

Solubility of the assemblage Pt-PtAs(melt) in basalt with implications for Pt-As complexing and As speciation

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Given the evidence in nature for a strong Pt-As association in magmas, we evaluated the effect of arsenic on platinum solubility in molten silicate. Two different approaches were employed. In the first (Type 1), vacuum-sealed quartz tubes contained a synthetic basalt analogue with Pt metal +/- arsenide melt encapsulated in a natural chromite crucible. Oxygen fugacity was fixed using solid oxide buffers, corresponding to ΔFMQ of -3.3 to +4.3. Experiments were done at 0.1 MPa, 1200°C for 1 to 4 days, then quenched in water. It was found that As was volatilized from samples and began to contaminate the oxygen buffer, leading to a systematic decrease in Pt and As solubility with time. To mitigate this problem, a second series of experiments (Type 2), done at ΔFMQ of +0.7 and +4.3, first equilibrated the basalt sample with (initially) pure Pt in a gas-mixing furnace, then with added arsenide melt in a sealed quartz tube, but without the solid oxide buffer; $f\text{O}_2$ was checked after using chromite/melt partitioning of vanadium. All Type 1 experiments contained Pt-Fe alloy + Pt-arsenide melt, whereas Type 2 runs contain Pt-arsenide melt only. In all experiments, the dissolved As content of the silicate melt increased significantly with $f\text{O}_2$, varying from 10 to 10,000 ppm, over the $f\text{O}_2$ range investigated. The average Pt contents of the Pt-saturated As-bearing glasses produced at ΔFMQ of +0.7 and +4.3 are 0.16 ppm and 0.18 ppm, respectively, compared to 0.02 ppm and 0.14 ppm Pt without As. At ΔFMQ of +0.7, the As content of the silicate melt is ~400 ppm, in which the Pt solubility is enhanced by 8-fold. Hence, the molar As/Pt required to affect this "excess" Pt solubility is ~7400. The As content of typical primitive basalts is ~0.1 ppm, compared to 1-10 ppb Pt, resulting in molar As/Pt of ~300-30; this suggests the solubility enhancement by As complexing will be insignificant in natural systems. Importantly, despite 800-10,000 ppm As in the glasses from Type 2 experiments saturated in Pt-arsenide melt, but not Pt metal, each contained Pt contents of <0.01 ppm, regardless of $f\text{O}_2$. This implies that the Pt level required for Pt-arsenide saturation in molten silicate is low, possibly leading to crystallization of such phases as sperrylite (PtAs_2) in sulfur-poor, As-bearing magmas.