

## Redox-limited magmatic degassing

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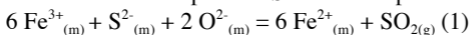
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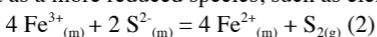
Studies of sulfur speciation in basaltic systems have long suggested that sulfur, present as either S<sup>2-</sup> or S<sup>6+</sup> within the melt, must undergo oxidation/reduction to degas as SO<sub>2</sub>. The question is: does this change in sulfur valence state balance with other multi-valent cations during degassing? To address this issue we have utilised a comprehensive analytical approach, based around micro-XANES synchrotron determination of Fe and S speciation, to understand the relationship between magma degassing and redox states.

Melt inclusions from the 2008 summit eruption of Kilauea Volcano, Hawaii, record significant sulfur degassing (~1400-110 ppm) but relatively homogenous major element compositions (FeO\* 10.8 +/- 0.14 wt%). Micro-XANES analyses of Fe speciation indicate there is a continuous correlation between decreasing Fe<sup>3+</sup>/ΣFe and decreasing sulfur content, in which in Fe<sup>3+</sup>/ΣFe decreases from 0.12 to 0.05, consistent with typical literature values for Kilauea Fe<sup>3+</sup>/ΣFe. Sulfur loss also coincides with a decreasing XANES sulfate peak from ~ 9% of total S to zero, although with some variability between inclusions.

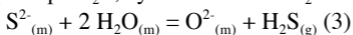
If sulfur degases as SO<sub>2</sub>, as predicted from gas emissions, the net reaction for coupled Fe-S redox is expected to be:



From this we would predict that degassing of the S should result in the reduction of all of the Fe<sup>3+</sup> in the melt. Clearly this is not the case. Instead, a major fraction of the S must be lost as a more reduced species, such as elemental S:



or perhaps H<sub>2</sub>S, by reaction with H<sub>2</sub>O dissolved in the melt:



However, neither elemental S or H<sub>2</sub>S are abundant in the gas plume, suggesting that rapid S oxidation immediately after degassing may be responsible for the dominance of SO<sub>2</sub> observed in the gas phase. Reactions (1) and (2) imply that sulfur degassing should decrease as *f*O<sub>2</sub> decreases, making it a self-limiting process that is not expected to go to completion, as observed. Loss of S as H<sub>2</sub>S is however, redox neutral (reaction 3)