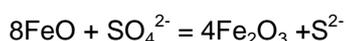


## An insight into the ‘magnetite crisis’ via magnetite hosted melt inclusions from the Pual Ridge.

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The solubility of sulphur in silicate melts has been demonstrated by Jugo (2005) to be an order of magnitude higher as the oxidised sulphate species ( $\text{SO}_4^{2-}$ ) than reduced sulphide ( $\text{S}^{2-}$ ). Thus in relatively oxidised arc magmas, where sulphate is the predominant species, S solubilities are extremely high. However, the removal of  $\text{Fe}^{3+}$  from the melt consequent to fractional crystallisation of Fe-Ti oxide results in a shift in the redox exchange:



This relationship quantifies that the modest change in the Fe redox ratio can have great influence on sulphur speciation. During evolution of arc magmas, magnetite is the first phase to appear on the liquid line of descent during fractional crystallisation that significantly lowers the total Fe and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  of the residual magma. This has led to the proposal that fractional crystallisation of magnetite may trigger sulphide saturation in the residual melt via the reduction of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (i.e. the “magnetite crisis”, Jenner et al., 2010).

Subaqueous quenched volcanic glasses provide the clearest record of magmatic evolution by fractional crystallisation. However, during the subaqueous eruption of oxidised arc magmas, significant concentrations of volatile species such as  $\text{CO}_2$ , S and some  $\text{H}_2\text{O}$  are lost from the resultant quenched glass. The behaviour of selenium has been traditionally thought to parallel that of sulphur in silicate melts (Palme and O'Neill, 2003) but has subsequently been shown to suffer less volatile loss upon quenching than S (Fig. 1).

In order to reconcile the observed chalcophile trace element behaviour during evolution by fractional crystallisation of oxidised arc magmas, precise determination of the sulphur speciation in the melt must first be obtained. However, as significant sulphur degassing occurs in oxidised arc magmas, the pre-eruptive sulphur

content of the melt cannot be analysed directly from the quenched glasses.

To circumvent this problem,  $\text{S}^*$  was established as the pre-eruptive ratio of S to Se. As Se is retained in oxidised arc magmas and can be measured in quenched glasses, it can be calibrated with the S/Se of MORBs and oxidised boninites to yield an estimate of the  $\text{S}^*$  in oxidised arc magmas (Jenner et al., 2010).

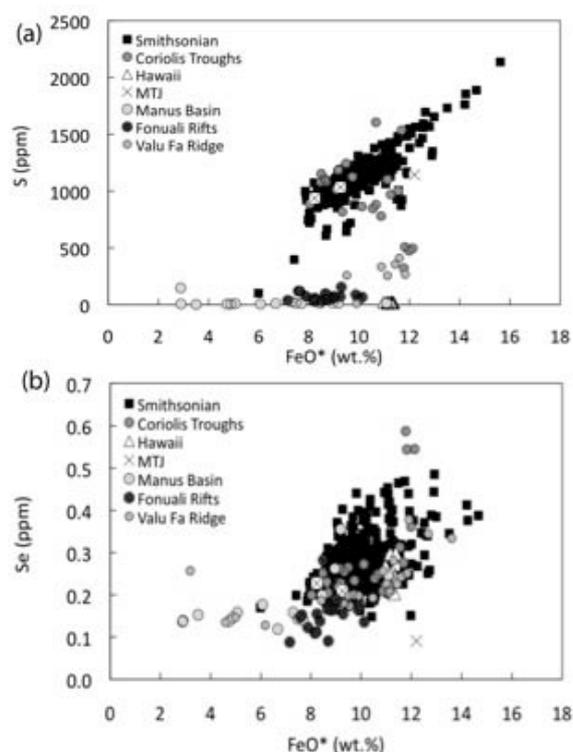


Fig. 1: Co-variation diagrams of (a) S and (b) Se vs.  $\text{FeO}^*$  (mass%) for glasses from the Manus and Lau basins in comparison with the MORB. Demonstrates that oxidized magmas lose S upon degassing whilst reduced melts retain their pre-eruptive S content (Jenner, et al., 2010).

Analysis of melt inclusions contained within Fe-Ti oxide phases is advantageous as volatile and chalcophile elements such as S

behave incompatibly in magnetite-ulvöspinel solid solution. Thus the melt inclusions trapped at the time of oxide crystallisation preserve the original, un-degassed volatile content.

Furthermore the analysis of melt inclusions, contained in phases separated from the Pual Ridge glasses, provides a unique opportunity for the validity of the S/Se method for the determination of the  $S^*$  to be tested. Electron Microprobe Analysis (EMPA) of melt inclusions contained within titanomagnetite separates from the Pual Ridge glasses (Fig. 2) have been shown to contain mean S concentrations of ~616 ppm, which is in accordance with the ~600 ppm predicted for the melt by the S/Se method.

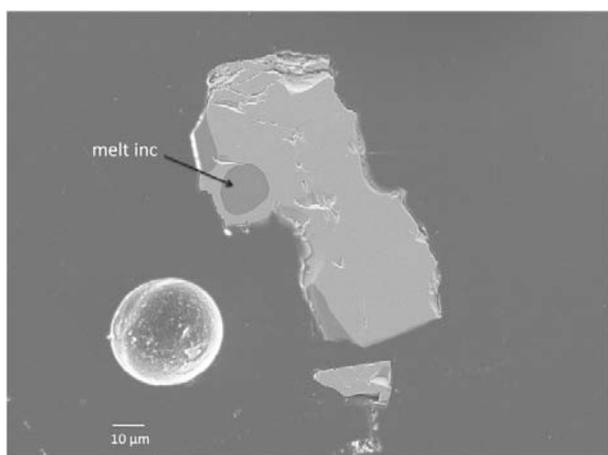


Fig. 2: Titanomagnetite phenocryst containing a silicate melt inclusion from the sample MD-7, Pual Ridge.

EMPA of melt inclusions contained in titanomagnetite phenocrysts from sample MD-7 evidence mean Cu concentrations of ~281 ppm, and is comparable with that measured for the quenched glass by LA-ICP-MS (Fig. 3; Jenner et al., 2010). The melt inclusions in the titanomagnetite phenocrysts record both the analysed peak Cu and the estimated peak S concentration in the melt immediately prior to sulphide saturation. This implies that magnetite crystallisation may trigger, but is not simultaneous with, sulphide saturation.

The Pual Ridge glasses record a fractional crystallisation sequence for which the major and trace element abundances of the residual melt have been thoroughly characterised (Jenner et al., 2010). However, only by the analysis of melt

inclusions contained within phases separated from the quenched glasses may the concentrations of volatile elements such as S, CO<sub>2</sub> and H<sub>2</sub>O be obtained directly.

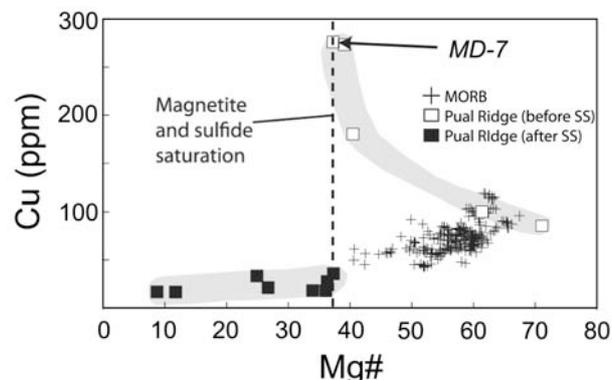


Fig. 3: Co-variation diagram of Cu vs. Mg#. Note the sharp decrease in Cu content of the melt at ~40 Mg#, representing magnetite induced sulphide saturation (Jenner et al., 2010).

Thus, in order to develop a greater understanding of the processes at play during evolution of arc magmas, the previously determined residual melt concentrations must be reconciled with melt inclusion data. Analysis of the melt inclusions contained within the phases separated from the subaqueous glasses over the fractionation interval evidenced by the Pual Ridge samples allows the validity of the 'magnetite crisis' to be rigorously tested. This is significant because it may relate to pre-enrichment of chalcophile trace elements and eventually to the formation of Cu-Au-Ag provinces and the development of the continental crust.

## REFERENCES

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