

Volatile/melt equilibrium in subvolcanic reservoirs: the partitioning of sulfur and chlorine

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Understanding volatile/melt equilibria is essential for the use of gas chemistry in volcanic monitoring as well as for the prediction of the likelihood of magmatic-hydrothermal ore deposit formation. The abundance of various S and Cl species in magmatic volatiles may provide information on magma chamber processes and also determines the efficiency of the extraction of economically important metals from the magma.

We conducted experiments in rapid-quench MHC pressure vessels and piston cylinder apparatus at 150 to 500 MPa and 800-1240 °C to identify the most important controls on the volatile/melt partition coefficients of S and Cl. Most experiments employed relatively high fluid/melt mass ratios of 0.33 to 16, which allowed precise estimation of the volatile phase composition at run conditions by mass balance calculations. The results show that the volatile/melt partition coefficients of Cl and both reduced and oxidized S strongly increase with increasing degree of melt polymerization, i.e. with melt composition evolving from mafic to felsic. At fO_2 less than 0.5 log units above the Ni-NiO buffer, S is primarily dissolved as FeS species in the silicate melt and its volatile/melt partition coefficients are mostly determined by the activity of FeO in the melt and the activity coefficients of dissolved FeS species. At 200 MPa confining pressure, pyrrhotite saturation limits the maximum H₂S concentration in the volatile phase to a few mol% in equilibrium with a wide range of melt compositions from basalt to rhyolites. At the sulfide/sulfate transition, the volatile/melt partition coefficients of S drop nearly an order of magnitude due to a remarkable change in the dissolution mechanism of S in the silicate melt. Oxidized S is present as sulfate species in melt, which is more easily accommodated by depolymerized melt structure resulting in exponentially increasing volatile/melt partition coefficients with increasing melt polymerization. It has also been shown, that alkali metal rich silicate melts are much more efficient at dissolving oxidized sulfur species than Ca-rich ones, which are in turn significantly more favorable to Mg-rich ones. Therefore, degassing of oxidized sulfur is the least efficient from alkaline mafic magmas and peralkaline rhyolites.

Volatile/melt partition coefficients of Cl decrease nearly 2 orders of magnitude from rhyolite to basalt melt compositions; therefore Cl degassing is rather inefficient from intermediate and mafic magmas. In the subvolcanic P-T regime, the chloride fraction of the volatile phase exsolving from typical calc-alkaline melts is composed of sub equal amounts of alkali metal- and Fe chlorides and HCl.

Decompression induced degassing may allow the extraction of most reduced S even from mafic magmas; whereas crystallization induced degassing will play an increasingly important role in the extraction of oxidized S and Cl at subvolcanic P-T conditions.