

**EXPERIMENTAL PARTITIONING OF Zr, Ti, AND Nb BETWEEN SILICATE LIQUID AND A COMPLEX NOBLE METAL ALLOY AND THE PARTITIONING OF Ti BETWEEN PEROVSKITE AND PLATINUM METAL.** Stephen R. Jurewicz and John H. Jones, Code SN4, NASA Johnson Space Center, Houston, TX 77058

**INTRODUCTION:** El Goresy et al.'s [1] observation of Nb, Zr, and Ta in refractory platinum metal nuggets (RPMNs) from Ca-Al-rich inclusions (CAIs) in the Allende meteorite led them to propose that these lithophile elements alloyed in the metallic state with noble metals in the early solar nebula. However, Grossman [2] pointed out that the thermodynamic stability of Zr in the oxide phase is vastly greater than metallic Zr at estimated solar nebula conditions.

Jones and Burnett [3] suggested this discrepancy may be explained by the very non-ideal behavior of some lithophile transition elements in noble metal solutions and/or intermetallic compounds. Subsequently, Fegley and Kornacki [4] used thermodynamic data taken from the literature to predict the stability of several of these intermetallic compounds at estimated solar nebula conditions.

Palme and Schmitt [5] and Treiman et al. [6], conducted experiments to quantify the partitioning behavior of certain lithophile elements between silicate liquid and Pt-metal. Although their results were somewhat variable, they did suggest that Zr partition coefficients were too small to explain the observed "percent" levels in some RPMNs. Palme and Schmitt also observed large partition coefficients for Nb and Ta. No intermetallic phases were identified.

Following the work of Treiman et al. [6], Jurewicz and Jones [7] performed experiments to examine Zr, Nb, and Ti partitioning near solar nebula conditions. Their results showed that Zr, Nb, and Ti all have an affinity for the platinum metal, with Nb and Ti having a very strong preference for the metal. The intermetallic phases  $(Zr,Fe)Pt_3$ ,  $(Nb,Fe)Pt_3$ , and  $(Ti,Fe)Pt_3$  were identified.

Curiously, although both experiments and calculations indicate that Ti should partition strongly into Pt-metal (possibly as  $TiPt_3$ ), no Ti has ever been observed in any RPMNs. Fegley and Kornacki [4] also noticed this discrepancy and hypothesized that the Ti was stabilized in perovskite which is a common phase in Allende CAIs.

**EXPERIMENTAL:** The current experiments were undertaken to determine: 1) the transition element partitioning behavior in a Fe-free system, 2) the effect of a complex Pt-Ir-Os-Ru alloy on transition metal partitioning, and 3) the partitioning behavior of Ti into Pt-metal in the presence of perovskite.

The Fe-free system experiments were performed using the technique described in Jurewicz and Jones [7]. The "CAI-like" liquid composition from our previous experiments was used except that FeO was deleted from the starting mix. The starting glass composition was spiked at the 1.0 wt.% level with the transition element oxide to be studied. Two micron platinum powder was blended into the doped mix as described by Jurewicz and Jones [7]. The experimental charge was then loaded into an alumina capsule and sealed in an evacuated silica glass tube with an additional crucible containing 100 mg of Cr-metal. The oxygen fugacity of the Cr-Cr<sub>2</sub>O<sub>3</sub> buffer is about one log unit greater than solar ( $10^{-16}$ ) at the run temperature of 1548K. The sealed silica tubes were run in a controlled atmosphere furnace with flowing CO/CO<sub>2</sub> providing a log  $f_{O_2}$  of -9.63 on the outside of the capsule. The charges were run for 48 hours.

The complex alloy experiments were similar to the above except that the original Fe-bearing CAI oxide mix and a metal mix of Pt, Os, Ir, and Ru in roughly equal atomic percentages, were used.

A mixed oxide "CAI-like" composition for the perovskite experiment was selected from Beckett [8] and was expected to crystallize substantial perovskite at the run temperature of 1548K. The initial oxide mix was melted in air at 1743K for 24 hours and then crystallized at 1548K for 150 hours. The resulting starting material contained about 20% vol. perovskite with olivine, fassaite, and spinel. The material was ground to a fine powder, blended with 2 micron Pt-powder, and loaded into an alumina capsule and run as per the previous experiments.

## PARTITIONING OF Zr, Nb, AND Ti: Jurewicz S.R. and Jones J.H.

**RESULTS:** The partitioning results are shown in Table 1 in addition to the previous results of Jurewicz and Jones [7] and Palme and Schmitt [5]. The results indicate that although Zr does partition into Fe-free Pt-metal, its partition coefficient is about the same as in the Fe-bearing system. Also, Zr does not appear to partition into the complex noble metal mix at all. Nb and Ti on the other hand, strongly partition into the metal in both the Fe-free and complex systems. Because Nb partitioned so strongly into the metal, only minimum D values were determined. The actual values are probably much higher, as suggested by Palme and Schmitt's [5] results.

Significantly, substantial Ti (5.8 +/- 0.6wt.%) was observed in the Pt-metal phase from the perovskite experiment and modal perovskite dropped to a few percent. Thus, perovskite decomposes in the presence of Pt-metal at solar oxygen fugacities and 1548K.

**DISCUSSION:** The observed Fe-free Zr partition coefficient, while similar to those previously observed, is still too small to account for "percent levels" of Zr in RPMNs. In addition, Zr does not tend to partition at all into a complex Os-Ru-Pt-Ir alloy, which more closely resembles natural RPMNs. Titanium appears to partition into Pt-metal even when the Ti is initially contained in perovskite. Our results suggest that the observed transition elements in RPMNs are not the result of a simple silicate/metal equilibration process and/or the RPMNs formed in a more oxidizing environment than that of solar composition.

TABLE 1. Partitioning results for all the experiments. Numbers in parentheses are two sigma deviations.

Tracer Wt%	$D_{Zr}^{Me/liquid}$	$D_{Nb}^{Me/liquid}$	$D_{Ti}^{Me/liquid}$
<b>Jurewicz and Jones (1992)</b>			
0.5	2.09(0.47)		
1.0	3.82(0.52)	> 10	151(60)
2.5	4.55(0.51)		
5.0	3.91(0.38)	> 55	5.94(4.93)
8.0	2.06(0.33)		
10.0		77(30)	1.49(0.10)
<b>Complex Noble Metal</b>			
1.0	nd <sup>1</sup>	> 40	14(5)
<b>Fe-free System</b>			
1.0	3.25(1.24)	> 22	400(145)
<b>Palme and Schmitt (1984)</b>			
	0.3-2.3	588-2700	

<sup>1</sup> Zr in the metal phase is below the detection limit of the electron probe.

**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] Jones J.H. and Burnett D.S. (1980) *Proc. Lunar Planet. Sci. Conf. 11th.*, 995-1001. [4] Fegley B., Jr. and Kornacki A.S. (1984) *Earth Planet. Sci. Lett.* **68**, 181-197. [5] Palme H. and Schmitt W. (1984) *Lunar and Planetary Science XV*, 623-624. [6] Treiman A.H. et al. (1991) *Lunar and Planetary Science XXII*, 1413-1415. [7] Jurewicz S.R. and Jones J.H. (1992) *Lunar and Planetary Science XXIII*, 645-646. [8] Beckett J.R. (1986) Ph.D. Thesis, Univ. of Chicago.