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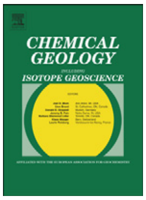

Experimental investigation of the S and S-isotope distribution between H_2O–S ± Cl fluids and basaltic melts during decompression

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ABSTRACT

Decompression experiments (from 400 to 70 MPa) were conducted to investigate sulfur (S) distribution and S-isotope fractionation between basaltic melts and coexisting fluids. Volatile-bearing [~3 to ~7 wt.% water (H_2O), ~300 to ~1200 ppm S, 0 to ~3600 ppm chlorine (Cl)] basaltic glasses were used as starting materials. The MgO content in the melt was either ~1 wt.% (Mg-poor basalt) or ~10 wt.% (alkali basalt) to investigate the possible role of compositional changes in basaltic systems on fluid-melt distribution of S and S-isotopes. The experiments were performed in internally heated pressure vessels (IHPV) at 1050 °C to 1250 °C, variable oxygen fugacities (fO_2; ranging from $\log(fO_2/\text{bar})$ ~ QFM to ~QFM + 4; QFM = quartz–fayalite–magnetite buffer) and at a constant decompression rate (r) of 0.1 MPa/s. The annealing time (t_A) at final pressure (p) and temperature (T) after decompression was varied from 0 to 5.5 h to study the fluid–melt equilibration process.

Sulfur and H_2O contents in the melt decreased significantly during decompression, while the Cl contents remained almost constant. No changes in H_2O and Cl content were observed with t_A, while S concentrations decreased slightly with $t_A < 2$ h; i.e., near-equilibrium fluid–melt conditions were reached within ~2 h after decompression, even in experiments performed at the lowest T of 1050 °C. Thus, fluid–melt partitioning coefficients of S ($D_S^{fl/m}$) were determined from experiments with $t_A \geq 2$ h.

The MgO (~1 to ~10 wt.%), H_2O (~3 to ~7 wt.%) and Cl contents (<0.4 wt.%) in the melt have no significant effect on $D_S^{fl/m}$. Consistent with previous studies we found that $D_S^{fl/m}$ decreased strongly with increasing fO_2; e.g., at ~1200 °C $D_S^{fl/m} \approx 180$ at QFM + 1 and $D_S^{fl/m} \approx 40$ at QFM + 4. A positive correlation was observed between $D_S^{fl/m}$ and T in the range of 1150 to 1250 °C at both oxidizing (QFM + 4; $D_S^{fl/m} = 52 \pm 27$ to 76 ± 30) and intermediate (QFM + 1.5; $D_S^{fl/m} = 94 \pm 20$ to 209 ± 80) redox conditions. Data compiled at 1050 °C and relatively reducing conditions (~QFM; $D_S^{fl/m} = 58 \pm 18$) indicate that the trends may be extrapolated to lower T, at least for intermediate to reducing conditions (~QFM + 1.5 to ~QFM).

The S-isotope composition in glasses of selected samples was measured by secondary ion mass spectrometry (SIMS). Gas–melt isotopic fractionation factors (α_{fl-m}) were calculated via mass balance. At 1200 °C an average α_{fl-m} of 0.9981 ± 0.0015 was determined for oxidizing conditions (~QFM + 4), while an average α_{fl-m} of 1.0025 ± 0.0010 was found for fairly reducing conditions (~QFM + 1). Furthermore, at lower T (1050 °C) an average α_{fl-m} of 1.0037 ± 0.0009 was determined for reducing conditions (~QFM). The data showed that equilibrium fractionation effects during closed-system degassing of basaltic melts at T relevant for magmatic systems (1050 to 1250 °C) can induce a S-isotope fluid–melt fractionation of about +4‰ in relatively reduced systems and of about −2‰ in relatively oxidized systems.

The reported experimental results are valuable for the interpretation of S and S-isotope signature in magmatic systems (e.g., in volcanic gasses or melt inclusions) and will help to elucidate, for instance, volatile transport processes across subduction zones and Earth's S cycle.

1. Introduction

Sulfur is the third most abundant volatile in natural silicate melts (besides H_2O and CO_2) and the highest concentrations are found in basaltic magmas which often contain ≫1000 ppm S (e.g., Perfit et al.,

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1983; le Roux et al., 2006; Moune et al., 2007; Wallace and Edmonds, 2011). During crystallization, S is mainly incorporated in accessory phases (mostly sulfides, e.g., Parat et al., 2011) but a significant fraction of S is also released to the fluid phase in late-stage crystallization processes or upon decompression due to high fluid–melt partitioning coefficients ranging from 1 to 2800 (Keppler, 1999; Newman and Lowenstern, 2002; Lesne et al., 2011a; Webster and Botcharnikov, 2011; Witham et al., 2012). Such magmatic S-bearing fluids have a crucial role in the formation of high T ore deposits (e.g., porphyry-type) and can be responsible for the release of high amounts of S to the atmosphere during volcanic eruptions, leading, e.g., to dramatic climate impact (see review of Oppenheimer et al., 2011).

The distribution of S between fluid and basaltic melt at (near-) equilibrium conditions has been investigated in several studies within the last decades; however, the dataset is still patchy. Most of the existing data on basaltic melt compositions (and other compositions) have been summarized in the review of Webster and Botcharnikov (2011). The available S fluid–melt partitioning data for basaltic systems were obtained for $T \approx 1050$ to 1150 °C and $\log(fO_2/\text{bar}) \approx$ QFM to QFM + 3.2 [hereafter differences of $\log(fO_2/\text{bar})$ to the quartz–fayalite–magnetite (QFM) buffer are given to specify fO_2] and a p range of 25 to 800 MPa (Teague et al., 2008; Moune et al., 2009; Beermann et al., 2011; Lesne et al., 2011a; Webster and Botcharnikov, 2011). Additional experiments of Gorbachev (1990) conducted at 500 MPa and 1100 °C are difficult to interpret because fO_2 is not reported.

None of the available studies systematically investigated the influence of T on the fluid–melt partitioning coefficient of S ($D_S^{fl/m}$) in basaltic systems. It is noteworthy that Lesne et al. (2011a) observed a significant compositional effect on $D_S^{fl/m}$ in basaltic systems implying that the data obtained in different studies at T of 1050 to 1150 °C for different compositions cannot be compiled to extract a general T effect on $D_S^{fl/m}$.

The influence of fO_2 on $D_S^{fl/m}$ in basaltic systems was investigated by Beermann (2010). The author observed, for instance, that $D_S^{fl/m}$ increases from 27 ± 7 at QFM + 3.2 to 200 ± 51 at QFM + 0.7 in Cl-bearing (~0.05 to ~0.55 wt.% Cl) trachybasaltic systems at 200 MPa and 1050 °C. The only systematic work investigating the influence of p on $D_S^{fl/m}$ in basaltic systems was published by Lesne et al. (2011a). The experiments were conducted under intermediate to oxidizing conditions (QFM + 1.7 to QFM + 3.1), at 1150 °C and 25 to 400 MPa and reveal that $D_S^{fl/m}$ increases strongly from ~10 to ~40 at 100 MPa up to ~600 to ~3000 at 25 MPa in basaltic systems.

Recent studies show that the role of other volatiles present in the melt phase may significantly influence $D_S^{fl/m}$. A strong dependence of $D_S^{fl/m}$ on the H_2O content in basaltic systems at 1050 °C, 300 MPa and ~QFM is indicated by the experimental results of Moune et al. (2009), but was not yet confirmed by systematic experimental investigations (see also review of Webster and Botcharnikov, 2011). Beermann (2010) observed a remarkable increase of $D_S^{fl/m}$ along with increasing Cl content in the basaltic systems, e.g., under oxidizing conditions (~QFM + 2) $D_S^{fl/m}$ increases from ~1 at ~0.05 wt.% bulk Cl in the system to ~96 at ~3.5 wt.% Cl. A similar positive correlation between Cl content and $D_S^{fl/m}$ was observed for phonolitic (Webster et al., 2009) and andesitic melts (Fiege et al., 2014a), while data of Botcharnikov et al. (2004) for rhyodacitc systems indicate a slight negative correlation between Cl content and $D_S^{fl/m}$. The influence of Cl on $D_S^{fl/m}$ is not fully understood; however, the studies suggested that this effect can possibly be attributed to changes in fluid and melt properties, to non-ideal mixing in the fluid phase and/or to interactions between the volatiles (e.g., H_2O, Cl, S) as well as between volatiles and cations within the melt and the coexisting fluid phase.

More experimental data and thermodynamic models on equilibrium distribution of S between fluid and (basaltic) melt are much-needed to interpret the composition of gases released from active volcanoes and to relate magmatic processes at depths with the response at the surface (via changes of the gas composition). However, two additional types of information are necessary to fully interpret the S (-isotope) signatures in volcanic gases: *i)* kinetic studies are required to check for the conditions (e.g., decompression rate = r) at which equilibrium fluid–melt S distribution is established during degassing of ascending magmas and *ii)* the S-isotope fractionation between fluid and silicate melt must be known to interpret the isotopic composition of volcanic gases.

Although disequilibrium distribution of S between fluids and melts may be of minor importance in basaltic systems due to the relatively low melt viscosity and fast diffusion of volatiles within basaltic melts (e.g., Zhang and Stolper, 1991; Watson, 1994; Freda et al., 2005; Persikov et al., 2010; Zhang and Ni, 2010; Zhang et al., 2010; Behrens and Stelling, 2011), kinetic effects may be expected for erupting basaltic magmas with very fast ascent rates (≥11 km/h; i.e., ≥0.1 MPa/s). However, all available studies on the fluid–melt distribution of S in basaltic systems are based on equilibrium experiments and kinetic experiments are needed to allow an estimation of times required for fluid–melt equilibration after decompression and to evaluate whether kinetic degassing effects of S occur in basaltic systems.

Degassing of S may be accompanied by S-isotope fractionation between fluid and silicate melt. The isotopic fractionation depends mainly on T (e.g., Sakai et al., 1982; Taylor, 1986) and on the speciation of S in both phases (e.g., Ohmoto and Rye, 1979; Mandeville, 2010), but the isotopic fractionation between S species in fluid and silicate melt at magmatic conditions is still not well constrained. The existing models (e.g., Marini et al., 1998; De Hoog et al., 2001) follow the approach of Sakai et al. (1982) and are based on one experimental study of the S-isotope fractionation between fluid and melt conducted by Miyoshi et al. (1984) as well as on theoretical data of Richet et al. (1977). However, Miyoshi et al. (1984) used molten salts as analogous to silicate melt phase and the applicability of the data to silicate melt systems can be questioned because the tendency to retain ^{34}S in salt melts (ionic bonding dominates) upon decompression is probably not equivalent to that in silicate melts (covalent bonding dominates). Fiege et al. (2014b) recently determined for andesitic systems at 1030 °C a fluid–melt S-isotope fractionation of +4 to +10‰ (i.e., melt becomes enriched in ^{34}S upon degassing) at relatively reducing conditions and of about −2‰ (i.e., melt becomes depleted in ^{34}S upon degassing) at relatively oxidizing conditions. The large scatter in fluid–melt S-isotope fractionation at reducing conditions (~QFM + 1) is attributed to the lack of experimental data at low fO_2, at which S in the fluid–melt system is fully reduced (≤QFM); i.e., the existing data were extrapolated from ~QFM + 1 to ~QFM. Thus, more experimental data are urgently needed to constrain the fractionation factor at reducing conditions (~QFM), to determine the T dependence of the fractionation and to test the applicability of the fractionation factors determined for an andesitic melt by Fiege et al. (2014b) to other silicate melt compositions. Notably, Fiege et al. (2014b) proposed a new model approach, which uses all four fluid–melt fractionation pairs *(SO_{2gas}–$SO_4{}^{2-}{}_{melt}$; H_2S_{gas}–$SO_4{}^{2-}{}_{melt}$; SO_{2gas}–$S^{2-}{}_{melt}$; H_2S_{gas}–$S^{2-}{}_{melt}$) and yields similar trends when compared to the approach of Sakai et al. (1982), which is based on three fractionation pairs (SO_{2gas}–H_2S_{gas}; $SO_4{}^{2-}{}_{melt}$–$S^{2-}{}_{melt}$; H_2S_{gas}–$S^{2-}{}_{melt}$). Here, we will focus on the approach of Fiege et al. (2014b), because it clearly delineates the fluid–melt fractionation pairs needed to model S-isotope fractionation in magmatic systems.*

In this study, degassing of basaltic melts containing up to 1200 ppm S was investigated via decompression experiments to study the influence of fO_2 and T on $D_S^{fl/m}$ and α_{fl-m} in basaltic systems. The experiments were performed at different redox conditions with $\log(fO_2/\text{bar})$ ranging from ~QFM to ~QFM + 4 and at T of 1050 to 1250 °C. The initial H_2O and Cl content in the melt varied in the range of ~3 to ~7 wt.% and 0 to ~3600 ppm, respectively, which allows us to determine the influence of bulk H_2O and Cl content on $D_S^{fl/m}$. To understand the possible influence of melt polymerization and, thus, of S-diffusivity and kinetics of S-degassing, the MgO content in the anhydrous starting glasses was either ~1 or ~10 wt.%; i.e., $X_{Mg} = MgO/(MgO + FeO_{tot})$ molar ratio in the melt ranges from ~0.2 to ~0.7 (FeO_{tot} = total iron concentration