Redox-limited magmatic degassing

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Studies of sulfur speciation in basaltic systems have long suggested that sulfur, present as either S^{2-} or S^{6+} within the melt, must undergo oxidation/reduction to degas as SO_2. 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 $Fe^{3+}/\sum Fe$ and decreasing sulfur content, in which in $Fe^{3+}/\sum Fe$ decreases from 0.12 to 0.05, consistent with typical literature values for Kilauea $Fe^{3+}/\sum Fe$. 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_2, as predicted from gas emissions, the net reaction for coupled Fe-S redox is expected to be:

$$6\,Fe^{3+}_{(m)} + S^{2-}_{(m)} + 2\,O^{2-}_{(m)} = 6\,Fe^{2+}_{(m)} + SO_{2(g)} \quad (1)$$

From this we would predict that degassing of the S should result in the reduction of all of the Fe^{3+} 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:

$$4\,Fe^{3+}_{(m)} + 2\,S^{2-}_{(m)} = 4\,Fe^{2+}_{(m)} + S_{2(g)} \quad (2)$$

or perhaps H_2S, by reaction with H_2O dissolved in the melt:

$$S^{2-}_{(m)} + 2\,H_2O_{(m)} = O^{2-}_{(m)} + H_2S_{(g)} \quad (3)$$

However, neither elemental S or H_2S are abundant in the gas plume, suggesting that rapid S oxidation immediately after degassing may be responsible for the dominance of SO_2 observed in the gas phase. Reactions (1) and (2) imply that sulfur degassing should decrease as fO_2 decreases, making it a self-limiting process that is not expected to go to completion, as observed. Loss of S as H_2S is however, redox neutral (reaction 3)