



The effect of sulphur on the glass transition temperature in anorthite–diopside eutectic glasses



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ABSTRACT

The effect of sulphur dissolved in anorthite–diopside eutectic (AD) glasses on the glass transition temperature (T_g) has been investigated via Differential Scanning Calorimetric measurements (DSC) and Thermogravimetric Analysis (TGA) under moderately reducing to oxidizing conditions.

In a series of AD glasses, we have measured the change in T_g as a function of S content present as SO₄²⁻ (HS⁻ is also identified to a lesser extent) and H₂O content. The AD glasses investigated have S contents ranging from 0 to 7519 ppm and H₂O contents ranging from 0 to 5.3 wt.%. In agreement with previous studies, increasing H₂O content induces a strong exponential decrease in T_g: volatile free AD glass has a T_g at 758 ± 13 °C and AD glass with 5.18 ± 0.48 wt.% H₂O has a T_g at 450 ± 11 °C. The change in T_g as a function of H₂O is well-reproduced with a third-order polynomial function and has been used to constrain T_g at any H₂O content. The effect of S on T_g is almost inexistent or towards a decrease in T_g with increasing S content. For instance, at ~2.4 wt.% H₂O, the addition of S induces a change in T_g from 585 ± 10 °C with 0 ppm S to 523 ± 3 °C with 2365 ± 138 ppm S; a further increase in S up to 7239 ± 90 ppm S does not induce a dramatic change in T_g measured at 529 ± 2 °C.

The limited effect of S on the glass transition temperature contrasts with recent spectroscopic measurements suggesting that S dissolution as SO₄²⁻ groups provokes an increase in the polymerization degree. We propose an alternative view which reconciles the spectroscopic evidence with the T_g measurements. The dissolution of S as SO₄²⁻ does not induce the formation of Si—O—Si molecular bonding through consumption of available non-bridging oxygens (NBO) but instead we suggest that Si—O—S molecular bonds are formed which are not detectable by DSC measurements but mimic the increase in glass polymerization. Therefore, spectroscopic measurements must be used with caution in order to extract melt physical properties.

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1. Introduction

Sulphur (S) is an important volatile element implied in volcanic system (Carroll and Webster, 1994; Paris et al., 2001; Scaillet et al., 2003; Clemente et al., 2004; Scaillet and Pichavant, 2005; Moune et al., 2009), playing a major role in degassing processes and related atmospheric changes (Carroll and Webster, 1994; Edmonds et al., 2003; Webster and Mandeville, 2007; Oppenheimer et al., 2011). The behaviour of S in magmas is complex owing to its variable oxidation state in silicate melts: under oxidizing conditions S is present as sulphate groups (SO₄²⁻ where sulphur is S⁶⁺), whilst under reducing conditions S is present as sulphide groups (where sulphur is S²⁻) (e.g. Fincham

and Richardson, 1954; Carroll and Rutherford, 1988; O'Neill and Mavrogenes, 2002; Jugo et al., 2005a,b; Moretti and Ottonello, 2005; Klimm and Botcharnikov, 2010; Baker and Moretti, 2011; Klimm et al., 2012).

The structure of a silicate glass can be described via a model involving Q-species (e.g. Grimmer et al., 1984; Brandiss and Stebbins, 1988; Merzbacher et al., 1990; Stebbins, 1995; Mysen and Richet, 2005). A Qⁿ unit represents a tetrahedral structural unit with n bridging oxygens (BO, n = 0 to 4). The abundance of each Qⁿ species is dependent on bulk composition (e.g. Maekawa et al., 1991; Mysen and Frantz, 1993; Frantz and Mysen, 1995; Malfait et al., 2007). The distribution of those individual Q-species can be related to the structure of melts, hence to their physical properties such as viscosity (e.g. Mysen et al., 1980; Mysen, 1998; Toplis and Dingwell, 2004; Neuville, 2006; Malfait et al., 2007).

The presence of volatile species influences the distribution of Q-species in silicate glasses. For instance, H₂O induces a strong melt depolymerisation when dissolving as OH groups (e.g. Farnan et al., 1987; Kummerlen et al., 1992; Zotov and Keppler, 1998; Zeng et al.,

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1999; Xue and Kanzaki, 2004, 2008; Mysen and Cody, 2005; Xue, 2009) according to the following general reaction:



In this dissolution mechanism, a water molecule breaks the bridge between two Q^n structural units changing, therefore, Q^n species into Q^{n-1} , less polymerized, species. Because molecular bonding is broken during this process, it impacts the melt physical properties such as viscosity. This common water dissolution mechanism is not the only one occurring in silicate melt and other dissolution mechanisms have been proposed. For instance, in highly depolymerized melt, water has been suggested to have an opposite effect, it induces an increase in the degree of polymerization (Romano et al., 2001; Xue and Kanzaki, 2004; Moretti and Ottonello, 2005; Giordano et al., 2009; Malfait and Xue, 2014).

Viscosimetric measurements on hydrous silicate melt (e.g. Scaillet et al., 1996; Richet et al., 1996; Whittington et al., 2000; Giordano and Dingwell, 2003; Robert et al., 2013) as well as glass transition temperature (T_g used as a proxy for viscosity) determination in hydrous silicate glasses (e.g. Deubener et al., 2003; Giordano et al., 2005; Morizet et al., 2007) confirm this fact. It is also consistent with the possible structural definition of glass transition temperature. The glass transition temperature is a temperature corresponding to a fixed relaxation time of the silicate melt structure which is thought to correspond to the exchange rate of the oxygens between tetrahedral units (Moynihan et al., 1976; Liu et al., 1988; Moynihan, 1995). As a result, there is a direct correlation between the change in the degree of polymerization induced by H_2O dissolution and the diminution in T_g value observed with increasing H_2O content (Dingwell et al., 1996, 1998; Giordano et al., 2008a,b).

In contrast to water, the effect of sulphur on viscosity or T_g is currently unknown. Recent spectroscopic investigations by Morizet et al. (2013) lead to the proposition that the presence of SO_4^{2-} induces an apparent polymerization of the melt which could therefore translate into an increase in melt viscosity or an increase in T_g . Whether this increase in polymerization corresponds to an increase in glass transition

temperature involving the formation of Si—O—Si molecular bonding is yet not clear. Morizet et al. (2013) suggested that the dissolution of S as SO_4^{2-} is accompanied by the formation of Si—O—S (their Eq. (9)) and hence might not be viewed as a true polymerization process.

In the present study, we investigated the change in T_g in anorthite–diopside eutectic glasses (AD) with known S and H_2O contents, similar to those investigated in Morizet et al. (2013). In the studied AD glasses S is dissolved mainly as SO_4^{2-} but also as HS^- , though in minor amounts. The choice for this composition is motivated by the fact that the obtained calorimetric results can be compared to both the spectroscopy of Morizet et al. (2013) and to the viscosity and T_g data obtained by Giordano et al. (2008a) on the same anorthite–diopside eutectic composition with various H_2O content. The results are discussed in terms of the effect of S and H_2O on T_g and the way sulphur dissolves into the silicate melt structure is also discussed.

2. Experimental and analytical methods

2.1. Experimental method

In the present study, we used the quenched glass samples investigated in Morizet et al. (2013) and additional glass samples were also synthesized. The dataset produced by Morizet et al. (2013) consists in glasses of anorthite–diopside eutectic composition (50.2 SiO_2 , 15.7 Al_2O_3 , 23.4 CaO and 10.6 MgO in wt.%). From a theoretical standpoint, the investigated glass composition is slightly depolymerised with an NBO/T close to 0.9 (i.e. NBO/T can have values from 0 to 4) using the method of Mysen (1988, 1990). The detailed glass compositions are provided in the Supplementary material and in Table 1. The starting composition preparation method is fully described in Morizet et al. (2013) and in most of the case it consists in mixing a starting volatile-free AD glass powder (ADVF in Table 1) with a known amount of elemental S (0 to ~5 wt.%, see Table 1). Prior to loading the obtained mixture into the Pt capsule a known amount of H_2O (up to 8.2 wt.% H_2O) is loaded at the bottom of the capsule using a microsyringe. For three

Table 1
Sample dataset, experimental conditions, volatile content and speciation.

Samples	Experimental conditions					ppm S ^a	S speciation ^c		wt.% H ₂ O ^b
	Pressure (MPa)	Temperature (°C)	Log f_{O_2} (ΔFMQ) ^d	Loaded S (wt.%)	Loaded H ₂ O (wt.%)		XSO_4^{2-}	XHS^-	
ADVF	0.001	1400	+5	0	0	0	0	0	0
AD1H-6 ^e	500	1450	> +1	0	1.2	0	0	0	1.03 (0.03)
AD2H-6 ^e	500	1450	> +1	0	8.2	0	0	0	4.55 (0.13)
AD-5-0	300	1250	+2.8	0	4.9	0	0	0	5.18 (0.48)
AD-3-0	300	1250	+2.8	0	2.6	0	0	0	3.01 (0.15)
AD-4-0	300	1250	+2.8	0	3.9	0	0	0	3.67 (0.17)
AD-4.7-0.5	300	1250	+2.8	0.5	4.7	2434 (567)	1	0	3.39 (0.10)
AD-5-1	300	1250	+1.9	1.0	4.8	3430 (136)	1	0	2.81 (0.27)
AD-4.5-1	300	1250	+2.1	1.0	4.6	4150 (974)	1	0	3.14 (0.24)
AD-5-3	300	1250	+1.8	3.0	4.7	6621 (355)	1	0	2.70 (0.09)
AD-5-5	300	1250	+2.3	5.0	4.9	7519 (3397)	0.97	0.03	3.68 (0.13)
AD4	300	1250	+2.0	0.25	4.6	2718 (598)	1	0	3.08 (0.12)
AD10	300	1250	+2.3	4.9	7.2	6973 (73)	1	0	3.70 (0.43)
AD12	300	1250	+1.2	5.1	2.2	671 (441)	1	0	1.77 (0.04)
AD20	300	1250	+2.1	1.1	5.2	1240 (25)	0.99	0.01	4.79 (0.19)
AD21	300	1250	+1.9	0.5	4.4	902 (26)	0.99	0.01	4.17 (0.11)
AD22	300	1250	+1.9	0.2	5.0	1025 (20)	0.99	0.01	4.34 (0.04)
AD23	300	1250	+1.2	1.0	5.5	1263 (91)	0.98	0.02	5.33 (0.14)
AD24	300	1250	+0.8	0.6	4.8	1075 (59)	0.98	0.02	4.17 (0.09)
AD5M-2 ^e	500	1450	> +1	0.7	2.6	7239 (90)	1	0	2.26 (0.05)
AD2M-5 ^e	500	1450	> +1	0.25	3.5	2365 (138)	1	0	2.50 (0.04)
AD10M-5 ^e	500	1450	> +1	1.6	3.2	5481 (324)	1	0	2.01 (0.04)

^a The S content is reported in Morizet et al. (2013) and has been determined via EPMA measurements. More than 20 spots were taken on each glass sample to obtain the standard deviation (numbers between brackets).

^b The wt.% H_2O was determined with micro-FTIR measurements on doubly polished plate. Three to five spectra were taken for standard error determination.

^c The S speciation was determined with Raman spectroscopy (see Supplementary material for typical Raman spectra). The HS^- contribution (peak located at 2575 cm^{-1}) is small and does not exceed 3% of the total S.

^d The log f_{O_2} has been calculated using the total H_2O content and is reported relative Fayalite–Magnetite–Quartz (FMQ) buffer.

^e Those samples were synthesized using piston–cylinder apparatus at 500 MPa. In the S-bearing experiments, the S was loaded prior the experiment in the Pt capsule as H_2SO_4 aqueous solution of 2, 5 and 10 $\text{mol}\cdot\text{L}^{-1}$ in concentration.

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