
There are some reports of the occurrences of metallic Zr, Hf, Nb and Ta in Pt-metal nuggets from Ca, Al-rich inclusions in carbonaceous chondrites. El Goresy et al. (1) found Nb, Ta, and Zr in Pt-metal nuggets from Allende inclusions and they concluded that "these four elements (Nb included) are very probably present in their metallic state." Metallic Nb and Ta was detected in an ultra-refractory inclusion from Ornans (2). Recently El Goresy et al. (3) reported the presence of metallic Zr and Hf in a metal crystal from a refractory inclusion in the C2 chondrite Evansi. In the C2 chondrite Evansi.

There are two possibilities for the incorporation of Zr, Hf, Ta etc. into Pt-metal nuggets: a) by equilibration of Pt-metal nuggets with a Ca, Al-rich melt under very reducing conditions. b) by condensation from a hot gas of solar (or some other) composition.

Recently Fegley and Kornacki (4, 5) pointed out the high stability of alloys of some refractory lithophile elements (Zr, Hf, Nb, Ta) with Pt-metals. The low activities of these elements in Pt-metals would facilitate their incorporation into Pt-metal grains in either of the above models although Fegley and Kornacki (5) favour the first possibility. In order to test this hypothesis we have experimentally determined Pt-metal/silicate partition coefficients for Zr, Hf, Nb, Ta, Cr and V. The experiments were done in the same way as those described by Rammensee et al. (6). Radioactive tracers were added as metals and as oxides. FeNi/silicates and PtFe/silicate partition coefficients were simultaneously determined. A tholeitic basalt and a Ca, Al-rich glass (average type B) were used as silicates. Experimental results are summarized in Table 1. All five elements show strong preference for Pt-metal compared to FeNi. V may behave similarly. The data for Nb are less reliable, since Nb was counted as NbO (T1/2 = 74 min.), which is a decay product of the 16.8 h Zr. No inactive carrier was added, resulting in extremely low concentrations of Nb. Nevertheless it appears that the behaviour of Nb is not too different from that of Ta. In a similar way Zr and Hf have nearly identical partition coefficients. This also indicates that the effect of absolute concentrations is negligible, since the concentration of Hf is about 50 times lower than that of Zr (ca. 10%)

In order to apply these results to conditions prevailing during melting of Ca, Al-rich inclusions we have recalculated the partition coefficients to the relevant conditions (7). The results are listed in Table 2. Because of the lower temperature and the more reducing conditions, the Pt-metal/silicate partition coefficients are significantly higher. The ratio of activities in metal to silicate was assumed to be the same for both conditions. In Table 3 the expected concentrations in Pt-metal nuggets from Ca, Al-rich inclusions are listed. Major uncertainties in these numbers result from the poorly known oxygen fugacity during melting of the inclusion, and the influence of other metals in the Pt-metal nuggets on the activities of Zr, Hf etc. Given these uncertainties we can draw three major conclusions from the data:

1) It is very unlikely to get Zr and especially Hf concentrations of more than 0.1% (the observed level (3)) in the metal nuggets by metal/silicate equilibration

2) In contrast, Nb and Ta can be enriched to the observed abundance level by this process. Their concentrations are generally more than 100% of Zr and Hf.

3) Pt-metal nuggets high in Nb and Ta should also contain Cr and V in the percent range. El Goresy et al. (1) have observed a few Pt-metal nuggets with high Cr concentrations. High Cr (5%) and some enrichment of V (0.6%) were found in metal nuggets from inclusion C1 by Wark and Wasserburg (8). The majority of the nuggets however do not appear to contain such high Cr or V concentrations (1).

ORIGIN BY CONDENSATION:

The fraction Z of e.g. Zr condensed in a Pt-metal alloy is given by

\[
\alpha_Z = 1/\left(1 + (p_{Zr}^{*}/\alpha_{Zr}^{*})/\rho_{Zr}^{*}\right)\]

\(\alpha_{Zr}^{*}\) activity coefficient of Zr in the alloy; \(\beta_{Zr}^{*}\) fraction of Zr metal atoms to all other species of Zr in the nebula; \(p_{Zr}^{*}\) vapor pressure of Zr metal; \(\rho_{Zr}^{*}\) maximum Zr vapor pressure in the nebula, assuming \(\beta<1\); \(X_{Zr}\) ratio of all Zr atoms (cosmic abundance) to the total number of condensed atoms.

The results of condensation calculations are listed in Table 4. The activity coefficients necessary for 50% condensation (\(\alpha = 0.5\)) are listed as function of temperature. In view of the results obtained in our experiments and the theoretical predictions, the numbers for Zr, Hf, Ta and Nb are not unreasonable. The ratio of activity coefficients for Zr (\(Y_{Zr}^{*}/Y_{Zr}^{*}\)) derived from our results is about 10^{-8}. Fegley and Kornacki (5) estimated the activity coefficient of ZrO2 in silicates to about 10^{-6} to 10^{-5}, based on data by Watson and Harrison on ZrO2 saturation in crustal magmas (9). With these activity coefficients we obtain Zr activity coefficients in Pt-metals of 10^{-5} to 10^{-4}. This is low enough to allow a significant fraction of Zr to condense as Zr metal. The difficulty for Ta and Nb is that the activity coefficients in silicates are not known and that the only information extracted from our data is the ratio of activity coefficients in metal to that in silicates. But it should be clear that the activity coefficients in metals are so low that condensation of Ta and Nb as metals should be no problem.

From Table 4 it is apparent that condensation of V as metal would require extremely low activities (less than 0.5%). The assumption of the lower fraction of 0.5% would result in two orders of magnitude higher activity coefficients than those listed in Table 4.
ON THE ORIGIN OF LITHOPHILE REFRACTORY ELEMENTS
Palme, H. and Schmitt, W.

Although we have only obtained a lower limit for the Pt-metal/silicate partition coefficient of V, it is very unlikely that the V activity coefficient is so low. The upper limit for the Pt-metal/silicate activity ratio deduced from our data is $10^{-3}$. Since the vapor pressure of Cr is lower than that of Co and Ni its fraction condensing together with Pt-metal alloys is extremely small. At 1600 K, for example, the condensed Cr fraction would be $10^{-7}$ assuming an activity coefficient of $10^{-3}$, which may be estimated from the experimental data. This Cr fraction would lead to a Cr content of about 800 ppm in the equilibrium condensate at 1600 K.

We therefore conclude that the presence of V and Cr in Pt-metal nuggets is the result of a metal-silicate equilibration. The observed contents of Nb, Ta, Zr and Hf, without corresponding enrichment of Cr and V indicates a condensation origin of these alloys. During partial melting of these inclusions the Pt-metal nuggets have not equilibrated with the Ca, Al-rich melt.


Table 1: Metal-silicate partitioning

<table>
<thead>
<tr>
<th>Silicate:</th>
<th>Basalt</th>
<th></th>
<th>Silicate: Ca, Al-rich glass</th>
<th>Metal:</th>
<th>FegO10 and Pt72Fe28</th>
<th>Metal:</th>
<th>FegO10 and Pt72Fe28</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 1700°C</td>
<td>T = 1700°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>log P(O2) = -10.24</td>
<td>log P(O2) = -10.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M/S (by weight)</td>
<td>M/S (by weight)</td>
<td>Fe/M</td>
<td>Pt/M</td>
<td>Fe/M</td>
<td>Pt/M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.53</td>
<td>3.14</td>
<td>Cr</td>
<td>0.53</td>
<td>8.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>0.0028</td>
<td>0.81</td>
<td>Ta</td>
<td>0.0011</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.13</td>
<td>2.83</td>
<td>Nb</td>
<td>0.03</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.00014</td>
<td>0.014</td>
<td>Zr</td>
<td>0.00076</td>
<td>0.097</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>0.016</td>
<td></td>
<td>Hf</td>
<td>0.00055</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>&gt;10</td>
<td></td>
<td>V</td>
<td>&gt;10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Recalculated of experimentally determined Pt-metal/silicate partition coefficients for melting conditions of Ca, Al-rich inclusions, assuming constant activities.

<table>
<thead>
<tr>
<th>M/S</th>
<th>approx. experim.</th>
<th>approx. Ca, Al-rich melting conditions</th>
<th>assumed species in silicate</th>
<th>Concentration in average type B inclusion</th>
<th>g/M</th>
<th>expected concentration in Pt-metal nuggets (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.014</td>
<td>0.3</td>
<td>Cr2O3</td>
<td>Zr</td>
<td>77</td>
<td>0.34</td>
</tr>
<tr>
<td>Hf</td>
<td>0.007</td>
<td>2.3</td>
<td>HfO2</td>
<td>Hf</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Ta</td>
<td>0.016</td>
<td>0.2</td>
<td>Ta2O5</td>
<td>Ta</td>
<td>0.28</td>
<td>550</td>
</tr>
<tr>
<td>Nb</td>
<td>0.13</td>
<td>1.6</td>
<td>Nb2O5</td>
<td>Nb</td>
<td>6</td>
<td>588</td>
</tr>
<tr>
<td>Zr</td>
<td>2.6</td>
<td>550</td>
<td>ZrO2</td>
<td>Cr</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>Hf</td>
<td>8.2</td>
<td>700</td>
<td>HfO2</td>
<td>V</td>
<td>550</td>
<td>&gt;126</td>
</tr>
</tbody>
</table>

Table 4: The activity coefficients $X$ required to obtain 50% condensation of Zr, Hf, Ta, Nb, and V in a refractory metal alloy. Condensation of oxides has not been considered. Solar nebula oxygen fugacity ($log$ (O$_2$/H$_2$O) = 3.14), and a total pressure of $10^{-3}$ atm. were assumed.

<table>
<thead>
<tr>
<th>$K$</th>
<th>Zr</th>
<th>Hf</th>
<th>Ta</th>
<th>Nb</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>3.6 x10^{-6}</td>
<td>3.5 x10^{-7}</td>
<td>1.2 x10^{-3}</td>
<td>2.3 x10^{-3}</td>
<td>1.6 x10^{-15}</td>
</tr>
<tr>
<td>1800</td>
<td>7.7 x10^{-8}</td>
<td>1.8 x10^{-8}</td>
<td>1.2 x10^{-5}</td>
<td>3.8 x10^{-5}</td>
<td>2.6 x10^{-14}</td>
</tr>
<tr>
<td>2000</td>
<td>1.1 x10^{-8}</td>
<td>5.7 x10^{-9}</td>
<td>1.2 x10^{-6}</td>
<td>3.8 x10^{-6}</td>
<td>6.8 x10^{-17}</td>
</tr>
</tbody>
</table>

© Lunar and Planetary Institute • Provided by the NASA Astrophysics Data System