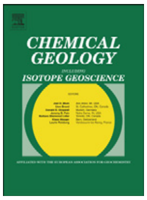

Effect of sulphur on the structure of silicate melts under oxidizing conditions

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ABSTRACT

In magmatic systems, sulphur is an important volatile element after C, H and O. Under oxidizing conditions, S dissolves in aluminosilicate melt as sulphate groups (SO_4^{2-}). The way SO_4^{2-} groups dissolve in the melt is currently poorly understood. We present experimental results of the effect of SO_4^{2-} dissolution on the aluminosilicate melt structure.

Glasses of haplogranitic (HPG) and anorthite–diopside eutectic (An–Di) compositions were synthesized at 300 MPa and 1250 °C and under oxidizing conditions (ΔFMQ + 1.7 to + 3.0). Starting compositions were equilibrated under fluid-saturated conditions with a mixture of S (0 to 5 wt.%) and H_2O (5 wt.%). The S and H_2O contents of the recovered glasses were determined with EPMA and FTIR, respectively. Solid state NMR was used to investigate the glass structure. Micro-Raman analyses were performed to identify S species present in glass and coexisting fluid phases.

The S content determined in glasses changes from 0 to 979 ppm and 0 to 7519 ppm for HPG and An–Di, respectively. S is present in the glasses as $M^{n+}SO_4^{2-}$ groups (M^{n+} is possibly Ca^{2+} in An–Di and Na^+ in HPG).

^{29}Si NMR analyses show important changes in the An–Di glass structure upon S dissolution. High S content in An–Di glasses induces a strong polymerization of the glass which we explain by the presence of non-bridging oxygen (NBO) promoting the dissolution of S as SO_4^{2-} groups. On the contrary, the dissolution of S within HPG melt does not produce visible changes in the silicate melt structure due to the low concentration in NBO in this melt composition.

The observed structural changes suggest that An–Di melt physical properties might be affected by S dissolution. S might produce large changes in melt viscosity, but opposite, as compared to H_2O for slightly depolymerized aluminosilicate melts.

1. Introduction

Sulphur (S) is an important volatile element in magmatic systems. The S output from volcanic emissions to the atmosphere has contributed greatly to the change in the chemistry of the Earth or other planets' atmospheres (e.g., Gaillard and Scaillet, 2009; Gaillard et al., 2011). Although this element is stored in small quantities in the Earth's interior (e.g. McDonough and Sun, 1995; Dreibus and Palme, 1996; Jugo et al., 2005a; Gaillard et al., 2013), it can take a large part of the fluid phase in many volcanic eruptions (e.g., Scaillet et al., 2003). Hence, the eruptive degassing of a large reservoir for S can have a dramatic impact on the climate (Oppenheimer et al., 2011).

The behaviour of S in silicate melts is not fully understood. One major experimental difficulty lies in the different oxidation state that S can take as a function of fO_2 conditions. S can be present as S^{2-} and S^{6+} for the most important species (e.g. Fincham and Richardson, 1954; Carroll and Rutherford, 1988; Paris et al., 2001; O'Neill and Mavrogenes, 2002; Fleet, 2005; Jugo et al., 2005a; Moretti and Ottonello, 2005; Wilke et al., 2008; Klimm and Botcharnikov, 2010; Jugo et al., 2010; Métrich and Mandeville, 2010; Baker and Moretti, 2011). The S content measured in silicate glass is dependent on fO_2 conditions experienced. Early studies conducted at 1 atm with gas mixture furnace (Fincham and Richardson, 1954; Katsura and Nagashima, 1974) showed that a minimum in S solubility in glasses synthesized at log $fO_2 = -5$ or -6 and between 1200 and 1300 °C. This minimum in S content is generally ascribed to a minimum in sulphur species fugacities (Carroll and Webster, 1994) in the gas phase.

Under oxidizing conditions, S is dissolved in silicate glass as sulphate (SO_4^{2-}) groups whereas it dissolves as sulphide (S^{2-}) groups under more reducing conditions (e.g. Carroll and Rutherford, 1988; Métrich and Clocchiatti, 1996; Jugo et al., 2005a,b). The dissolution of S is defined

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by two chemical reactions involving the interaction with a fluid phase (Fincham and Richardson, 1954):

$$SO_2^{fluid} + O^{2-\,melt} \leftrightarrow \frac{3}{2} O_2^{fluid} + S^{2-\,melt} \tag{1}$$

and

$$SO_2^{fluid} + \frac{1}{2} O_2^{fluid} + O^{2-\,melt} \leftrightarrow SO_4^{2-\,melt}. \tag{2}$$

Eq. (1) applies to the dissolution of S in silicate melts under reducing conditions and Eq. (2) applies to the dissolution of S under oxidizing conditions.

The composition of the melt greatly influences the solubility of S with a central role for FeO (Haughton et al., 1974; Carroll and Webster, 1994; O'Neill and Mavrogenes, 2002; Baker and Moretti, 2011; Beermann et al., 2011), SiO_2 (Moretti and Ottonello, 2005), and possibly H_2O in FeO-poor melts (Clemente et al., 2004; Prouteau and Scaillet, 2013).

A silicate glass in the broad sense (a melt containing SiO_2) is 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. In complex silicate melts where other oxides than SiO_2 are present, Al_2O_3 is also considered as a network forming cation (AlO_4 tetrahedra) whereas other cations (for example, Ca, Mg, Na and K) are either network modifiers or charge balancing cations (e.g. Neuville and Mysen, 1996; Lee and Stebbins, 2000).

The notation Q^n is often employed where n represents the number of bridging oxygen (BO) per tetrahedron. The abundance of each Q^n species is controlled by the following general equation (e.g. Maekawa et al., 1991; Mysen and Frantz, 1993; Frantz and Mysen, 1995; Malfait et al., 2007):

$$2Q^n \overset{K}{\longleftrightarrow} Q^{n+1} + Q^{n-1} \quad \text{with } n = 3,\ 2,\ 1 \tag{3}$$

where K is the equilibrium constant of the reaction. Thus, the structure and physical properties (in particular viscosity) of a silicate glass are related through the distribution of these different Q^n units (e.g. Mysen, 1998; Neuville, 2006; Malfait et al., 2007). It is currently assumed that the Q^n distribution (Eq. (3)) in glasses will represent the equilibrium frozen-in at the glass transition temperature, Tg (e.g. Brandiss and Stebbins, 1988; Farnan and Stebbins, 1994; Maekawa and Yokokawa, 1997). The presence of volatile species induces a change in this equilibrium reaction. In particular, H_2O plays a major role in silicate melt by breaking the bonds in between tetrahedra changing a BO in NBO (non-bridging oxygen) therefore inducing a depolymerization of the silicate melt (e.g. Farnan et al., 1987; Kummerlen et al., 1992; Zotov and Keppler, 1998; Zeng et al., 1999; Xue and Kanzaki, 2004, 2008; Xue, 2009).

Although Eq. (2) is generally accepted for the S dissolution mechanisms in silicate melts under oxidizing conditions, the role of Eqs. (1)–(2) on Eq. (3) is currently unknown. In other words, both the effect of S on the physical properties of silicate and the way S atoms influence the melt structure, hence Eq. (3), are unclear. Recent work conducted at high pressure in the $Na_2O–SiO_2$ system by Tsujimura et al. (2004) suggests that S produces a change in the network structure of silicate glass. They concluded that the dissolution of S involves the polymerization of the melt resulting from a change in the melt composition as Na is exsolved into the fluid phase. This possible mechanism needs to be explored further by conducting experiments on more complex silicate glass compositions of geological interest.

We present experimental results aimed at investigating the possible effects of S on the silicate glass structure with implications on silicate melt physical properties. We have chosen two different starting compositions reflecting two different melt structures: one fully polymerized (only BOs, NBO = 0) and one slightly depolymerized (both BOs and NBOs are present). The experiments were conducted at 300 MPa and 1250 °C under oxidizing conditions. The spectroscopic results are discussed in terms of polymerization/depolymerization of the glass upon S dissolution and the impact of this finding is discussed in terms of the qualitative effect of S as compared to the effect of H_2O onto the silicate melt physical properties.

2. Experimental method

The synthetic haplogranitic (HPG) and anorthite–diopside eutectic (An–Di) compositions in the $Na_2O–K_2O–Al_2O_3–SiO_2$ and $CaO–MgO–Al_2O_3–SiO_2$ systems were prepared from a mixture of oxides (SiO_2, Al_2O_3 and MgO) and carbonates (Na_2CO_3, K_2CO_3 and $CaCO_3$). The absence of iron is imposed by the analytical needs for investigating the melt speciation with NMR which cannot be used on Fe-bearing materials. The theoretical compositions are reported in Table 1 along with the electron probe micro-analyses (EPMA) for major elements of all the samples. The starting compositions were prepared by mixing all oxides and carbonates together and by melting the powders twice at 1400 °C for a few hours.

Elemental sulphur (up to 1 wt.% S for HPG, up to 5 wt.% for An–Di) was added to the starting powders prior the experiments by thorough grinding in an agate mortar ensuring homogeneous distribution down to a 100 micron scale (see Table 2). During the experiments, the S combines with available O atoms to oxidize as sulphates (SO_4^{2-}). For instance, S can oxidize by combining with available O present in the fluid phase following Eq. (4):

$$S + O_2^{fluid} \leftrightarrow SO_2^{fluid}. \tag{4}$$

H_2O was added as liquid water together with the solid starting material in the platinum capsules. As shown in Table 1, the initial water content (initial H_2O) ranges from 1.5 to 4.9 wt.% for HPG samples and from 3.9 to 4.9 wt.% for An–Di samples. We synthesized several S-free samples and with different H_2O contents (see Table 1, for example HPG-5-0 and AD-5-0) so the individual effect of H_2O and S on the glass structure can be compared. For these S-free samples, the synthesized glasses are undersaturated with respect to H_2O solubility. At 300 MPa and 1250 °C, we estimated the H_2O solubility at 6.2 and 6.5 wt.% for AD and HPG glass composition according to the H_2O solubility model VolatileCalc (Newman and Lowenstern, 2002) for both HPG and AD compositions.

The sample nomenclature is organized as follows: the letters indicate the composition, the first number gives the initial H_2O loaded and the second number gives the initial S content loaded into the experiments. For example, AD-5-0 corresponds to the sample synthesized with 5 wt.% H_2O and 0 ppm S added to the charge.

Because compositional changes with S dissolution in An–Di melt composition were observed (see Section 4), we also synthesized three volatile-free glasses with different MgO contents. Those glasses are reported in Table 1 and denoted as AD (9.2 wt.% MgO), AD + 2 wt.% MgO (10.6 wt.% MgO) and AD-2 wt.% MgO (7.0 wt.% MgO). The three glasses were synthesized at 1400 °C and 1 bar. In doing so, we tried to mimic the change in the wt.% MgO observed in S-bearing glasses synthesized at high pressure (see Table 1).

Experiments were conducted in an Internally Heated Pressure Vessel (IHPV) at 1250 °C and 300 MPa and for run duration of 3 h. Recent work (e.g., Liu et al., 2007; Beermann et al., 2011) suggests that under those experimental conditions, such run durations allow equilibrium conditions to be reached. We have calculated the diffusion length (Zhang, 2010) using the diffusivity equation of Freda et al. (2005) for hydrous basalt. After 3 h, the diffusion is less than a mm in length suggesting our run duration is long enough to reach equilibrium distribution of S at the capsule scale, though in the richest S-bearing