PHASE EQUILIBRIUM CONSTRAINTS ON THE CONDITIONS OF FORMATION OF LAURITE + IPGE ALLOY

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To more completely assess the origin of associated laurite (RuS$_2$) and Ru-Os-Ir (IPGE) alloys which are found as inclusions in near-liquidus phenocrysts, such as chromite, we conducted experiments to evaluate the effects of T and f$_{S_2}$ on phase relations in the system Ru-Os-Ir-Cu-S. Cu-S melt (added as a flux) + IPGE metals were held in silica crucibles, and experiments were done in both vertical-tube gas-mixing furnace apparatus (low f$_{S_2}$) and evacuated silica tubes (higher f$_{S_2}$ buffered by Pt-PtS) at 1200-1250°C for 1-3 days. The solubility of Cu in run-product laurite and alloy was found to be negligible. At constant f$_{S_2}$ of 10$^{-1}$ atm, the two-phase field of laurite and alloy is restricted to only the most Ru-rich bulk compositions (X$_{Ru}$ > 0.75) at 1250°C, and slightly expands to encompass more Ru-poor compositions (X$_{Ru}$ > 0.5) at 1200°C. At this f$_{S_2}$, laurites show virtually no change in composition over the temperature range examined, remaining very close to pure RuS$_2$. An increase in sulfur fugacity to 10$^{-0.37}$ atm at 1200°C and 10$^{-0.05}$ atm at 1250°C resulted in a considerable expansion of the two-phase field, with both laurite and alloy dissolving considerably more Os + Ir. For example, at 1250°C and f$_{S_2}$ of 10$^{-0.05}$, the Os and Ir content of laurite increases to ~20 and ~12 wt%, respectively. Coexisting alloy in both sets of high f$_{S_2}$ experiments contain less than 10 wt% Ru.

The compositions of coexisting laurite and IPGE alloy defined by our high f$_{S_2}$ experiments show remarkable similarity to coexisting PGM compositions preserved in natural chromitites from several localities. In some cases, however, natural laurite-alloy pairs contain a few percent less Ru than compositions defined by our experiments. Consideration of the effects of T and f$_{S_2}$ on binary IPGE phase relations suggests that reasons for this discrepancy are 1) natural laurite-alloy equilibration temperatures are lower than 1200-1250°C or 2) the f$_{S_2}$ at which the pairs form is higher than our experiments. In the case of 1), a change in the composition of laurite-alloy pairs requires an external source of sulfur, which would be precluded once the minerals are trapped in a sulfur-impermeable host phase. Given that high temperature entrapment is inferred by textural relations, we suggest 2) is the most likely cause of this distinction. Limits on the f$_{O_2}$ of magmas that may precipitate alloy-laurite pairs stems from the requirement that such magmas remain sulfide-liquid undersaturated, at least until PGMs are trapped in their chromite host. Using the thermodynamic model of Wallace and Carmichael (1993), we have estimated that a magma with ~10 mole% FeO will achieve sulfide liquid saturation at f$_{O_2}$ less than FMQ-0.8 at the conditions of our high f$_{S_2}$ experiments. Magmas with less iron require still lower f$_{O_2}$ for sulfide saturation. Such conditions are reasonable for terrestrial basaltic magmas, lending support to the notion that coexisting laurite + alloy are primary phenocrysts, as suggested by textural relations.