

Sulfur content at sulfide saturation in oxidized magmas

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ABSTRACT

Accurate estimates of the sulfur content in silicate melts at sulfide saturation are required to explain magmatic processes such as the origin and budget of sulfur in some volcanic eruptions and the transfer of Cu, Au, and other precious metals from the mantle to the crust via partial melting of the mantle. A model that links S speciation, S content at sulfide saturation (SCSS), S content at anhydrite saturation (SCAS), and changes in oxygen fugacity (fO_2) is presented. The model predicts an exponential increase in the SCSS with increasing fO_2 from fayalite-magnetite-quartz (FMQ) because of the contribution of sulfate species in the melt. The predicted SCSS ranges from 1300 ppm (at FMQ – 1) to 1500 ppm (at FMQ + 0.5) for mid-oceanic-ridge basalts (MORB), is up to 7500 ppm (at FMQ + 2) for backarc and oceanic-island basalts, and can be as high as 1.4 wt% (at FMQ + 2.3) for island arc basalts. For the mantle wedge above subducting slabs, the SCSS ranges from 1500 ppm (at FMQ + 0.4) to 4500 ppm (at FMQ + 1.7). Disequilibrium experiments show textural evidence that is consistent with the model predictions. Thus, sulfide-undersaturated magmas can be formed at relatively low degrees of melting in metasomatized mantle sources without the need to invoke sulfide elimination by oxidation at high fO_2 . Estimates of the amount of S that can be transported by silicate melts need to account for the enhanced capacity of silicate melts to dissolve S when sulfate species are present, even if sulfides are the stable S-bearing phase.

INTRODUCTION

An understanding of the behavior of S is relevant for the understanding of magmatic processes for several reasons. Sulfur content in fumarolic emissions is often used to detect renewed volcanic activity (Symonds et al., 1994). Volcanic activity can produce large SO_2 emissions, which can be carried to the stratosphere during explosive eruptions and have severe short-term impact on global climate (Robock, 2000). The behavior of chalcophile and siderophile elements (e.g., Ni, Cu; Au, Pt, Pd) in magmatic systems is dictated by S as sulfide (S^{2-}), and sulfide saturation exerts a primary control on the genesis of metalliferous deposits (Imai et al., 1993; Sillitoe, 1997). Early studies (e.g., Fincham and Richardson, 1954; Haughton et al., 1974; Wendlandt, 1982) focused on sulfide-bearing and sulfide-saturated systems because sulfides are the most commonly observed S-bearing phases in magmatic systems (Desborou et al., 1968; Mitchell and Keays, 1981). However, the anhydrite-bearing eruptions of El Chichón volcano in 1982 (Luhr et al., 1984) and Mount Pinatubo in 1990 (Bernard et al., 1991) demonstrated that sulfate species (S^{6+}) are significant in some magmatic systems. Furthermore, estimates of S content and speciation in magmas (e.g., Metrich and Clacchiatti, 1996; Rowe et al., 2007) show that sulfate species are more common in magmatic systems than previously acknowledged. Experimental determination of the S content in silicate melts shows unequivocally that magmas can carry more S

when S^{6+} is the dominant species (Carroll and Rutherford, 1985, 1987; Luhr, 1990; Jugo et al., 2005a). Estimates of S speciation in natural and experimental samples showed that the transition from sulfide-dominated to sulfate-dominated systems occurs over a narrow fO_2 interval (roughly from fayalite-magnetite-quartz [FMQ] to FMQ + 2; Wallace and Carmichael, 1994; Jugo et al., 2005b). This fO_2 range is significant because it overlaps with the fO_2 conditions prevalent during magma generation in arc settings (Parkinson and Arculus, 1999) and the fO_2 conditions prevalent in backarc, island arc, and oceanic-island magmas at the time of eruption (Ballhaus, 1993). Despite these advances, there is little understanding of (1) how mixed speciation controls the S content in silicate melts that are sulfide- or sulfate-saturated, (2) the fO_2 conditions under which sulfide and sulfate phases can coexist in equilibrium, and (3) the potential implications of the above for the behavior of S in magmatic systems.

Part of the problem in understanding the role of S in magmatic systems is caused by what has been commonly referred to in the literature as “the sulfur solubility minimum” (e.g., Kress, 1997; Moretti and Ottonello, 2005). The concept is based on experiments in which a S-bearing gas is equilibrated with silicate melts but in the absence of crystalline sulfide or sulfate phases (e.g., Katsura and Nagashima, 1974). As discussed in detail in Jugo et al. (2005a), such “S solubility minimum” describes the distribution of a trace element (S) between two coexisting phases (a gas phase and a silicate melt) but does not describe the S contents required to

saturate a silicate melt in either sulfides or sulfates. In this contribution I present a model that integrates changes in S speciation as a function of fO_2 (Jugo et al., 2005b; Wilke et al., 2008) and S content data at sulfide and sulfate saturation (Carroll and Rutherford, 1985, 1987; Jugo et al., 2005a) to predict changes in the S content at sulfide saturation with changes in fO_2 .

RATIONALE

In contrast to other polyvalent cations (such as Fe), which can form minerals containing both ferrous (Fe^{2+}) and ferric (Fe^{3+}) species (such as magnetite), sulfide (S^{2-}) and sulfate species (S^{6+}) do not coexist in any mineral. The only relevant phases in which S^{2-} and S^{6+} species can coexist are silicate melts and volatile phases. Because here the main goal is to understand the behavior of S in silicate melts prior to the exsolution of gas phases, only three S-bearing phases are taken into account: sulfide, sulfate, and silicate melt. Sulfur speciation in silicate melts changes from sulfide to sulfate in the fO_2 range of FMQ < fO_2 < FMQ + 2. Within that range, the total S content below saturation with any condensed phase can be expressed as

$$\{S\}_T = \{S^{2-}\} + \{S^{6+}\}, \quad (1)$$

where $\{S\}_T$ refers to the total S content; $\{S^{2-}\}$ is the contribution from sulfide species dissolved in the melt; and $\{S^{6+}\}$ is the contribution from sulfate species dissolved in the melt. Because S^{2-} and S^{6+} species are the only S species present in silicate melts, the sulfide and sulfate fractions relative to the total dissolved S, $X(S^{2-}) = \{S^{2-}\}/\{S\}_T$ and $X(S^{6+}) = \{S^{6+}\}/\{S\}_T$, satisfy the relation

$$X(S^{2-}) + X(S^{6+}) = 1. \quad (2)$$

For silicate melts representative of natural magmas, the S content at sulfide saturation is always lower than the S content at sulfate saturation (Carroll and Rutherford, 1985, 1987; Luhr, 1990; Jugo et al., 2005a). Therefore, it is reasonable to assume that for $X(S^{2-}) > 0.5$ (i.e., when sulfides are the dominant species), increasing the total S content will eventually trigger sulfide saturation, and the total S content in the melt can be expressed as

$$\{S\}_T = SCSS = [S^{2-}] + \{S^{6+}\}, \quad (3)$$

where SCSS is the S content at sulfide saturation, and $[S^{2-}]$ is the S^{2-} contribution to the melt at sulfide saturation. (The squared brackets, $[S^{2-}]$, are

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used to distinguish from $\{S^{2-}\}$, the S contribution from sulfide species below sulfide saturation.)

As equation 3 shows, the total S content in the melt at sulfide saturation has a contribution from sulfate species dissolved in the melt, even if a condensed sulfate phase is not present. However, the contribution from sulfate species is dependent on fO_2 , and for any given fO_2 the following relationship must be satisfied:

$$\{S^{6+}\}/[S^{2-}] = X(S^{6+})/X(S^{2-}). \quad (4)$$

Using equations 4 and 2, the SCSS (equation 3) can be expressed as

$$SCSS = [S^{2-}]/(1 - X(S^{6+})). \quad (5)$$

As shown in Jugo et al. (2005b), the change in $X(S^{6+})$ as a function of fO_2 is best described by a sigmoidal function of the form

$$X(S^{6+}) = A/(1 + \exp(B - C\Delta FMQ)), \quad (6)$$

where ΔFMQ is fO_2 relative to the FMQ oxygen buffer, and A, B, and C are the coefficients controlling the shape of the sigmoidal curve. For S speciation in basaltic melts, those coefficients were determined to be $A = 0.86$, $B = 2.89$, and $C = 2.23$ (Jugo et al., 2005b). The ideal behavior of a system in which S dissolves only as sulfide or sulfate species should result in a coefficient $A = 1$, but the nonlinear regression of the available data in Jugo et al. (2005b) converged to $A = 0.86$. Jugo et al. (2005b) interpreted this deviation from ideal behavior as the result of sulfite (S^{4+}) species present in the melt, as suggested by Metrich et al. (2002). However, Wilke et al. (2008) conducted systematic X-ray absorption near-edge structure (XANES) studies and showed that the presence of sulfite species in quenched glasses is an analytical artifact caused by beam-sample interaction. Therefore, S is present in the silicate melts solely as a combination of S^{2-} and S^{6+} species, and coefficient A should converge to unity ($A = 1$). Combining equations 5 and 6 and using $A = 1$ in equation 6, we can now calculate how the SCSS increases solely as a function of increasing fO_2 :

$$SCSS = [S^{2-}](1 + \exp(2.23\Delta FMQ - 2.89)). \quad (7)$$

A similar expression can be derived for a sulfate-dominated system (in which we assume that sulfate saturation is reached first):

$$SCAS = [S^{6+}](1 + \exp(2.89 - 2.23\Delta FMQ)), \quad (8)$$

where SCAS (S content at anhydrite saturation) is used for simplicity, even though the saturating sulfate phase may be a sulfate liquid and not crystalline anhydrite at high temperature (e.g., Jugo et al., 2005a).

The exponential curves defined by equations 7 and 8 increase in opposite directions and intersect at a critical fO_2 value that defines the conditions at which magmas could be simultaneously saturated with sulfide and sulfate (crystalline or as immiscible liquids). At this fO_2 the magma can be expected to dissolve the maximum possible amount of S. This critical fO_2 value, for simultaneous sulfide and sulfate saturation, is defined by

$$\Delta FMQ_c = 1.29 + 0.45(\ln[S^{6+}] - \ln[S^{2-}]), \quad (9)$$

where ΔFMQ_c refers to the critical fO_2 for simultaneous saturation of sulfide and sulfate. The main limitation of this approach is that equations 7, 8, and 9 use parameters that were derived from S speciation data in quenched basaltic melts (natural and experimental), and application to melts of different composition assume that composition does not affect S speciation significantly.

COMPARISON OF THE MODEL TO EXPERIMENTAL DATA

Figure 1 shows experimental data of the S content as a function of fO_2 for trachyandesitic melts similar to those erupted by El Chichón volcano (Carroll and Rutherford, 1985, 1987) and for basaltic melts (e.g., similar to those thought to be feeding the magmatic system at Mount Pinatubo; Jugo et al., 2005a). The curves shown were generated using equations 7 and 8 above. The two curves are different because differences in melt composition (basalts versus andesites/trachyandesites), water content (anhydrous versus hydrous), pressure (1.0 GPa versus 200 MPa), and temperature (1300 °C versus 1025 °C) affect the S content. The values

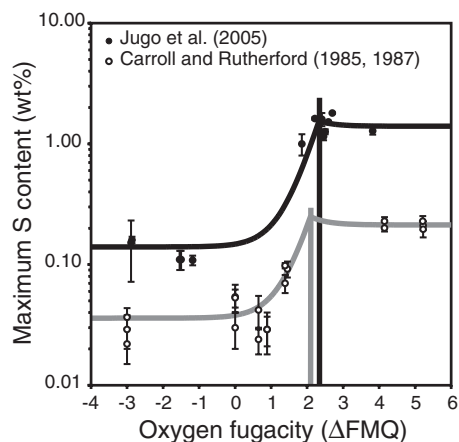
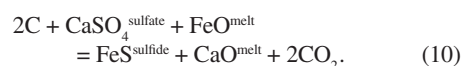


Figure 1. Experimental data of the S content at sulfide and sulfate saturation as a function of fO_2 and fit of the curves described in equations 7, 8, and 9. The data from Carroll and Rutherford (1985, 1987) are for hydrous trachyandesitic melts at ~1025 °C and ~200 MPa. The data from Jugo et al. (2005a) are for anhydrous basaltic melts at 1300 °C and 1 GPa.

used for $[S^{2-}]$ and $[S^{6+}]$ are the averages of the experimental data for sulfide-saturated runs and sulfate-saturated runs in each study and correspond to the horizontal parts of the curves in the figure. Only the averages of sulfide-saturated data at $fO_2 \leq FMQ$ and sulfate-saturated data at $fO_2 > FMQ + 3$ were used ($[S^{2-}] = 0.037$ wt% and $[S^{6+}] = 0.213$ wt% for the trachyandesitic melts at 1025 °C and 200 MPa; $[S^{2-}] = 0.13$ wt% and $[S^{6+}] = 1.28$ wt% for the basaltic melts at 1300 °C and 1.0 GPa). The data at intermediate fO_2 ($FMQ < fO_2 < FMQ + 3$) were not used to construct the curve, and the fit of the curve with the data also validates the approach used (to merge S speciation with data of the S content at saturation). The vertical lines are the critical fO_2 values (ΔFMQ_c) calculated from equation 9 and do not coincide ($\Delta FMQ_c = +2.08$ for the trachyandesites and $\Delta FMQ_c = +2.32$ for the basalts) because ΔFMQ_c depends on the difference between $[S^{2-}]$ and $[S^{6+}]$.

EXPERIMENTAL TESTS FOR THE S CONTENT AT SATURATION FOR TRANSITION FROM SULFIDE TO SULFATE

As a test to verify this model, disequilibrium experiments were designed and completed in a piston-cylinder apparatus. The experimental charges consisted of a synthetic andesitic glass mixed with anhydrite and loaded into graphite capsules. The capsules were heated to 1300 °C to ensure that no silicate crystals would form and pressurized to 1 GPa to enhance S dissolution in the silicate melt. The capsules were kept at run conditions for short periods, ranging from 15 min to 1 h, in order to prevent equilibrium. Carbon from the graphite capsules initiates a reduction reaction:



Thus, carbon-sample interaction creates a reduction front that moves toward the center of the capsule. This likely involves CO_2 (and CO) moving inwards and other species moving outwards. Quenching prior to complete equilibration preserved the reduction profile, recording the continuum from sulfide to sulfate speciation in each experiment. Figure 2 shows the textures caused by the advance of the reduction front in one of those disequilibrium experiments. The change in S speciation across these reduction fronts is documented in Wilke et al. (2008). Between the sulfide- and sulfate-saturated domains there is a narrow gap with higher glass content than the sulfide-saturated or the sulfate-saturated regions. Microprobe analyses to measure changes in S contents in this narrow gap were attempted. However, the gap is ~25 μm wide, and tests with a 15- μm -diameter beam

showed that crystalline S-bearing phases were almost invariably included within the activation volume and did not allow estimation of the S content across the gap. The experiment is not identical to the conditions stated for Equation 10 because sulfide precipitation and sulfate dissolution likely cause local changes in melt composition. However, the gap can be interpreted as the region in the moving reduction front that causes the maximum possible S content in the melt, thus dissolving sulfate droplets such as those seen at the right of the picture, prior to causing sulfide saturation (left side of the picture). A decrease in S solubility in this transition region is not consistent with the textures observed because it would result in the opposite texture: a band with more concentration of crystalline S-bearing phases.

DISCUSSION AND CONCLUSIONS

The most significant aspect of the calculations is that equation 7 predicts that the SCSS will increase exponentially in the fO_2 range in which sulfide and sulfate species coexist (from $fO_2 = FMQ$ to the fO_2 at which a sulfate phase can saturate from the melt, at about $fO_2 = FMQ + 2$). Below $fO_2 = FMQ$, sulfate species contribute less than 5% to the total S in the silicate melt and are negligible. Thus, relative to systems in which S^{2-} accounts for more than 95% of the S species (i.e., at $fO_2 \leq FMQ$, e.g., MORB), the SCSS doubles at $FMQ + 1.3$, increases fourfold at $FMQ + 1.8$, and fivefold at $FMQ + 1.9$. Above $fO_2 = FMQ + 2$, sulfate dominates and the contribution to the SCAS from sulfide species is trivial. This change in S behavior has significant implications for magmatic systems formed and evolving at $fO_2 > FMQ + 1$. For example, sulfide elimination at the source during partial melting of the mantle is thought to be the main requirement for incorporation of highly siderophile elements (HSE) in silicate melts (because in the absence of a metal phase these elements show strong chalcophile behavior). Under reduced conditions, a large degree of partial melting would be required to eliminate sulfides by dissolution. Keays (1995), for example, estimated that a mantle source would require ~25% melting before sulfide phases could be eliminated by dissolution (based on a bulk S content of the mantle of 250 ppm and a SCSS in the melt of 1000 ppm). Alternatively, it has been proposed that magmas generated at $fO_2 \geq FMQ + 2$ would result in Cu and Au (and HSE) enrichment in silicate melts because sulfide phases would not be stable (Mungall, 2002). This is significant because elimination of sulfides by oxidation should produce magmas rich in HSE at low degrees of partial melting (Jugo et al., 2005a; Mungall et al., 2006). However, because of the exponential increase in the SCSS with increasing fO_2 , elimination of sulfide phases in the

mantle source does not require partial melting in excess of 25% (Keays, 1995) or fO_2 conditions exceeding $FMQ + 2$ (Mungall, 2002). Figure 3 illustrates this by outlining the expected SCSS and SCAS for different tectonic settings. For example, if island arc magmas are formed in the mantle wedge in the range $FMQ + 0.5 < fO_2 < FMQ + 1.7$ as estimated by Parkinson and Arculus (1999) we should expect the SCSS to range from 1500 ppm (at $FMQ + 0.5$) to 4500 ppm (at $FMQ + 1.7$; white box in Fig. 3). The low end of the range is not significantly different from the SCSS in reduced (e.g., MORB) magmas (SCSS = 1300 ppm). However, the SCSS at the upper fO_2 end is three times higher than in MORB magmas. If Keays' (1995) approach is used, only 6% melting would be required to eliminate mantle sulfides by dissolution if melting occurs at $FMQ + 1.7$ (assuming a mantle with 250 ppm S; McDonough and Sun, 1995). Metasomatism is thought to increase the amount of S in the mantle wedge to ~500 ppm (de Hoog et al., 2001). Even assuming that all S added during metasomatism is stabilized as sulfides, ~11% melting would be required to eliminate sulfides by dissolution if melting occurs at $FMQ + 1.7$. As a consequence, partial melting in metasomatized sources should result in (1) the release to the melt of the HSE inventory trapped in sulfides, or (2) a change to conditions in which HSE content in the silicate melt is controlled by metal-melt, oxide-melt or silicate-melt equilibria. Furthermore, Alard et al. (2000) showed that mantle sulfides in metasomatized sources are either interstitial (along grain boundaries) or enclosed (mostly in olivine). They showed that the interstitial sulfides (Cu-rich pentlandite) have higher Cu and higher Pd/Ir than the enclosed sulfides (mostly monosulfide solid solution). Because low degrees of partial melting would preferentially eliminate interstitial sulfides, melting of metasomatized sources should result in Cu-rich magmas with high Pd/Ir and would likely cause fractionation of HSE. Thus, the total inventory of HSE in the melt will depend on the relative proportion of enclosed sulfides that are shielded during melting and retained in the mantle residue.

Application of the model to magmas from several tectonic settings at different fO_2 ranges (Ballhaus, 1993) indicates that sulfate species will dominate in island arc basalts (IAB), backarc basalts (BAB), and oceanic-island basalts (OIB) compared to mid-oceanic-ridge basalts (MORB), and therefore the SCSS should be high in IAB, BAB, and OIB (Fig. 3). For example, in MORB, the SCSS increases from 1300 ppm (at $FMQ - 1$) to 1500 ppm (at $FMQ + 0.5$; black band in Fig. 3); in BAB and OIB, the SCSS increases from 1400 ppm (at FMQ) to 7500 ppm (at $FMQ + 2$; dark-gray box in Fig. 3); and in IAB, the SCSS increases from 2000 ppm (at $FMQ + 1$) to 1.4 wt% (at $FMQ + 2.3$) where sul-

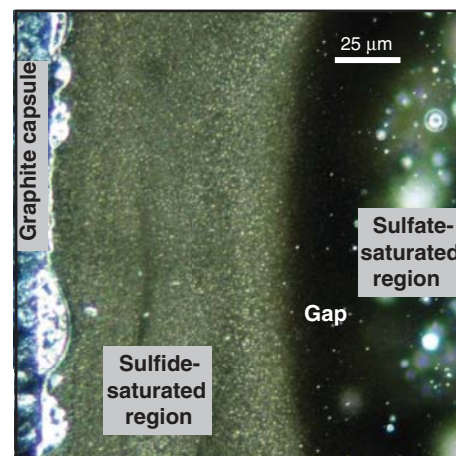


Figure 2. Detail of one of the dis-equilibrium experiments quenched to preserve the reduction front imposed by enclosing a sulfate-saturated andesitic melt in a graphite capsule. A gap with few visible sulfides or sulfates separates the sulfate-saturated region (right) from the sulfide-saturated region (left).

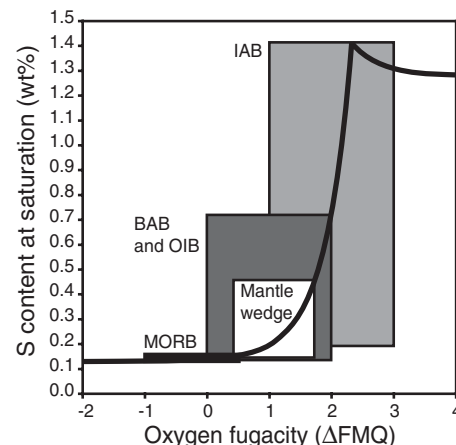


Figure 3. Predicted S content at sulfide and sulfate saturation for the mantle wedge above subduction zones and for basaltic melts from different tectonic settings. Oxidation states for the fields shown are from Ballhaus (1993) and Parkinson and Arculus (1999). The curve is the same curve shown in Figure 1. IAB— island arc basalts; BAB— backarc basalts; OIB— oceanic-island basalts; MORB— mid-oceanic-ridge basalts.

fate saturates (light-gray box in Fig. 3). Above $FMQ + 2.3$, sulfides are not stable and the maximum S content is controlled by the SCAS. These values were calculated using experimental data for basaltic melts at 1300 °C and 1.0 GPa (Jugo et al., 2005a). Further work is needed to fully evaluate the role of pressure and composition (in particular, alkalinity). However, the exponential trend is likely to remain and therefore should be taken into account when estimating the amount of S that can be transported in magmas.

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