

EXPERIMENTAL AND THEORETICAL CONSTRAINTS ON THE ORIGIN OF LITHOPHILE ELEMENT-PT ALLOYS. A.H. Treiman,* J.H. Jones* and B. Fegley, Jr.**

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Electron microbeam analyses by El Goresy et al. [1] of Pt-metal nuggets in Ca-, Al-rich inclusions (CAI) of the Allende meteorite have indicated the presence of Nb, Zr and Ta. The lack of noticeable accessory phases that could have contributed to the nugget analyses has led to the suggestion that these elements, which are ordinarily difficult to reduce to metal, were in solid solution with Pt [1]. This possibility has been questioned by Grossman [2], who noted that (even under solar conditions) Zr is 10^7 more stable in the oxidized state than in reduced form. However, Grossman's observation did not take into account the known nonideal behavior of Zr-Pt solid solutions [3]. Jones and Burnett [4] noted that it was possible to form the types of nuggets reported by El Goresy, because the activity coefficient of Zr in Pt was $<10^{-12}$ [3]. However, Jones and Burnett were concerned that U, which was experimentally found to strongly alloy with Pt, was not found in the nuggets as well [4]. Fegley and Kornacki [5] extended this concern by noting that, if Zr-Pt alloys were indeed present, it would be expected that Ti-Pt solution should also have occurred. Thus, the study of El Goresy et al. [1] has raised as many questions as answers.

We have begun a systematic survey of the partitioning of lithophile elements between Pt-Fe alloys and silicate liquid. Our aim is to better quantify the tendencies of lithophile elements to alloy with Pt and to better constrain the redox conditions of early solar system processes. These experiments are somewhat difficult and here we only report preliminary data for Zr and Hf.

Experimental and analytical. Pt wire was placed in an alumina crucible with a basaltic powder that had been spiked with either a Zr or Hf oxide tracer. The basaltic powder was originally of eucritic composition but lost most of its FeO during the experiment by reduction to metal. The crucible with the experimental charge was sealed inside an evacuated silica tube with a second crucible containing Cr metal. The oxygen fugacity of the Cr-Cr₂O₃ buffer at 1600 K is about a log unit above that of solar and is approximately 2.5×10^{-16} bar. The charge was suspended at temperature in a Deltech furnace for ~1 day. Longer times at temperature were limited by oxygen diffusion through the silica glass tube.

To provide some constraints on the thermochemistry of the alloying process, we endeavored to saturate the silicate system with an oxide of the tracer. In this way, the activity of the oxidized species would be known and an activity coefficient for the tracer in the alloy could be calculated. Because we added more tracer than was necessary for analysis, our experiments may not fall in the Henry's law region — at least not for the silicate system.

Analyses were performed on the ARL SEMQ of the University of Arizona, using wavelength dispersive analysis. Even so, the overlap between the Pt M- α and the Zr L- α lines made Zr analysis of the Pt difficult. We used prorated analyses of pure Pt at the Zr peak location to correct our Zr analyses for any contribution from Pt.

Experimental Results. The experimental charges were quite complex. The silicate assemblage, after being highly reduced, was no longer above the liquidus at 1325°C and a variety of crystalline phases were found, in addition to glass. In most cases the silicates were free of FeO, which had all entered the Pt. Because much of the Fe in the experimental charge was originally ferric, we have confidence that equilibrium between the charge and the buffer was closely approached. In some charges, however, detectable FeO in the silicates may be attributed to exhaustion of the buffer by diffusion of oxygen through the silica tube and reoxidation of alloyed Fe. Thus, our Pt/silicate liquid partition coefficients (D) should probably be viewed as lower limits to the true D value.

The metal assemblage was also somewhat complicated. The Pt metal was not a single phase but consisted of solid Pt-Fe nuggets surrounded by a quenched Pt-Si liquid. Thus,

partitioning techniques, such as those of Palme and Schmitt [6], which have relied on macroscopic separation of Pt from silicate and subsequent neutron activation analysis, could be compromised by the presence of more than one phase in the alloy assemblage. Alternatively, it is possible that the experiments of Palme and Schmitt, which were performed at 1700°C, contained no solid Pt, but only a liquid Pt alloy.

Analytical Results. Our preliminary partition coefficients are given in Table 1. In some cases the low levels of the tracer in the Pt-Si liquid allow only lower limits to be placed on the solid Pt/liquid Pt partition coefficient.

Discussion. Our data appear to confirm the results of Palme and Schmitt [6], whose experiments were performed at 1700°C and under more oxidizing conditions. Palme and Schmitt then extrapolated their experimental results to conditions appropriate for the formation of Allende CAI. Our D values, which were obtained at conditions slightly more oxidizing than solar, are not very different from the lower limits of the extrapolated results of Palme and Schmitt (Table 1). Correction for the difference between our experimental f_{O_2} and solar would make for better agreement between our results and the upper limits estimated by Palme and Schmitt. This agreement between two very different techniques gives us confidence that our results are reasonable. One caveat, however, is that the Pt-Fe alloy of [6] could have been molten or partially molten. How this might affect their results is still unclear.

Palme and Schmitt used their extrapolated partition coefficients to calculate the composition of Pt metal condensates [6]. Their results indicated that it would be difficult to produce nuggets with percent levels of Zr under solar conditions. However, such concentration levels could probably be achieved under conditions only modestly more reducing. Our calculations and those of [5] indicate that Zr should reach percent levels in nuggets formed at f_{O_2} 's of only 2-3 log units below solar.

Therefore, our preliminary experiments, the experiments of [6], and the calculations of [5] are all in general agreement and suggest that the apparent rarity of Zr-bearing nuggets [7] is consistent with the reducing conditions (relative to solar) necessary for their formation. This agreement between experimental and theoretical studies further emphasizes the question of why an element such as Ti [5] that is 100X more abundant and probably more easily alloyed with Pt has not been found in Allende nuggets. Titanium partition coefficients for Pt/silicate liquid may help resolve this issue.

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References. [1] El Goresy A. et al., (1978) *Proc. Lunar Planet. Sci. Conf. 9th.*, 1279-1303. [2] Grossman L. (1980) *Ann. Rev. Earth Planet. Sci.* 8, 559-608. [3] Brewer L. and Wengert P.R. (1973) *Metall. Trans.* 4, 83-104. [4] Jones J.H. and Burnett D.S. (1980) *Proc. Lunar Planet. Sci. Conf. 11th.*, 995-1001. [5] Fegley B., Jr. and Kornacki A.S. (1984) *Earth. Planet. Sci. Lett.* 68, 181-197. [6] Palme H. and Schmitt W. (1984) *Lunar and Planetary Science XV*, 623-624. [7] Wark D.A. (1983) Ph.D. Thesis, University of Melbourne.

Table 1
Summary of Preliminary Results for the Partitioning
of Lithophile Elements Between Pt and Silicate Liquid**

Element	D(solid Pt-Fe/Liquid Pt-Si)	D(Solid Pt-Fe/Silicate Liquid)
Zr	>10	0.27 (0.3-2.3)
Hf	>70	0.13 (0.2-1.6)
Fe	65	>100
Si	0.015	0.002

* T= 1325°C (1600 K); $\log f_{O_2} = -15.6$ (Cr-Cr₂O₃)

Numbers in parentheses from Palme and Schmitt (1984).