

HIGHLIGHTS AND BREAKTHROUGHS

Anhydrite: An important sulfur binder limiting the climatic impact of subaerial volcanic eruptions

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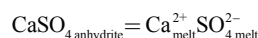
Abstract: Gaseous sulfur compounds are critical climate active volatile components released by volcanoes. Volcanic eruptions can emit massive amounts of H₂S and SO₂ into the atmosphere, which react with oxygen and H₂O to sulfuric acid. Formation of H₂SO₄ aerosols, which have on a geological timescale short-term residence times of month or years, may have global climatic impact. The phase stability of sulfur-bearing minerals such as anhydrite in erupting magmas may be a key controlling factor limiting SO₂ emission during subaerial volcanic activity (Huang and Keppler, January 2015 issue of *American Mineralogist*). **Keywords:** Sulfur fluid/melt partition behavior, anhydrite stability, degassing, volcanic eruptions

Release of sulfur-bearing volcanic gas into the troposphere may cause local and distal acid haze and rain leading to crop failure and disease, e.g., in Europe during the Iceland Laki eruption 1783–84 (Thordarson and Self 2003). Injection of sulfur-bearing gas into the stratosphere followed by formation of sulfuric acid aerosols is capable to increase the Earth's albedo significantly. The climatic eruption of Mt Pinatubo in 1991, yielding about 5 km³ of erupted magma (Dense Rock Equivalent, DRE) (Scott et al. 1996) and more than 17 Mt SO₂ gas (Bluth et al. 1992), decreased the global surface temperature by 0.5 °C for the following two years of eruption (McCormick et al. 1995). Volcanic super-eruptions, emitting hundreds of km³ DRE and Gt of SO₂, are suggested to decrease surface temperatures dramatically (Self and Blake 2008). Severe climatic impact due to the formation of large igneous provinces accompanied by massive H₂S and SO₂ degassing over time periods of a few million years may have triggered mass extinctions in Earth's history (e.g., Courtillot 1999; Self et al. 2008).

The physicochemical properties of silicate melts coexisting with sulfur-bearing phases (minerals, fluids, and gases) have been investigated for more than half a century and are summarized in Behrens and Webster (2011). Spectroscopic techniques provide evidence that sulfur species are dissolved in silicate melts mainly as S²⁻ and SO₄²⁻ depending on f_{O_2} (Wilke et al. 2011). Saturation of sulfur-species at pre-eruptive P and T conditions depends on bulk silicate melt composition, P , T , $a_{\text{sulfur-species}}$ in the fluid and the stability of sulfur-bearing minerals, ranging from 10 to 100 ppm level in felsic melts (Keppler 2010; Huang and Keppler 2015) to >1 wt% in basaltic melt (Beermann et al. 2011).

Degassing of sulfur components from ascending and erupting magma depends on numerous physicochemical parameters such as bulk melt composition, f_{O_2} , sulfur-species content, fluid composition, phase stability of sulfur-bearing minerals (e.g., anhydrite and pyrrhotite), fluid/melt partitioning, mobility of sulfur-species, and decompression rate. Although intensively experimentally studied, to date sulfur-species saturation data even in simplified rhyolitic melt compositions vary by a factor of 10 at oxidized conditions (Huang and Keppler 2015). At P , T , X conditions where silicate melt coexists with sulfur-bearing minerals, solubility can be defined as sulfur concentration at sulfide saturation (SCSS) under reducing conditions and at anhydrite saturation (SCAS) under oxidizing conditions (Baker and Moretti 2011).

Experimental studies on sulfur-species solubility of silicate melts at sulfur-bearing mineral saturation and fluid/melt partitioning are still highly important to improve thermodynamic models for the behavior of sulfur-species in silicate melts, hydrous fluids and gases. Especially, there is a need for experimental data sets in simplified compositional systems to improve rigorous thermodynamic models that describe sulfur-species saturation in silicate melts and fluid/melt partitioning quantitatively. Huang and Keppler (2015, this volume) investigated systematically sulfur-species saturation in a simplified hydrous rhyolitic melt. At reducing conditions, within the stability field of wollastonite, $a_{\text{S}^{2-}, \text{fluid}}$ and bulk CaO content were varied. At oxidizing conditions, within the stability field of anhydrite, H₂SO₄ concentration of fluid as well as bulk CaO content was varied (SCAS). At reducing conditions, the sulfur content of the melt increases linearly with sulfur content in the fluid, resulting in a sulfur fluid/melt partition coefficient ($D_s^{\text{fl/m}}$) of about 500. Variation of CaO melt concentration has no measurable effect on $D_s^{\text{fl/m}}$. In contrast, at oxidized conditions within the stability field of anhydrite, an inverse correlation between sulfur and CaO concentration in the melt is observed. Within error, at 850 °C and 2 kbar the solubility product $K = [\text{CaO}][\text{SO}_3]$ is constant leading to a rigorous thermodynamic model based on the simple reaction



that was suggested by Carroll and Rutherford (1987). Similar inverse correlations are observed for S²⁻ and FeO concentration in hydrous albitic melt coexisting with FeS at reducing conditions (Bradbury 1983) and F vs. CaO concentrations at fluorite saturation in hydrous haplogranite melt (Dolejš and Baker 2004). The temperature dependence of the solubility product $K = [\text{CaO}][\text{SO}_3]$ corresponds to a ΔH_r of 238 kJ/mol. Together with a $D_s^{\text{fl/m}}$ of 100–150, depending slightly on CaO melt content, this enables to model the SO₂ degassing potential of felsic melts.

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Huang and Keppler (2015) provide clear evidence that CaO limits SO₂ degassing potential of felsic magma significantly by stabilizing anhydrite.

Magmatic sulfur-bearing minerals are commonly observed in volcanic systems. At reducing conditions pyrrhotite and Cu-Fe sulfides, and at oxidizing conditions anhydrite and h  y  ne are often stable in sub-volcanic magma chambers (Parat et al. 2011). This limits H₂S/SO₂ degassing during volcanic eruptions and may be an important key factor for the equilibrium of global temperature preventing us from a Snowball Earth.

Improvements of thermodynamic models are highly needed for a deeper understanding of the complex behavior of sulfur components in volcanic systems. It is necessary to investigate systematically the effect of melt polymerization on sulfur-species saturation and fluid/melt partitioning. On top of that, the experimental results of Huang and Keppler (2015) motivate to determine the solubility product of additional magmatic sulfur-bearing mineral phases, e.g., pyrrhotite in basaltic melts and h  y  ne in phonolitic melts, coexisting with aqueous fluids. Experimental investigations of the effect of mixed volatiles (e.g., H₂O and chlorine) on sulfur-species saturation and fluid/melt partitioning are in progress and will refine the understanding of sulfur species degassing processes (Botcharnikov et al. 2004; Stelling et al. 2008; Beermann et al., in review). Additional important keys to elucidate H₂S/SO₂ degassing processes are experimental studies on the diffusion of sulfur-species in hydrous melts (Behrens and Stelling 2011), the dynamics of fluid bubble formation and bubble growth controlled by magma ascent rate (Nowak et al. 2011; Fiege et al. 2014; Marxer et al. 2015) and potential post-eruptive binding reactions and adsorption processes of gaseous sulfur-species with volcanic ash particles (Schmauss and Keppler 2014).

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