

ANIONIC Pt IN SILICATE MELTS AT LOW OXYGEN FUGACITY: SPECIATION, PARTITIONING AND IMPLICATIONS FOR CORE FORMATION PROCESSES ON ASTEROIDS. E. Médard¹, A. M. Martin¹, K. Righter², A. Malouta³, C.-T. Lee³, ¹Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058 (medard@lpi.usra.edu), ²NASA Johnson Space Center, Mailcode KT, 2101 NASA Parkway, Houston, TX 77058, ³Dept of Earth Science, Rice University, MS-126, 6100 Main St., Houston, TX 77005

Introduction: Most siderophile element concentrations in planetary mantles can be explained by metal/silicate equilibration at high temperature and pressure during core formation. Highly siderophile elements (HSE = Au, Re, and the Pt-group elements), however, usually have higher mantle abundances than predicted by partitioning models, suggesting that their concentrations have been set by late accretion of material that did not equilibrate with the core. The partitioning of HSE at the low oxygen fugacities relevant for core formation is however poorly constrained due to the lack of sufficient experimental constraints to describe the variations of partitioning with key variables like temperature, pressure, and oxygen fugacity. To better understand the relative roles of metal/silicate partitioning and late accretion, we performed a self-consistent set of experiments that parameterizes the influence of oxygen fugacity, temperature and melt composition on the partitioning of Pt, one of the HSE, between metal and silicate melts. The major outcome of this project is the fact that Pt dissolves in an anionic form in silicate melts, causing a dependence of partitioning on oxygen fugacity opposite to that reported in previous studies.

Experiments: High-pressure, high-temperature piston-cylinder experiments were performed at 1.2-2.0 GPa and 1650-2250 K under a large range of oxygen fugacities between IW-8 and IW+2 (where IW is the oxygen fugacity of the iron-wüstite buffer). The experiments involve equilibration between a metallic melt and a silicate melt in graphite, MgO or Al₂O₃ capsules. Composition of the quenched metal alloys and the silicate glasses were measured by EPMA. Pt concentrations in glasses were then analyzed by LA-ICP-MS. The investigated metallic alloys include ternary Pt-Fe-Si and Pt-Fe-C alloys, as well as binary Pt-Si alloys in Fe-free experiments. Activity models were built from literature data (steel-making industry) fitted to asymmetric regular solution models [1] to compare the partitioning data obtained in different metallic systems.

Pt speciation in silicate melts at low oxygen fugacity: In Fig. 1, the slope of the line representing the partition coefficient as a function of oxygen fugacity is very close to 2 between IW (log fO₂ = -6) and IW-6, which is the range of fO₂ for core formation on most

terrestrial planets and large asteroids [2,3,4]. This indicates that the partitioning reaction involves the release of one oxygen atom from the silicate. One possible reaction involves formation of the Pt²⁻ anion:

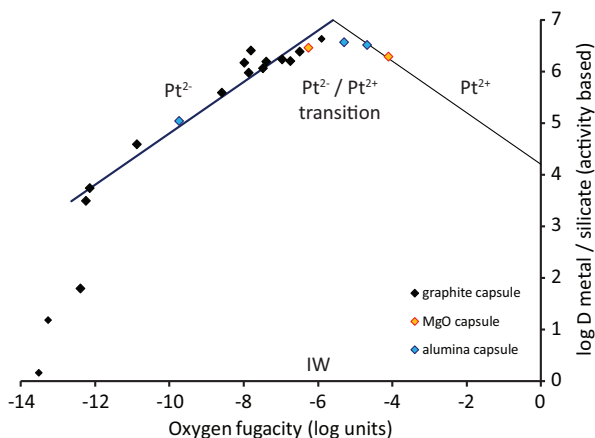
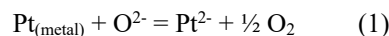
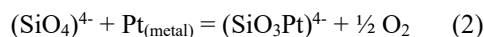


Fig. 1. Metal/silicate partition coefficient of Pt as a function of oxygen fugacity for experiments at 1.2-2.0 GPa and 1900-1980 °C.

The valence and speciation of Pt has also been investigated in some of the experimental silicate glasses using X-ray Absorption Fine Structure Spectroscopy (XAFS) on the 13ID-E beamline at the Advanced Photon Source (Argonne National Labs). Spectra acquired at the Pt L_{III} edge do not resemble that of any known cationic or neutral Pt compound. They are, however, very similar to the spectra of platinum silicides (Pt₂Si, PtSi) [5], suggesting the presence of Pt-Si bonds in the silicate melts. Substitution of Pt for O in the silicate network agrees with the observed oxygen fugacity dependency of the partitioning, according to the reaction:



Although an ionic representation as platinide anion Pt²⁻ is convenient, the Si-Pt bond is likely partially covalent, as is the case for the Si-O bond. Due to the high electronegativity of Pt, charge transfer in platinum silicide show, however, a partial ionic character, with an overall charge flow onto Pt [6].

Metal/silicate partitioning: [1] have shown that metal/silicate partitioning of Pt is independent of pressure, and suggest that temperature is the only important parameter. The temperature dependency is given by their equation (9). Here we give a corrected version since there was an error in the published equation (D is expressed using mass concentrations at infinite dilution of Pt in a pure iron core):

$$\log D_{Pt}^{M_{metal}/silicate} = 0.8703 + 13345/T \quad (3)$$

Our experiments in MgO and Al₂O₃ capsules confirm that there is no influence of the silicate melt composition on the partitioning. Silicate melts in those oxide capsules are strongly enriched in MgO and Al₂O₃, but the partition coefficient do not vary (Figure 1). The data used to calibrate equation (3) have been obtained at an average oxygen fugacity close to the IW buffer. The influence of oxygen fugacity according to Figure 1 and equation (2) can be incorporated to give a new partitioning equation:

$$\log D_{Pt}^{M_{metal}/silicate} = 0.8703 + 13345/T + 0.5dIW \quad (4)$$

Where dIW is the oxygen fugacity relative to the IW buffer, in log units.

Core formation on Vesta: Small asteroids are more likely to record equilibrium core formation processes, since their low gravity is less likely to attract late accreting bodies, and no recent geological processes affected them. Models based on siderophile elements partitioning [2,4] and on silicon isotope fractionation [7] indicate that core/mantle differentiation on Vesta happened at 1700-2000 K and IW-2 to IW-4. Those conditions largely overlap with our experimental conditions. Predicted Pt concentrations for the Vestan mantle varies between 10⁻⁵ and 10⁻⁸ times the CI chondrite values. [8,9] show that HSE concentrations in Vestan (HED) meteorites have a large range of variations. Samples with a high HSE content show chondritic spectra, consistent with overprinting by late accretion, whereas samples with the lowest concentrations show fractionated HSE spectra, possibly consistent with equilibrium core formation. Measured lowest Pt concentrations in HED are 10⁻⁵ to 10⁻⁶ [8,9], overlapping with our model calculations. It is thus possible that Pt concentrations in some HED meteorites record equilibrium core formation conditions, particularly if the Vestan core formed at the high-T (2000 K), low-fO₂ (IW-4) end of the proposed models. Note that our model does not account for the influence of light elements on partitioning. Addition of Si to the

metallic alloys is expected at such low fO₂, and can significantly change the metal/silicate partition coefficients [10].

Aubrite parent body: Mantle (or basaltic) samples that show a record of core formation should be characterized by relatively low and fractionated HSE spectra. Aubrites meteorites are particularly interesting, because they formed under extremely reducing conditions (IW-6 to IW-8) [11]. The lowest Pt concentration in aubrites is 3.10⁻⁴ times the CI chondrites [12] in the most fractionated samples. Assuming aubrites are mantle samples, and the core of the aubrite parent bodies comprises 40 % of the asteroid mass [12], this concentration can be reached in the window 1900 K / IW-8 to 2250 K / IW-6.

Conclusions and perspectives: Since Pt dissolves as negatively charged species at low oxygen fugacity, equilibrium Pt partitioning models predicts that Pt concentrations will be highest in the most reduced planetary bodies. Pt concentrations in the reduced mantles of Vesta and the aubrite parent body can be explained by simple core / mantle equilibrium models, without the need for a late accretion phase. For larger planetary bodies (Earth, Mars, and the Moon), predicted mantle concentrations are still too low, and late accretion of material that does not equilibrate with the core is required. However, the effect of pressure on negatively charged Pt in silicate melts is largely unknown, and partition coefficients at higher pressures could be consistent with equilibrium core formation processes.

References: [1] Médard E., et al. (2015) *GCA*, 162, 183-201. [2] Righter K., Drake M. J. (1996) *Icarus*, 124, 513-529. [3] Wade J., Wood B. J. (2005) *EPSL* 236, 78-95. [4] Steenstra E. S., et al. (2016) *GCA*, 177, 48-61. [5] Rossi G. (1987) *Surface Science Reports*, 7, 1-101. [6] Naftel S. J., et al. (1997) *Thin Solid Films*, 309, 580-584. [7] Pringle E. A., et al. (2013) *EPSL*, 373, 75-82. [8] Dhaliwal J. K., et al. (2016) *LPSC 47*, Abstract #2644. [9] Day J. M. D., et al. (2016) *Reviews Min. Geoch.*, 81, 161-238. [10] Righter K., et al. (2017) *LPSC 48*, this meeting. [11] Mittlefehldt D. W., et al. (1996) *GCA*, 60, 867-882 [12] van Acken D., et al. (2012) *MAPS*, 47, 1606-1623.