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HIGHLIGHTS AND BREAKTHROUGHS

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

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

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35 Release of sulfur-bearing volcanic gas into the troposphere may cause local and distal acid haze
36 and rain leading to crop failure and disease, e.g. in Europe during the Iceland Laki eruption 1783-
37 84 (Thordarson and Self, 2003). Injection of sulfur-bearing gas into the stratosphere followed by
38 formation of sulfuric acid aerosols is capable to increase the Earth's albedo significantly. The
39 climatic eruption of Mt Pinatubo in 1991, yealding about 5 km³ of erupted magma (Dense Rock
40 Equivalent, DRE) (Scott et al. 1996) and more than 17 Mt SO₂ gas (Bluth et. al. 1992), decreased
41 the global surface temperature by 0.5 °C for the following two years of eruption (McCormick et
42 al. 1995). Volcanic supereruptions, emitting hundreds of km³ DRE and Gt of SO₂, are suggested
43 to decrease surface temperatures dramatically (Self and Blake, 2008). Severe climatic impact due
44 to the formation of large igneous provinces accompanied by massive H₂S and SO₂ degassing over
45 time periods of a few million years may have triggered mass extinctions in Earth's history (e.g.
46 Courtillot 1999, Self et al. 2008).

47 The physicochemical properties of silicate melts coexisting with sulfur-bearing phases
48 (minerals, fluids and gases) have been investigated for more than half a century and are
49 summarized in Mineralogical Reviews 73 by Behrens and Webster (2011). Spectroscopic

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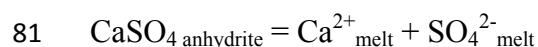
50 techniques provide evidence that sulfur species are dissolved in silicate melts mainly as S^{2-} and
51 SO_4^{2-} depending on f_{O_2} (Wilke et al. 2011). Saturation of sulfur-species at pre-eruptive P and T
52 conditions depends on bulk silicate melt composition, P, T, $a^{\text{sulfur-species}}$ in the fluid and the
53 stability of sulfur-bearing minerals, ranging from 10 to 100 ppm level in felsic melts (Keppeler,
54 2010; Huang and Keppeler, this issue) to >1 wt% in basaltic melt (Beermann et al., 2011).

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

64 Experimental studies on sulfur-species solubility of silicate melts at sulfur-bearing
65 mineral saturation and fluid/melt partitioning are still highly important to improve
66 thermodynamic models for the behavior of sulfur-species in silicate melts, hydrous fluids and
67 gases. Especially, there is a need for experimental data sets in simplified compositional systems
68 to improve rigorous thermodynamic models that describe sulfur-species saturation in silicate
69 melts and fluid/melt partitioning quantitatively. Huang and Kepper (this issue) investigated
70 systematically sulfur-species saturation in a simplified hydrous rhyolitic melt. At reducing
71 conditions, within the stability field of wollastonite, $a^{S^{2-}, \text{fluid}}$ and bulk CaO content were varied.
72 At oxidizing conditions, within the stability field of anhydrite, H_2SO_4 concentration of fluid as
73 well as bulk CaO content was varied (SCAS). At reducing conditions, the sulfur content of the

74 melt increases linearly with sulfur content in the fluid, resulting in a sulfur fluid/melt partition
75 coefficient ($D_S^{fl/m}$) of about 500. Variation of CaO melt concentration has no measurable effect
76 on $D_S^{fl/m}$. In contrast, at oxidized conditions within the stability field of anhydrite, an inverse
77 correlation between sulfur and CaO concentration in the melt is observed. Within error, at 850°C
78 and 2 kbar the solubility product $K = [CaO][SO_3]$ is constant leading to a rigorous
79 thermodynamic model based on the simple reaction

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83 that was suggested by Carroll and Rutherford (1987). Similar inverse correlations are observed
84 for S^{2-} and FeO concentration in hydrous albitic melt coexisting with FeS at reducing conditions
85 (Bradbury 1983) and F vs. CaO concentrations at fluorite saturation in hydrous haplogranite melt
86 (Dolejš and Baker, 2005). The temperature dependence of the solubility product $K = [CaO][SO_3]$
87 corresponds to a ΔH_R of 238 kJ/mol. Together with a $D_S^{fl/m}$ of 100-150, depending slightly on
88 CaO melt content, this enables to model the SO_2 degassing potential of felsic melts. Huang and
89 Keppler (this issue) provide clear evidence that CaO limits SO_2 degassing potential of felsic
90 magma significantly by stabilizing anhydrite.

91 Magmatic sulfur-bearing minerals are commonly observed in volcanic systems. At
92 reducing conditions pyrrhotite and Cu-Fe sulfides, and at oxidizing conditions anhydrite and
93 häüyne are often stable in sub-volcanic magma chambers (Parat et al. 2011). This limits H_2S/SO_2
94 degassing during volcanic eruptions and may be an important key factor for the equilibrium of
95 global temperature preventing us from a Snowball Earth.

96 Improvements of thermodynamic models are highly needed for a deeper understanding of
97 the complex behavior of sulfur components in volcanic systems. It is necessary to investigate

98 systematically the effect of melt polymerisation on sulfur-species saturation and fluid/melt
99 partitioning. On top of that, the experimental results of Huang and Keppler (this issue) motivate
100 to determine the solubility product of additional magmatic sulfur-bearing mineral phases, e.g.
101 pyrrhotite in basaltic melts and h a yne in phonolitic melts, coexisting with aqueous fluids.
102 Experimental investigations of the effect of mixed volatiles (e.g. H₂O and chlorine) on sulfur-
103 species saturation and fluid/melt partitioning are in progress and will refine the understanding of
104 sulfur species degassing processes (Botcharnikov et al., 2004; Stelling et al., 2008; Beermann et
105 al., submitted). Additional important keys to elucidate H₂S/SO₂ degassing processes are
106 experimental studies on the diffusion of sulfur-species in hydrous melts (Behrens and Stelling,
107 2011), the dynamics of fluid bubble formation and bubble growth controlled by magma ascent
108 rate (Nowak et al., 2011; Fiege et al., 2014; Marxer et al. submitted) and potential post-eruptive
109 binding reactions and adsorption processes of gaseous sulfur-species with volcanic ash particles
110 (Schmauss and Keppler, 2014).

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