MO AND W ANOMALIES IN CAI's: SIGN OF HIGH TEMPERATURE CONDENSATION, OR SUBSOLIDUS ALTERATION?

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Grossly inconsistent results are produced by different indicators of the oxygen fugacity under which Ca-Al-rich inclusions (CAI's) formed (1, 2). On the one hand, anomalies in Mo and W in CAI's indicate fO2 values 3 to 4 orders of magnitude more oxidizing than for the canonical solar nebula (3). On the other hand, the presence of Ti3+ and the lack of anomalies in Ce indicate fO2's more reducing than in a gas of solar composition (4, 5). Two different solutions to this dilemma have been proposed: either (a) the metal formed at high temperature under relatively oxidizing conditions before being introduced into the silicates which crystallized under more reducing conditions (1, 6); or (b) after crystallization of the CAI, the metal was selectively altered and lost some Mo and W (7).

We have performed a series of laboratory experiments to determine under what conditions subsolidus processes (the second alternative) might have mobilized and removed Mo and W. In each experiment, mm-sized pieces of two different alloys A and B (Table 1) containing Mo and W were heated in sealed, evacuated, silica tubes at an fO2 controlled by a solid buffer. Each tube contained some CaO "getter" to react with and remove gaseous Mo and W oxide species. Afterwards, the metal alloys were sectioned and analysed by SEM (in future by INAA) for evidence of Mo or W mobilization and loss. Experimental conditions ranged from 730°C-1200°C, from Cr/Cr2O3-Ni/NiO buffer (and also in air), and from 24-88 hours (see Fig. 1). Conditions included some temperatures not far below the final CAI crystallization temperature, and fO2 values both more and less oxidizing than the canonical solar nebula.

Table 1: Starting compositions of metal alloys (wt.%) V Fe Ni Mo Ru W Os Ir Pt Sum

<table>
<thead>
<tr>
<th>Alloy</th>
<th>V</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Ru</th>
<th>W</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00</td>
<td>9.5</td>
<td>1.9</td>
<td>19.0</td>
<td>16.8</td>
<td>2.6</td>
<td>13.1</td>
<td>13.1</td>
<td>23.9</td>
<td>100.0</td>
</tr>
<tr>
<td>B</td>
<td>4.00</td>
<td>44.0</td>
<td>43.2</td>
<td>1.90</td>
<td>1.68</td>
<td>0.26</td>
<td>1.31</td>
<td>1.31</td>
<td>2.39</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Results: see Fig. 1 and footnotes. We found that V was mobilized at fO2's equal to or greater than the Fe/FeO buffer, and was concentrated in veins of VFe oxide in the metal.

However, the most significant result was that, for the range of experimental conditions employed, no significant mobilization or loss of Mo and W from the metal was observed if Fe was not oxidized. (This result is also consistent with thermodynamic calculations showing that the free energies of formation of FeO, MoO2 and WO2 are similar. At temperatures and oxygen fugacities where Fe and FeO coexist, W and Mo are calculated to distribute themselves approximately equally between metal and oxide, assuming ideal solid solution in both phases.) At the Ni/NiO buffer and in air, a coating of Fe oxide formed on the metal and Mo and W were partly mobilized. However, in these cases, not all of the Mo and W escaped, and much of the Mo and W concentrated in the surface Fe oxide layer. In a related series of experiments, our co-workers Köhler et al. (8) found no Mo or W losses at the Fe/FeO buffer, but they did find significant, and approximately equal, losses of about 50% of the Mo and W at the Ni/NiO buffer.

Conclusions. The major conclusion is that in CAI's, wherever Mo and W anomalies are observed in all-metal nuggets (nuggets without any associated Fe oxide), Mo and W were not removed secondarily after solidification of the CAI i.e. the nuggets were deficient in Mo and W from the beginning, and this primary feature presumably resulted from their formation at high temperatures under substantially more oxidizing conditions than in solar gas (3). All-metal nuggets are the most common (and often the only) type of opaque grain in Type A and Type C CAI's; many such nuggets have been analysed and contain Mo and W anomalies (9). In Type B CAI's, nuggets are also typically at least as numerous as Fe-oxide-bearing grains, and in many cases such nuggets also display Mo and W anomalies e.g. (1). Therefore, for the majority of CAI's and opaque grains, secondary loss of Mo and W does not appear to be the cause of Mo and W anomalies. Furthermore, wherever anomalies are observed in CAI's, Mo is always more depleted than W, a fact readily accounted for by high temperature condensation (3) but not by subsolidus loss. Our co-workers have
shown that, during subsolidus loss, Mo and W are approximately equally depleted (8). (Careless readers please note: we are not arguing against subsolidus, in situ, alteration of metal, which we believe played a major role in the formation of Frondlings. We are merely arguing that Mo and W anomalies pre-dated such alteration.)

Implications. The schizophrenia described in the opening paragraph remains uncured. Consequently, it seems that in the part of the nebula where CAI's formed, high temperature oxidizing conditions temporarily proceeded more reducing conditions. The gas then became oxidizing again at lower temperature and some metal grains were altered to Frondlinge. This sequence is untidy because it goes against the simple, popular concept of an initially $H_2$-rich, reducing, nebular gas which became more oxidizing as the $H_2$ dispersed and temperature fell.


Fig. 1 Summary of experimental conditions and results.

Key: $\bullet$ = no Mo, W mobilization; no Fe oxide formation.

$\Delta$ = Mo, W mobilized; Fe oxide coating formed.

Numbers refer to points on Figure. 1 = (Cr$_2$O$_3$, 930°C, 88 hr.) No oxides, no loss V, Mo, W. 2 = (MnO, 930°C, 88 hr.) No oxides, no loss V, Mo, W. Mn entered from buffer, made MnPt & MnRu phases. 3 = (FeO, 930°C, 45 hr.) No loss V, Mo, W. Alloy A - no oxides. Alloy B - V mobilized into VFe oxide inclusions. 4 = (FeO, 1130°C, 46 hr.) As for (3). 5 = (NiO, 730°C, 70 hr.) Fe oxide coating; V, Mo, W mobilized. Alloy A - Mo concentrates in coating, W loss. Alloy B - V, Mo, W concentrate in coating. 6 = (NiO, 930°C, 67 hr.) Fe oxide coating; V, Mo, W mobilized and partly lost. 7 = (NiO, 1200°C, 68 hr.) Ni enters from buffer; V, Mo, W mobilized; V, Mo, W lost. 8 = (Air, 830°C, 14 hr.) Fe oxide coating; mobilization V, Mo, W and concentration in coating; V, Mo, W loss.