PLATINUM PARTITIONING AT LOW OXYGEN FUGACITY: IMPLICATIONS FOR CORE FORMATION PROCESSES.

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Introduction: Highly siderophile elements (HSE = Au, Re, and the Pt-group elements) are tracers of sili-cate / metal interactions during planetary processes. Since most core-formation models involve some state of equilibrium between liquid silicate and liquid metal, understanding the partioning of highly siderophile ele-ments (HSE) between silicate and metallic melts is a key issue for models of core / mantle equilibria and for core formation scenarios. However, partitioning models for HSE are still inaccurate due to the lack of sufficient experimental constraints to describe the variations of partitioning with key variable like temperature, pressure, and oxygen fugacity. In this abstract, we describe a self-consistent set of experiments aimed at determining the valence of platinum, one of the HSE, in silicate melts. This is a key information required to parameterize the evolution of platinum partioning with oxygen fugacity.

Experimental and analytical techniques: High-pressure, high-temperature piston-cylinder experiments are being performed at 2.0 GPa and 1900 °C with a large range of oxygen fugacities between IW-7 and IW+2 (where IW is the oxygen fugacity of the iron-wüstite buffer). Most experiments involve equilibration between a metallic melt and a silicate melt (of basaltic composition) in graphite capsules. A few experiments were run in Al_2O_3 or MgO capsules. Oxygen fugacity is set by the interaction of variably oxidized starting materials with graphite containers [1], and by external oxygen buffers in graphite-free experiments. Composition of the metallic phases and the silicate glasses are measured by EPMA. Pt concentrations in all glasses are then analyzed by LA-ICP-MS. The valence and speciation of Pt in silicates and metals is also being investigated in some selected samples using X-ray Absorption Near-Edge Spectroscopy (XANES) on the 13ID-E beamline at the Advanced Photon Source (Argonne National Labs).

The composition of the investigated metallic alloys varies widely, including pure Pt, a series of Pt-Fe(-C-Si) alloys, and Pt-Si alloys in iron-free experiments. Thermodynamic activity models were constructed from literature data (mostly from the steel-making industry) in order to compare the partioning data obtained in different metallic systems. Silicate melts are broadly basaltic, and include a natural tholeiitic basalt, and synthetic equivalents in simplified systems (CMAS, CMAS-Ti, CMAS-Na).
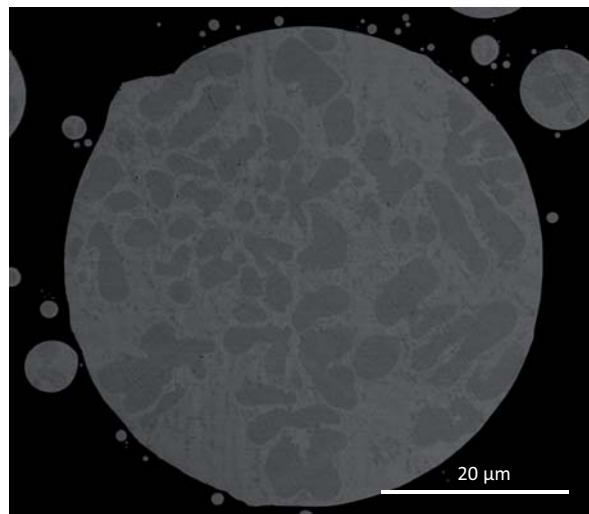

Fig.1. SEM/BSE image of a bead of Pt-Fe-Si alloy that quenched to a Si-poor alloy (dark) and a Si-rich alloy (bright). The black area is the equilibrium silicate glass.

Platinum speciation - the partitioning point of view: The dissolution of metals in silicate melts is often assumed to occur through formation of a metal oxide. The valence of a dissolved metal can then be estimated from the partioning as a function of fO_2 as follows [2]:

$$Pt(metal) + n/4\ O_2 = Pt^{n+}O_{n/2}(silicate)$$
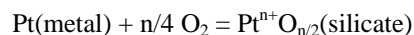
where n is the valence of dissolved Pt. The equilibrium constant of this reaction is given by:

$$K = \frac{a_{PtO_{n/2}}^{silicate}}{a_{Pt}^{metal} \cdot f_{O_2}^{n/4}} = \frac{1}{D_{metal/silicate}^{Pt} \cdot f_{O_2}^{n/4}}$$

By plotting the partition coefficient as a function of fO_2 in log units, all other parameters (temperature, pressure, melt composition) being kept constant, one can solve for the valence of dissolved platinum.
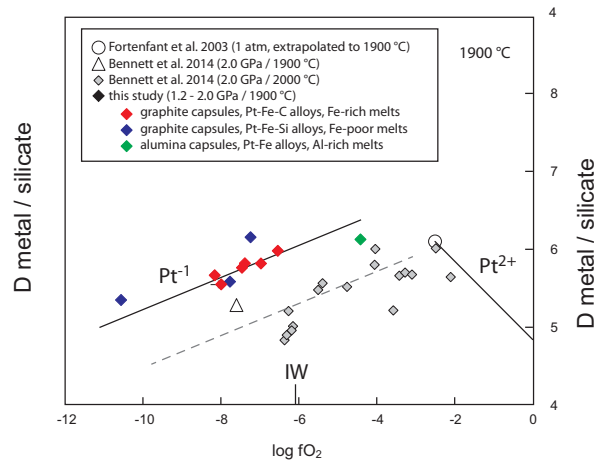
Fig.2. Evolution of partition coefficients as a function of oxygen fugacity at 1900 °C. Partition coefficients are true partition coefficients based on activities. The slopes of the D vs fO₂ trends followed by our data are typical of a -1 valence.

Contrary to expectations, for the investigated range of oxygen fugacities, the slope is positive, and very close to 0.25, as expected for a -1 valence. A similar behavior was suggested by [3] and our previous data [4]. This slope indicates that the dissolution reaction for Pt metal in silicate melts at fO_2 of IW-7 to IW+1 produces oxygen. Although some complex-forming reactions could produce oxygen together with Pt-(CO), Pt-Si or Pt-S complexes, the most likely species is the platinide anion Pt⁻, an anion already known to exist in a few binary compounds [5]:

$$Pt(metal) + \tfrac{1}{2} O^{2-}(silicate) = Pt^-(silicate) + \tfrac{1}{4} O_2$$
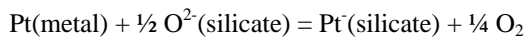
Our experiments thus strongly suggest that Pt is dissolved in an anionic form at oxygen fugacities at or below the IW buffer, a behavior that was previously hidden by data dispersion caused by formation of nanonuggets at the low oxygen fugacity relevant for core formation processes [4]. The presence of another metallic anion, Au⁻, in silicate melts, was already suggested in the earliest HSE studies by [6], for oxygen fuacities around or below IW. Preliminary results at even lower oxygen fugacities may also suggest the presence of Pt^{2-}. The transition between Pt^{2+} and Pt⁻ would be around IW+2. Dissolution of Au and Pt in anionic form in silicate melts at low oxygen fugacities is not surprising, since these elements have the highest electronegativities of all the transition metals, and their anions would be stabilized by favorable electronic structures and relativistic effects.

Platinum speciation - the spectroscopic point of view: Pt concentrations in our experiments are high enough to be investigated by X-ray spectroscopy on synchrotron. XANES investigations on the Pt L-edge are being performed in order to confirm the exact nature and valence of the Pt species. Preliminary results indicate a valency of +4 in the investigated experiments. When compared to the partitioning data, theses results suggests that Pt⁻ is an unstable species, as already suggested by the study ot the few synthesized Pt⁻ bearing compounds. Either Pt⁻ reacts with other valence-changing elements on quench (as was observed for Cr^{2+} [7]), or Pt- is extremely sensitive to the X-ray beam used in the experiments. A new set of experiments devoid of any transition metal other than platinum will be analyzed using variable beam exposure time in order to solve this issue.

Conclusions: Assuming an average oxygen fugacity of IW-2 during core formation processes [8], at least Pt and Au (and possibly other higly siderophile elements) would have been in an anionic form in silicate melts during core segregation processes. This fact have been previously hidden by the presence of nanonuggets in experiments under the relevant oxygen fugacities. The decrease in partition coefficient at low fO_2 caused by the negative valence can provide a partial solution to the excess-siderophile problem. Addition of a late veneer is, however, still required to explain the HSE concentration in the Earth's mantle, unless plqnetqry differenciation occurred under exceptioannally low oxygen fugacities.

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