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Formation of trace minerals from magmatic melts - new insights from a HRTEM study of the Pt-As system

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It is an interesting question how trace minerals in magmatic systems manage to crystallize even though their constituents are present in the melt only in low ppm to ppb abundances. A good case in point are the platinum-group minerals. Very often, the PGE form minerals with ligands that are as rare as the noble metals, including As, Sb, Te, Bi, and Sn; and yet many PGE phases with these rare ligands are the first minerals that crystallize from a cooling sulfide or silicate melt. How do these constituents manage to find each other to form macroscopic crystals? Do perhaps preferential nano-associations of the PGE with their anionic ligands exist in the melt at high temperature, well before any macroscopic (μm-sized) PGE minerals become stable phases?

In order to enlighten that problem, we have studied the system Pt-As in FeS matrix at magmatic temperature (950°C). In that system, Pt is always a cationic species. Arsenic, on the other hand, can switch from cationic to anionic depending on pS_2:

As + n/4 S_2 (starting mix) = As^{n+} + n/2 S^{2-} (run products), i.e. at high pS_2, and

n M + m As (starting mix) = n M^{m+} + m As^{n-} (run products), i.e. at low pS_2,

where M refers to any redox-sensitive transition metal (here Fe) in the charge. The more As is present as anionic species, the lower the partition coefficient of Pt between monosulfide (mss) and sulfide melt ($D_{Pt}{}^{mss/melt}$), apparently because Pt^{n+} and As^{n-} form molecular associations strong enough to prevent Pt from partitioning into the mss lattice. Monosulfide grains were sectioned with focussed ion beam (FIB) techniques and investigated with HRTEM to make visible any Pt-As associations that may have been trapped accidentally by growing mss. Indeed, crystalline $PtAs_2$ nanophases do exist. The phases were found to form platelets < 10 to 50 nm in diameter and 1 nm in thick. The nanophases were identified in experimental charges that were grossly undersaturated with respect to macroscopic (μm-sized) $PtAs_2$ crystals. Tentatively, we conclude that many trace minerals in magmatic systems may assemble from pre-nucleating clusters or fundamental nano-sized builing blocks whose compositions mimic that of the macroscopic mineral. The pre-nucleation clusters may form well before the respective trace mineral becomes a thermodynamically stable phase.