



The solubility of sulfur in hydrous basaltic melts

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ABSTRACT

Experiments were performed to determine the sulfur solubilities of hydrous basalts from Vesuvius, Etna and Stromboli (Italy). The melts were equilibrated at 1050 and 1200 °C with H₂O and sulfur (added as pyrrhotite), and at pressures ranging from 250 to 2000 bar. Most experiments were performed under oxidising conditions (NNO + 2), and a few under reducing conditions (NNO – 1), with melt water contents of 0.5–3.5 wt.%. Sulfur contents in glasses were determined by electron microprobe and range from 860 up to 6700 ppm. No compositional effect is found between the three alkali basaltic melts. The fugacities of S-bearing species were derived using an MRK equation of state applied to an O–H–S fluid, knowing H₂ and H₂O fugacities, and range from 50 up to 3000 bar. A thermodynamic species-based model is derived from our results along with available data in the literature, assuming that sulfur dissolution results from the additive contributions of both H₂S and SO₂ dissolution reactions. Compared to similar models developed for silicic melts, basalt compositions requires the incorporation of an Fe term, which accounts for the strong association between Fe and S in silicate melts, and considers the elevated Fe content of mafic melts. The model shows that, at any fixed f_{S_2} , the sulfur solubility in hydrous basalt displays a pronounced minimum around NNO, the position of which depends on temperature. The minimum in sulfur solubility coincides with the redox range where the abundance of S₂ in the fluid reaches its maximum compared to either H₂S or SO₂ species. Such a minimum in solubility is in agreement with experimental constraints at 1 bar under carefully controlled f_{O_2} and f_{S_2} . Calculated proportions of dissolved species in the melt depend on the prevailing f_{S_2} and f_{O_2} , being in general agreement with available spectroscopic models. Calculations of gas saturation pressures, which classically consider only H₂O and CO₂ dissolved volatiles, are strongly affected by S-bearing species. At f_{O_2} close to, or higher than, NNO + 1, omission of sulfur species may result in underestimates of gas saturation pressures of 1 kbar or more. The same happens at f_{O_2} below NNO – 1.

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1. Introduction

The understanding of the behaviour of volatile components in magmas is crucial for the modelling of magmatic and volcanic processes (e.g., Carroll and Webster, 1994; Moretti and Ottonello, 2005; Burgisser and Scaillet, 2007; Gaillard et al., 2011, 2013; Oppenheimer et al., 2011a; Oppenheimer et al., 2011b; Prouteau and Scaillet, 2013). For instance, constraining the sulfur solubility in melts is essential because of their important role on ore deposit processes (e.g., Jugo, 2009; Botcharnikov et al., 2010; Jégo et al., 2010; Scaillet, 2010; Simon and Ripley, 2011; Jégo and Pichavant, 2012). There has been also considerable interest in the potential influence of volcanic sulfur emissions on atmosphere chemistry of terrestrial planets (e.g., Robock, 2000; Gaillard et al., 2011; Halevy et al., 2007; Gaillard and Scaillet, 2009). On a shorter time scale, volcanic sulfur emissions have been shown to be a useful tool for the prediction of volcanic eruptions (Aiuppa et al., 2007; Oppenheimer et al., 2011a; Oppenheimer et al., 2011b). For instance, comparison between calculated fluid compositions and volcanic

gases can provide robust constraints on both the depth and mode of degassing, as well as on the amount of free fluid in magma reservoirs (Moretti et al., 2003; Scaillet and Pichavant, 2003, 2005; Burgisser et al., 2008, 2012; Wallace and Edmonds, 2011). As a matter of fact, various studies have shown that high volatile contents are common in basaltic magmas associated with subduction zones (Sisson and Grove, 1993a; Roggensack et al., 1997; Wallace, 2001; Pichavant et al., 2002; Marianelli et al., 2005), sulfur species being the most abundant volatiles in magmas after H₂O and CO₂.

A complete description of the degassing behaviour of ascending magmas requires to understand the interactions between the different volatile species, as well as their different solubilities. However, modelling sulfur has proven to be a difficult task (e.g., Moretti and Ottonello, 2005; Baker and Moretti, 2011), essentially because it occurs under multiple valence states (Connolly and Haughton, 1972): from S^{2–} under reduced conditions, to S⁶⁺ under oxidised conditions (Fincham and Richardson, 1954; Carroll and Rutherford, 1985, 1987, 1988; Carroll and Webster, 1994). For example, Métrich and Clacchiatti (1996) showed that, at NNO + 2, the ratio of S⁶⁺/S_{tot} dissolved in Etnean basalts is equal to 0.96. Mysen and Richet (2005a) and Mysen and Richet (2005b) have suggested that the S dissolution mechanism

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is linked to the polymerization state of the melt, the ratio NBO/T (non bridging oxygen/tetrahedral cation). Recent spectroscopic studies have indeed illuminated the complex role of sulfur on silicate melts structure (e.g., Klimm and Botcharnikov, 2010; Klimm et al., 2012a; Klimm et al., 2012b; Morizet et al., 2013).

Following the pioneering work of Fincham and Richardson (1954), several experimental studies have been carried out to determine the solubility and speciation of sulfur in anhydrous basaltic melts under both reduced (e.g., O'Neill and Mavrogenes, 2002) and oxidised (Jugo et al., 2005, 2010) conditions. Various experimental studies have also determined the solubility of sulfur in hydrous silicic melts (Luhr, 1990; Carroll and Webster, 1994; Botcharnikov et al., 2004; Clemente et al., 2004; Webster and Botcharnikov, 2011). By contrast the sulfur solubility in hydrous basaltic melts, which are conditions relevant to arc magmatism, remains comparatively less explored (Luhr, 1990; Liu et al., 2007; Moune et al., 2009; Beermann et al., 2011; Prouteau and Scaillet, 2013). With the aim of filling such a gap, sulfur solubility experiments in hydrous basaltic melts, mostly under oxidised conditions, are presented in this study. Then, along with available data in the literature, we propose a thermodynamic model of sulfur solubility in hydrous basaltic melts, using a species-based approach (e.g., Stolper, 1982) which has already proven to be successful for the description of sulfur behaviour in hydrous rhyolitic melts (Clemente et al., 2004). We discuss how such a model can be used to calculate sulfur species and to retrieve the fugacities of H₂S and SO₂ species, with the aim of improving estimates of the conditions of magma storage, based on the volatile contents of trapped melt inclusions.

2. Experimental techniques

2.1. Apparatus

Experiments were performed in an internally heated pressure vessel (IHPV), working vertically using either Ar (to generate oxidised conditions) or Ar–H₂ mixtures (to generate reduced conditions) as the pressurising medium (Scaillet et al., 1992). Platinum or gold capsules (up to 4), were placed together in a sample holder, made of thin Al₂O₃ tube, which was hung from a Pt-wire on top of a double-wound molybdenum furnace. Temperature was controlled by two type-S thermocouples, placed along the length of the capsules. The temperature gradient along the capsules was always less than 10 °C. Experiments were ended by using a drop quench technique (Di Carlo et al., 2006): a high electrical current was passed through the Pt-wire which was melted. Thereafter, capsules felt in the cold part of the vessel (<100 °C). The cooling rate is estimated to be about 100 °C/s.

2.2. Starting materials and capsule preparation

Experiments were conducted on three alkali basalts (Table 1): VES-9 (tephrite) comes from a medieval strombolian eruption of Vesuvius, ET02PA27 (K-basalt, here named ETN-1) comes from a lava flow of the 22/11/2002 eruption on the southern flank of Mount Etna (supplied by N. Métrich) and PST-9 (basalt) is a golden pumice coming from a 10 cm thick layer erupted at Stromboli in the period AD 800–1600 (Di Carlo et al., 2006). The three starting materials have been already used to determine their water and carbon solubilities (Lesne et al. 2011a; Lesne et al. 2011b). The natural samples were powdered and melted in a Pt crucible at atmospheric pressure, at 1400 °C during 3 h in order to get homogeneous and nominally anhydrous glasses. The resulting glasses were analysed by electron microprobe. Their compositions are listed in Table 1. Because sulfur diffusion is lower than that of CO₂ and H₂O (Freda et al., 2005), starting materials were dry powdered glasses. This optimises the distribution of sulfur in the charge and minimises the duration of experiments, hence the problem of iron loss toward the capsule walls.

Table 1
Starting glasses.

	PST-9 ^a	VES-9 ^b	ETN-1 ^c
SiO ₂	49.40	48.26	47.41
TiO ₂	0.80	0.96	1.65
Al ₂ O ₃	15.80	14.59	17.12
Fe ₂ O ₃	8.50	8.40	11.26
MnO	0.20	0.14	0.17
MgO	8.00	6.76	5.70
CaO	12.70	12.83	10.81
Na ₂ O	2.30	1.81	3.41
K ₂ O	1.90	5.58	1.97
P ₂ O ₅	0.40	0.65	0.51
Total	100.00	100.00	100.00

All analyses normalised to 100% anhydrous.

^a Basalt from Stromboli, Italy.

^b Basalt from Vesuvius, Italy.

^c Basalt from Etna, Italy.

For each composition, batches of powdered basalt mixed with sulfur were prepared by weighing about 100 mg of glass powder with appropriate amounts of pyrrhotite (up to about 3 mg). The resulting mixture contains about 0.1–1 wt.% of S (Table 2) and was thoroughly mixed in an agate mortar under acetone for several minutes, and then dried out. It has been shown that the starting form of sulfur added (elemental, pyrrhotite or anhydrite) has no detectable effect on the stability of sulfur-bearing phases (Clemente et al., 2004), which is why we have used pyrrhotite in our experiments. Using pyrrhotite has the added advantage of compensating for Fe loss out of the capsule.

Platinum capsules were used for experiments at 1200 °C, and gold capsules at 1050 °C (all with 2 cm height, 2.5 mm inner and 3.0 mm outer diameters). One advantage of using Pt capsules is that the formation of PdAuFe sulphide phases (Pichavant et al. 2006) is minimised compared to AuPd alloys. It is not totally suppressed, however. The disadvantage of using platinum capsule is that it reacts with iron to form a Fe–Pt alloy (e.g., Grove, 1982; Sisson and Grove, 1993b). However, as pointed out above, the iron loss is minimised by the fact that sulfur was added as pyrrhotite, as long as the run duration remains short, that is in the order of a few hours in the temperature range explored in the present study (see below, Merrill and Wyllie, 1973). Deionised and distilled water was first added, so as to reach conditions slightly below H₂O saturation for a system without sulfur at the applied experimental conditions. Then, between 30 and 100 mg of the powdered basalt glass + pyrrhotite mixture was loaded into capsules which were welded shut with a graphite arc welder. Weighing during capsule preparation and after the experiment allowed to check for any volatile loss. Capsules showing less than 0.0003 mg difference were considered successful.

2.3. Experimental conditions

Experiments were performed in the pressure range of 250 to 2000 bar, and mostly at 1200 °C and under oxidised conditions (NNO + 2, see below), since holding S in noble metal containers is less problematic than at low *f*O₂. Pure Ar was added in the autoclave to impose oxidised conditions (imposed by the intrinsic *f*H₂ of the vessel, which is about 0.3 bar, i.e. Pichavant et al., 2009, 2014). In addition, a few reducing experiments (NNO – 1, see below) were also conducted at 1050 °C and 1200 °C. The reducing conditions were obtained by imposing a known H₂ pressure in the vessel so as to achieve more reducing conditions (around at NNO – 1, Table 2, see Scaillet et al., 1992). The short run durations prevented the use of either H₂-membranes or solid sensors to monitor the *f*H₂. Experiments done over the years with the same vessel show that the *f*H₂ reached at the target P–T is 2–4 times that initially loaded (e.g., Di Carlo et al., 2010). Hence the

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