



The effect of melt composition on the partitioning of oxidized sulfur between silicate melts and magmatic volatiles

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Abstract

Experiments were conducted at 500 MPa and 1240 °C in a piston cylinder apparatus to assess the effect of melt composition on the melt/volatile partition coefficient of sulfur ($D_S^{\text{melt/volatile}}$), which was used as a measure of the silicate melt's capacity to dissolve oxidized sulfur species. Iron-free, three- and four-component silicate melts were equilibrated with H₂O–S fluids with sulfur concentrations ≤ 2 mol% at an oxygen fugacity imposed by the Re–ReO₂ buffer (1.4 log units above the Ni–NiO buffer). At these conditions, SO₂ (S⁴⁺) is predicted to be the dominant sulfur species in the volatile phase and sulfate (S⁶⁺) is the dominant sulfur species in the silicate melt. The values of $D_S^{\text{melt/volatile}}$ were calculated by mass balance. The results show that $D_S^{\text{melt/volatile}}$ values increase exponentially with decreasing the degree of polymerization of the silicate melt structure. For example, in calcium-aluminosilicate melts, $D_S^{\text{melt/volatile}}$ changes from 0.005 to 0.3 as the degree of melt polymerization changes from the equivalent of a rhyolite to the equivalent of a basalt. At a constant degree of melt polymerization, $D_S^{\text{melt/volatile}}$ in equilibrium with sodium-aluminosilicate (NAS) melts is more than an order of magnitude higher than in equilibrium with calcium-aluminosilicate (CAS) melts, and more than two orders of magnitude higher than in equilibrium with magnesium-aluminosilicate (MAS) melts. The value of $D_S^{\text{melt/volatile}}$ changes from 0.014 in MAS glasses to 3.4 in NAS glasses for the most depolymerized compositions in each series. Potassium has a similar effect on sulfate dissolution to that of Na. The variation of $D_S^{\text{melt/volatile}}$ in equilibrium with various calcium–sodium aluminosilicate (CNAS), magnesium–sodium aluminosilicate (MNAS) and magnesium–potassium aluminosilicate (MKAS) melts indicates that alkalis are only available for sulfate complexation when they are present in excess compared to the required amount to charge balance for the Si⁴⁺ to Al³⁺ substitution in the melt structure. Calcium has a moderate, Mg has a very minor affinity to replace alkalis in this charge balancing role. Apparent equilibrium constants are provided to predict the available amount of various network modifiers for sulfate complexation and, therefore, the presented data can be used to predict $D_S^{\text{melt/volatile}}$ for geologically relevant melt compositions.

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1. INTRODUCTION

Sulfur is the fourth most abundant volatile element in magmas after hydrogen, oxygen and carbon. Sulfur impacts society through volcanic degassing as well as by being an

essential component required for the formation of magmatic sulfide and hydrothermal ore deposits. Sulfate aerosol released into the atmosphere during volcanic eruptions is effective at blocking solar irradiation and may exert significant short term climatic impacts (Brasseur and Granier, 1992; Minnis et al., 1993; McCormick et al., 1995; Briffa et al., 1998; Robock, 2000). Various sulfur bearing species serve as ligands for the transportation of chalcophile and highly siderophile elements in silicate melts and magmatic volatiles (Hedenquist and Lowenstern, 1994; Williams-Jones and Heinrich, 2005; Zevin et al., 2007;

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Botcharnikov et al., 2010; Zajacz et al., 2010, 2011, 2012b; Pokrovski and Dubrovinsky, 2011; Jago and Pichavant, 2012), as well as control the precipitation of numerous ore-forming elements in the magmatic-hydrothermal environment and in magmatic sulfide ore deposits (Barnes, 1997). The above two types of mineralizations are our major resources of Cu, Mo, Ni, Au, Ag, Pb, Zn and platinum group elements.

Unlike all other major volatile elements in magmas (H, C, O, Cl), sulfur changes its oxidation state in the oxygen fugacity (fO_2) regime of typical arc magmas (Wallace and Carmichael, 1994; Metrich et al., 2009; Jugo et al., 2010; Klimm et al., 2012a,b). The two most abundant forms of S in silicate melts are sulfide (S^{2-}) and sulfate (S^{6+}) based on X-ray Absorption Near Edge Structure (XANES) Spectroscopy data on quenched silicate glasses (Metrich et al., 2009; Jugo et al., 2010; Wilke et al., 2011; Klimm et al., 2012a,b). The transition between these two oxidation states is very sharp and occurs in the middle of the characteristic fO_2 range of arc magmas. However, sulfur displays radically different behavior in these two oxidation states. The S^{2-} anion is dominantly associated with Fe or H in silicate melts and volatiles, and its concentration in these phases is primarily limited by the saturation of Fe-rich liquid or solid sulfide phases (Fincham and Richardson, 1954; Mathez, 1976; Carroll and Rutherford, 1985; Li and Naldrett, 1993; O'Neill and Mavrogenes, 2002; Clemente et al., 2004; Stelling et al., 2011; Klimm et al., 2012b). On the other hand, S^{6+} has a strong affinity to associate with oxygen, and it is present as sulfate species in silicate melts (Metrich et al., 2009; Jugo et al., 2010; Klimm and Botcharnikov, 2010; Wilke et al., 2011; Klimm et al., 2012b). Its maximum dissolved concentration is typically limited by the saturation of anhydrite, except for some alkali-rich, silica undersaturated magmas which may saturate primary magmatic sodalite and scapolite group minerals that contain sulfur (Carroll and Rutherford, 1985, 1987; Parat et al., 2011). The limits on the maximum concentrations of sulfur in silicate melts imposed by the saturation of sulfate phases are typically much higher than those imposed by the saturation of Fe-rich sulfides (Carroll and Rutherford, 1985; Jugo et al., 2005b; Jugo, 2009; Zajacz et al., 2012a); therefore, oxidized arc magmas often contain significantly larger concentrations S dissolved in the silicate melt as shown by data obtained from silicate melt inclusions in minerals (Wallace, 2005; Wallace and Edmonds, 2011). The solubility mechanism of S^{2-} in silicate melts is relatively well understood. Reduced sulfur is known to be dissolved dominantly as FeS species, therefore the activity of Fe in the melt and the activity coefficients of FeS(melt) species are the most critical variables determining its solubility behavior (O'Neill and Mavrogenes, 2002; Moretti and Ottonello, 2005; Moretti and Baker, 2008; Zajacz et al., 2013). However, less systematic data exist on the effect of silicate melt composition on the solubility of sulfate species. It may be expected that various cations exhibit different degrees of affinity to bind with the sulfate anions in the silicate melt structure, and therefore, silicate melt composition may have a significant effect on sulfate solubility. This is apparent when comparing the solubilities of anhydrite or

the volatile/melt partition coefficients of S between various studies that used different melt compositions (Carroll and Rutherford, 1985, 1987; Jugo et al., 2005b; Jugo, 2009; Keppler, 2010; Backnaes and Deubener, 2011; Webster and Botcharnikov, 2011; Zajacz et al., 2012a). The effect of melt composition has also been included in the thermodynamic model of Moretti and Ottonello (2005), which, however, must have relied on standard state thermodynamic properties of sulfate salts and an optimization to fit sulfate solubility data mostly obtained at ambient pressure published in the metallurgic literature.

Here I present experimental melt/volatile partition coefficients for oxidized S obtained at a pressure (P) of 500 MPa and a temperature (T) of 1240 °C with the purpose of assessing the effect of melt composition on the solubility of sulfate species. Sulfur partitioning has been compared between ternary magnesium-, calcium-, sodium- and potassium-aluminosilicate melts, as well as various quaternary compositions at nearly identical degree of melt polymerization. Also, the effect of the degree of melt polymerization has been systematically investigated using calcium- and sodium aluminosilicate melts. Sulfur partitioning between silicate melts and low density aqueous fluids is interpreted as a function of the predicted availability of various network modifier cations for sulfate complexation in the silicate melt.

2. METHODS

2.1. Experimental strategy

I have equilibrated synthetic silicate melts with a volatile phase containing ~2 mol% S at an fO_2 imposed by the Re-ReO₂ buffer assemblage. Aqueous volatile phase rather than sulfate salt melt was chosen to impose a predictable activity of oxidized S species, as the exchange reactions between sulfate salt melts and silicate melt would likely modify the composition of both the silicate and sulfate salt melt, in particular when quaternary or higher order silicate melt compositions are used. Whereas, in low-density volatiles, it can be expected that oxidized S is dominantly present as gaseous SO₂, or potentially minor additional H₂SO₄ or SO₃ species, and the composition of the aqueous fluid phase is not significantly influenced by the co-existing silicate melt (Binder and Keppler, 2011; Borisova et al., 2014). The molar SiO₂:Al₂O₃: $\sum Me_{2/n}O$ ratio, where Me stands for network modifiers (e.g. Na, K, Ca and Mg) with a valence state of n , was selected to be 0.64:0.1:0.26. This composition falls relatively close to the ternary eutectic points in the calcium-aluminosilicate (CAS) and magnesium-aluminosilicate (MAS) systems (Ehlers, 1987). This corresponds to a non-bridging oxygen/tetrahedral cation (NBO/T) value of 0.38, where $NBO/T = [Na + K + 2 * (Ca + Mg) - Al]/(Al + Si)$ using the mole fraction of the elements as concentration units. The value of NBO/T was kept constant for a set of experiments using various ternary and quaternary melt compositions. In addition, two sets of experiments were conducted with CAS and sodium-aluminosilicate (NAS) melts varying NBO/T between 0 and 0.4 while maintaining the molar Si/Al ratio close to 3. The

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