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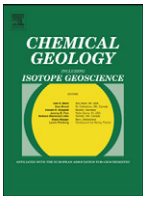

Partitioning of sulfur and chlorine between aqueous fluid and basaltic melt at 1050°C, 100 and 200 MPa

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ABSTRACT

The partitioning of S and Cl between aqueous fluid and basaltic melt of Mt. Etna has been experimentally investigated at 1050 °C, $\log fO_2$ ~ FMQ + 0.5, FMQ + 2.3, and FMQ+2.8 at 200 MPa as well as at ~FMQ+2.8 at 100 MPa by using $HCl_{(aq)}$ and native S as chlorine and sulfur source. At given P–T–fO_2 conditions, the partitioning of S and Cl between fluid and melt typically demonstrates non-linear dependence on S and Cl contents in the system, and only at low concentrations of S (below ~2 wt.%) and Cl (below ~1 wt.%) in the fluid is the Henrian behavior observed. The partition coefficients of S (D_S, wt.% S_{fluid} / wt.% S_{melt}) ranged between 3 ± 1 and 96 ± 24 at 200 MPa and between 6 ± 2 and 73 ± 18 at 100 MPa at $\log fO_2 \geq$ FMQ+2.3, and between 164 ± 13 and 236 ± 26 at 200 MPa and FMQ+0.5. The partition coefficients of Cl (D_{Cl}, wt.% Cl_{fluid}/wt.% Cl_{melt}) ranged between ~2 ± 1 and 17 ± 1 at 200 MPa and between ~3 ± 2 and 19 ± 1 at 100 MPa at $\log fO_2 \geq$ FMQ+2.3, and between ~2 ± 1 and 9 ± 1 at 200 MPa and at FMQ+0.5.

At oxidizing conditions (FMQ+2.3 and FMQ+2.8) sulfur and chlorine demonstrate mutual interaction by favoring partitioning of both volatiles into the fluid relative to melt together with effective extraction of Ca and K from the melt into the fluid. Such interaction indicates that both, S and Cl may change their speciation by effective extraction of Ca and K from the melt and by mutual reactions between species rather than by competitive bonding with extracted cations. These observations are also an indication that bulk activity coefficients of S and Cl in the fluid are decreased, which in turn decrease non-ideality of mixing between interacting fluid species compared to S-deficient aqueous chloridic fluids.

The non-linear dependence of Cl fluid–melt partitioning on the concentration of Cl in the fluid can be described by a simple square root function.

The data also indicate that Cl may affect the solubility of H_2O in basaltic melt which increases by 0.5 mol of H_2O per 1 mol of Cl. It can be presumably attributed to the incorporation mechanism of HCl into the melt structure, i.e. Cl^- may complex with network-modifying cation(s) and H^+ may bond with half of non-bridging oxygen. The square root behavior of Cl partitioning between many aluminosilicate melts and aqueous fluid may thus be explained by the exchange reaction of one Cl ion from the fluid with two oxygen ions in the melt. Correlations between the mechanisms and the partitioning behavior of S between fluid and melt could not be carved out.

At 100 MPa and oxidizing conditions (~FMQ+2.3 and FMQ+2.8), the S/Cl ratio in the fluids and S contents in the coexisting melts closely match the compositions of fluids and compositions of olivine hosted melt inclusions from the 2002–2003 eruption of Mt. Etna. At S/Cl fluid ratios of ~5 to 7, measured during passive degassing, experimentally determined melt S contents were similar to primitive magma which contains ~0.27 to 0.33 wt.% S. Whereas at S/Cl fluid ratios of ~2 to 4 determined during mild strombolian activity, coexisting melts contained 0.18 to 0.27 wt.% S which is similar to partially degassed, slightly evolved melts. This indicates that primitive melts of Mt. Etna might have been more oxidizing than previously determined on melt inclusions.

1. Introduction

Volcanism is typically accompanied by degassing of large amounts of volatiles (e.g., H_2O, CO_2, S, and halogens). The composition of emitted volcanic gases is often closely linked to the eruptive energy (e.g., Edmonds et al., 2001, 2002; Di Liberto et al., 2002; Conde et al.,

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2014). The dissolution and exsolution processes of volatiles in magmatic system are governed by the initial contents of volatiles in the magma and the partitioning mechanism of volatiles between magmatic phases which can be strongly influenced due to changes in redox conditions. The release of multicomponent fluids during eruptive or quiescent magma degassing imposes the relative proportions of individual volatile components and their interaction relationships in the melt and in the fluid. In particular S and Cl have strong controls on the properties of magmatic fluids, acting as indicators for the conditions of magmatic degassing, and may bear information on potential changes in the eruption style. Sulfur is typically present in two valence states in silicate melts (sulfate, S^{6+} and sulfide, S^{2}) (e.g., Carroll and Rutherford, 1988; Wallace and Carmichael, 1994; Jugo et al., 2005, 2010) and in most magmatic fluids (sulfur dioxide, SO_2 and hydrogen sulfide, H_2S) (e.g., Holloway, 1977, 1987; Moretti and Papale, 2004). The change in S speciation can reflect prevailing redox conditions at depth (Scaillet et al., 1998; Burgisser and Scaillet, 2007; Burgisser et al., 2008; de Moor et al., 2013) and even elucidate buffering redox reactions in low-density volcanic gases (Giggenbach, 1987, 1993; Ohba et al., 1994; de Moor et al., 2013). Chloridic fluids are well-known for their strong non-ideal behavior at *P*–*T*–*X* conditions relevant to magmatic systems (e.g., Sourirajan and Kennedy, 1962; Bodnar et al., 1985; Shmulovich et al., 1995; Duan et al., 2006; Driesner and Heinrich, 2007) The influence of chlorine on the activity of other fluid components exerts strong controls on magma degassing (e.g., Webster et al., 2014 and references therein).

Sulfur and chlorine are present only in minor amounts in the atmosphere making them easily measurable in volcanic plumes by remote spectroscopy (e.g., Burton et al., 2003; McGonigle, 2005; Oppenheimer et al., 2011). The correlation between fluid composition, in particular the S/Cl ratio, and eruptive activity, as observed on many volcanoes worldwide, points to a close link between magma storage conditions and magma degassing processes (e.g., Aiuppa et al., 2002, 2004; Allard et al., 2005; Burton et al., 2007; de Hoog et al., 2001; Johnson et al., 2010; Métrich et al., 2004; Stremme et al., 2011). However, due to high uncertainty in finding correlation factors which control degassing in natural magmatic systems, our understanding and ability to model magma degassing are largely based on a quantitative determination of volatile partitioning laws obtained from experimental studies. Experimental simulation ensures controls on *P*–*T*–*X*–fO_2–time conditions and provides data series required for the development and calibration of magma degassing models.

Studies focused on the partitioning behavior of both volatiles, S and Cl, between aluminosilicate melt and aqueous fluid are scarce and have been published for rhyodacite by Botcharnikov et al. (2004), for phonolite to trachyte by Webster et al. (2009), for andesite by Zajacz et al. (2012) and Fiege et al. (2014), for the system basalt and H–O–S–Cl–C-fluids by Lesne et al. (2011), and phonolite–trachyte and H–O–S–Cl–C–F-fluids by Webster et al. (2014). The study of Zajacz et al. (2012) includes seven experiments with S and Cl focusing on their fluid–melt partitioning at low S and Cl contents in the system. Lesne et al. (2011) investigated closed-system decompression-driven partitioning of H_2O, S, Cl, and CO_2 starting from four different starting system compositions which included two different basalts, similar to Stromboli (Italy) and Masaya (Nicaragua). Fiege et al. (2014) focused on kinetic controls on the partitioning of S and Cl between fluid and andesitic melt, similar to the Krakatau (Indonesia) andesite, during decompression. However, only the studies of Botcharnikov et al. (2004) and Webster et al. (2009) cover a wide range of S and Cl concentrations in systems, which is necessary to understand in general the partitioning behavior of components between phases. Botcharnikov et al. (2004) showed that S increases the partitioning of Cl, whereas Cl decreases the partitioning of S into the fluid, because of the increase in S solubility at FeS saturation in rhyodacite in the presence of Cl at reducing conditions. In sulfate-dominated systems (at $\log fO_2 > \text{FMQ}+1$, where FMQ is the Fayalite–Magnetite–Quartz oxygen buffer), Webster et al. (2009) demonstrated that S and Cl concentrations in the melt vary inversely with each other and that both S and Cl mutually enforce partitioning into the fluid. Fiege et al. (2014) pointed out that the addition of Cl to sulfate-dominated systems and increasing decompression rate enhance the partitioning of S into the fluid as well.

In order to extend our knowledge on the general behavior of S and Cl in mafic magmatic systems, we have investigated experimentally S and Cl partitioning between aqueous fluid and basaltic melt in a wide range of S and Cl system concentrations. Such data are crucial because basaltic magmas are prominent sources for S and Cl degassing to the atmosphere (e.g., Thordarson and Self, 1996; Thordarson et al., 1996; de Hoog et al., 2001; Halmer et al., 2002; Grainger and Highwood, 2003; Highwood and Stevenson, 2003; Stevenson et al., 2003; Textor et al., 2003; Thordarson and Self, 2003). For example Mt. Etna, one of the world's most active and best surveyed volcanoes emits annually about ~6 Mt SO_2 (Halmer et al., 2002) and, considering Mt. Etna's mean S/Cl plume ratios (Aiuppa et al., 2004), ~0.5 Mt of Cl into the atmosphere. Mt. Etna is one of the best candidates for experimental studies, because of the large existing database on natural gas and melt compositions (e.g., Métrich et al., 1993, 2004; Aiuppa et al., 2004; Clocchiatti et al., 2004; Andronico et al., 2005; Spilliaert et al., 2006a,b; Viccaro et al., 2006, 2008; Corsaro et al., 2007, 2009; Ferlito et al., 2008, 2009) which offers a direct comparison between natural and experimental data. In order to investigate early-stage degassing processes at depth, experiments were carried out at conditions relevant to magma storage and early-stage ascent of basaltic magma (1050 °C, 200 and 100 MPa, reduced and oxidizing redox conditions, i.e. at $\log fO_2 \sim \text{FMQ}+0.5$, FMQ+2.3, and FMQ+2.8).

2. Experimental methods

2.1. Starting materials

The starting glass was prepared from a trachybasalt lava rock sample collected from the southern flank of Mt. Etna near Rifugio Sapienzia, 1892 m a.s.l. (provided by Max Wilke, University of Potsdam, Germany). These trachybasalts erupted from the upper vents of Etna as described in detail by Métrich et al. (2004). This rock sample has been already used as starting material in former studies on the solubility of H–O–Cl–± F fluids as well as on the solubility and speciation of S in basaltic magmas (Chevychelov et al., 2008; Stelling et al., 2008; Jugo et al., 2010; Beermann et al., 2011; Botcharnikov et al., 2011).

Starting glass was prepared from the crushed and ground rock samples (<200 μm grain size). The rock powder was poured into a platinum crucible, fused in a 1 atm furnace in air at 1600 °C, and was subsequently quenched in a water bath after 3 h of melting. The quenched glass was crushed again and ground to grain sizes < 200 μm, The ground glass was fused again for 0.5 h at 1600 °C in air and quenched in a water bath again. Finally, the crystal- and vesicle-free glass was ground to grain sizes <200 μm. The chemical composition of the starting glass was determined by electron microprobe analysis (EPMA) (Table 1).

All experiments were performed under fluid-saturated conditions. In order to maintain almost constant fluid/melt mass proportions in the charges ~11 to 13 wt.% or ~9 to 11 wt.% of the total initial fluid was added to the system for runs at 200 MPa and 100 MPa, respectively. Hence, the amount of free fluid in the experiment was ~5 to 6 wt.% as estimated from the added amount of fluid and from the solubility of H–O–Cl-fluids in basaltic melts at 200 MPa, 1050 °C (Stelling et al., 2008) and at 100 MPa, 1200 °C (Alletti et al., 2009). The initial Cl concentration of the starting glass was 0.06 wt.% Cl and it was considered in the mass relations of starting charges in the experiments (Table 2).

2.2. Experimental techniques

The strategy was to create a series of experiments with systematic changes in Cl and S contents at nearly fixed oxygen fugacity (fO_2). Thus, gold capsules (length = 15 mm, inner diameter = 2.8 mm, wall