

The importance of sulfur as ligand to the PGE – Implications for the enrichment of PGE in magmatic sulfides

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Previous studies have shown that PGE dissolve as oxides species in silicate melts (i.e. associated with O^{2-} as a ligand). However, the majority of these studies were carried out using synthetic CMAS ($CaO-MgO-Al_2O_3-SiO_2$) silicate melt compositions. Conversely natural melts contain appreciable FeO and variable S , raising the question whether PGE solubilities derived from CMAS systems are directly relevant to natural silicate melts. In addition to oxygen, dissolved S^{2-} may associate with the PGE as a ligand, and enhance their solubility in silicate melt when compared to a S -free melt. Furthermore, deciphering the role of S^{2-} as a ligand to the PGE will improve our understanding of the enrichment of PGE in magmatic sulfides.

In order to test if PGE associate with S^{2-} as a ligand, the effect of S on the solubility of the PGE in silicate melts was investigated. Therefore, a natural picrite was equilibrated with Ru (or Pt) metal at $1300^{\circ}C$ in a 1-atm vertical gas mixing furnace under controlled fS_2 and fO_2 . Results show that the solubility of Ru in picrite increases more than one order of magnitude in S -bearing experiments compared to S -free melts at identical fO_2 . Ruthenium thus shows a distinct preference to bond with dissolved S^{2-} , which may also be applicable for other PGE, since initial results show that also Pt solubility in silicate melts increases in the presence of S^{2-} .

In order to evaluate the importance of S^{2-} as a ligand to Ru (or other PGE) relative to O^{2-} from these results, it is necessary to assess how much O^{2-} is available as a ligand to the PGE. The relevant oxygen fraction is the one that partitions into the silicate melt from the gas atmosphere via the oxidation of multivalent elements. Because Fe is the most abundant multivalent element in basalts, oxygen absorbed by the silicate melt is directly related to its Fe^{3+}/Fe^{2+} ratio and can thus be quantified. At FMQ ~ 1500 ppm O^{2-} are absorbed by the silicate melt, compared to 140 ppm S^{2-} (at $\log fS_2 = -2.3$). Combining these abundances with Ru concentrations in the experimental glasses at FMQ (S-free: ~ 0.025 ppm Ru; S-bearing: ~ 1 ppm Ru) indicates that the preference that Ru has to associate with S^{2-} is ~ 800 times larger than with O^{2-} . This simple estimate clearly shows that sulfur has a major control on Ru solubility in silicate melts, which may also be valid for other PGE, as illustrated by Pt in our experiments.

Conventionally it is thought that sulfide melt needs to fully equilibrate with large volumes of magma in a turbulent magma chamber to efficiently scavenge the PGE. Our experiments favour modified mechanism: At the onset of sulfide melt saturation, PGE will be extracted directly into the sulfide liquid, owing to their pre-existing association with S^{2-} . The proposed mechanism allows sulfides to be highly enriched in PGE, and removes the need for complex processes that allow complete equilibrium between a small fraction of sulfide liquid and a much larger volume of magma.