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Sulfur partitioning between magmatic phases at sulfide-sulfate transition - Implications for metal mobility

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Sulfur is a volatile component that participates in a number of processes from magma generation to volcanic eruption affecting magma properties and controlling mobility of many different elements. These effects depend on abundance and proportions of redox-sensitive S species and on their partitioning between magmatic phases.

Literature data and our experiments at 100 to 500 MPa and temperature of 1000-1250°C demonstrate that S partitioning in magmas is largely controlled by T, fO_2 and fS_2 as well as by melt composition. Furthermore, we found that Fe has a fundamental influence on S speciation in silicate liquids with upto 90% decrease in S^{6+}/S_{tot} ratio as FeO content increases from 0 to 18 wt% at fixed fO_2 . It implies that the reaction constant of sulfide-sulfate transition is highly sensitive to melt composition opening the transition range from ca. 2 log fO_2 units in typical basaltic-andesitic melts to 4-4.5 log fO_2 units between Fe-poor and Fe-rich melts.

Change in S^{6+}/S^{2-} has important influence on activity coefficients of S-bearing species affecting S partitioning between silicate melt, fluid and S-rich phases and mobilization of metals. It is further complicated by the presence of Cl in the magma decreasing (by 30-40%) fluid/melt partition coefficient of oxidized S but having only small effect on partitioning of reduced S.

In contrast to available models, experimental basalts demonstrate enhanced ability to dissolve S close to sulfide-sulfate transition. It has important implications for the stability of S-rich phases and mobility of metals in the processes of melting and crystallization.

Sulfur speciation in melt and fluid as well as sulfur partitioning into S-rich phases imposes major control on the

mobility of metals. For instance, Au partitioning is mostly controlled by S²⁻ with increasing contribution of Cl-bearing ligands as sulfide sulfur converts into sulfate. On the other hand, partitioning of metals between silicate melt and FeS liquids and solids is weakly affected by redox change at sulfide-sulfate transition.

In contrast to available models of S solubility, basalts demonstrate enhanced ability to dissolve S close to sulfide-sulfate transition. It has important implications for the stability of FeS phases in the processes of melting and crystallization as will be illustrated by new empirical model of S solubility.