



## **Experimental determination of the solubilities of Ir, Pt, Pd and Au in sulfide- and sulfate-saturated basaltic melts at 1300 °C and 1 GPa: Implications for HSE fractionation in subduction zones.**

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It is well established that the behavior of the highly siderophile elements (HSE = Re, Os, Ir, Ru, Rh, Pt, Pd, Au) in the Earth's mantle and crust is dominantly controlled by sulfide phases. However, the oxidation state in arc magmas at their source may be too high to stabilize sulfides, and little is known about the behavior of the HSE under such conditions. To determine how destabilization of sulfides under relatively high  $fO_2$  affects the behavior of Ir, Pt, Pd and Au in basaltic melts, we conducted two sets of anhydrous experiments at 1300 °C and 1.0 GPa using a piston-cylinder apparatus. The main difference between the two sets of experiments is the contrasting  $fO_2$  imposed. The first set of experiments were equilibrated at oxygen fugacities lower than  $\Delta\log fO_{2(FMQ)} = -1$  (FMQ = fayalite-magnetite-quartz  $fO_2$  buffer) and produced sulfide-saturated melts. The second set of experiments were equilibrated at oxygen fugacities equal to or higher than  $\Delta\log fO_{2(FMQ)} = +1.9$  and produced sulfate-saturated melts. In both cases metals were added as discrete pieces of Pt<sub>90</sub>Ir<sub>10</sub> and Au<sub>80</sub>Pd<sub>20</sub> alloys (the latter was also used in some cases as container for the experiments). Run products consisted of glasses of basaltic composition, a sulfur-bearing

phase (Fe-sulfide, Ca-sulfate), a lherzolitic mineral assemblage (olivine, orthopyroxene, clinopyroxene, spinel) and residual HSE phases. The compositions of coexisting olivine and spinel were used to estimate the  $fO_2$  in all experiments. Concentrations of the HSE in the glasses were determined by LA-ICP-MS. The concentrations of Pd and Au in oxidized (sulfate-saturated) melts (Pd =  $11.9 \pm 1.2$  ppm; Au =  $4.7 \pm 0.9$  ppm) were significantly higher than the concentrations of these metals in reduced, sulfide-saturated melts (Pd =  $0.63 \pm 0.31$  ppm; Au =  $0.52 \pm 0.08$  ppm). For Pt, the content was similar in sulfide and sulfate saturated melts ( $1.23 \pm 0.46$  and  $1.6 \pm 0.3$  ppm, respectively), whereas Ir behaved opposite to Pd and Au, its concentration being slightly higher in the reduced melts with respect to oxidized melts ( $0.24 \pm 0.08$  and  $0.07 \pm 0.02$  ppm, respectively). In addition, laser ablation profiles indicate that polymetallic alloys were present (as nano-scale nuggets) in all experiments, regardless of  $fO_2$ . Textural and compositional data from residual HSE phases enclosed in sulfides indicate that Pd is strongly chalcophile, whereas Pt and Ir have a stronger affinity for Fe-based alloys. In contrast, Au did not show preference for the sulfide or the Fe-alloy phase. These results support the hypothesis that except for Pd and Au, the HSE reside in mantle sulfides mostly as melting-resistant atomic clusters and micro alloys (e.g., Lorand et al., 1999). We suggest that in metasomatized, and sufficiently oxidized arc sources, mantle sulfides are not stable, and Au and Pd behave as incompatible elements, being fractionated during partial melting from other highly siderophile elements, which are retained in alloys.

Lorand, J-P., Pattou, L., and Gros, M., 1999, Fractionation of platinum-group elements and gold in the upper mantle: A detailed study in Pyrenean orogenic lherzolites: *Journal of Petrology*, v. 40, p. 957-981.