

Evolution and differentiation of sulphur in sub arc environment

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Understanding the processing of sulphur through the subduction zone system remains one of the major challenges in geoscience. Not only is sulphur a tracer of magmatic processes but produces economically important deposits and can have a short term effect on climate. High S-concentrations in arc magmas (>1000ppm) are often explained by the presence of S⁶⁺ (sulphate ions) related to the prevalence of oxidizing conditions. Yet, the behaviour of sulphur in magmatic systems at mid to deep crustal conditions (>5kbar) has been neglected. Evidence of this behaviour from natural samples is limited and previously experimental simulation faced many challenges, particularly, oxygen fugacity (fO_2) control at high-pressures conditions.

Recent studies [1] [2] have suggested that the transition from S²⁻ to S⁶⁺ (sulphide to sulphate melt species) takes place in an $\log fO_2$ window of ΔFMQ 0 to +2 at 2kbar and 1000°C. In this study we explore this equilibrium at higher pressures of 10 and 15kbar. Piston cylinder experiments were performed using a synthetic basaltic andesite from Laguna del Maule (Chile) doped with S (3000 ppm), Cl (1500 ppm), with 5.5 wt% water added. 1.5 wt.% carbon was added by reaction of Ca(OH)₂ with air. Temperatures were between 850-950°C and fO_2 was controlled from ΔFMQ -0.5 to +5.5 using the new solid oxygen buffers technique [3].

Our results suggest a strong control of oxygen fugacity over phase relations. At reduced conditions ΔFMQ -0.5 and +1 crystallisation of plagioclase is suppressed and as result Al₂O₃, CaO contents of the melt are higher by 2-3wt.% compared to the higher fO_2 conditions. At low fO_2 the sulphide pyrrhotite is stable as expected but it's stability reaches up to ΔFMQ +3 at 10 and 15 kbar. Within this pyrrhotite field sulphur solubility increases strongly above ΔFMQ +3, suggesting an additional sulphate component is increasing in the melt. The 'sulphate only' stability field was reached by ΔFMQ +5 as shown by switch to anhydride crystals. Thus, the S²⁻ to S⁶⁺ transition at 10 and 15kbar appears to occur at a higher oxygen fugacity than the ΔFMQ range of 0 to +2 proposed for 2kbar [1].

[1]Klimm *et al.* (2012) *Chem. Geol.* **322-323**, 250-267 [2] Masotta and Keppler (2015) *GCA* **158**, 79-102 [3]Matjuschkin *et al.* (2015) *Contrib. Mineral. Petrol.* **169**, 9