PHOSPHORAN-OLIVINE IN OPAQUE ASSEMBLAGES OF THE NINGQIANG CARBONACEOUS CHONDRITE: IMPLICATION TO THEIR PRECURSORS. Ying Wang¹, Xin Hua¹,² and Weibiao Hsu¹, ¹Laboratory for Astrochemistry and Planetary Sciences, Purple Mountain Observatory, Nanjing, 210008, China (y_wang@pmo.ac.cn); ²Dept. of Mechanical/Aerospace Engineering, Arizona State University, Tempe, AZ 85287.

Introduction: Opaque assemblages (OAs) are very complex objects in CV3 chondrites. They consist of Ni-rich metal, Fe-oxides, sulfides, phosphates, silicates, refractory Pt-group element metals (PGMs) and their oxides. OAs occur in CAIs, chondrules, and matrix of CV3 chondrites [1,2]. Some of the phases are refractory and others are volatile. They can consist of highly reduced or highly oxidized minerals. OAs were once thought to have condensed from the solar nebula, assembled and captured by host CAIs [1]. Later experimental studies revealed that OAs were not nebular condensates but low-temperature alteration (exsolution, oxidation and sulfidation) products of pre-existing homogeneous metal alloys within CAIs and chondrules [2]. Recent in situ O isotopic analyses of magnetite in OAs of Ningqiang further indicated that OAs were aqueous alteration products of pre-existing metal within chondrules and matrix [3,4]. However, the origin of OA precursors is still controversial. They could be metal grains directly condensed from the solar nebula and incorporated into CAIs and chondrules [5] or they were locally produced during CAI and chondrule formation [2].

As a companion study of OAs in Ningqiang, we report here the first occurrence of phosphoran-olivines (P-olivines) in OAs and discuss its implication to the origin of OA precursors.

Results: In Ningqiang, numerous round to oblate OAs with sizes from 10 to 600 µm are found in chondrules and matrix (Fig.1). They are mainly composed of Ni-rich metal, magnetite, pyrrhotite, with minor amounts of pentlandite, whitlockite, P-olivine, pyroxene, and trace amounts of nano-sized PGE alloys. The average composition of Ni-rich metal is Ni₆₄Fe₃₄Co₂, and some grains contain Pt up to 1 %, but none has detectable P. Olivines in OAs are phosphorous (0.2 ~ 2.7 % P₂O₅) [7], the syenitic pipe from the Pine Canyon (up to ~ 6 % P₂O₅) [8] and the metapelitic gneisses from the Ötz Valley (up to ~ 8.8 % P₂O₅) [9].

Because of their similar ionic radius and charge, P can reside in the crystal lattice of olivine by substituting Si at tetrahedral sites and gain charge balance via the vacancies of octahedral sites [10].

The distribution coefficient for P in olivine in equilibrium with a melt is only 0.02-0.04 [11]. The occurrence of P-olivine is indicative of rapid crystallization from P-rich melts [7-10]. In pallasites, Fe metal and olivine are the two major co-existing phases. P-olivine often appears as a rim along the edge of a normal olivine crystal. P-olivines in pallasites were thought to have formed by subsolidus reaction of olivine with P-bearing metal [6]. However, the distribution coefficient of P between metal and silicate is far greater than 1 [12], which means that P would preferentially participate into the metallic phase. It is possible that P-olivine formed by redox reaction of pre-existing olivine with P-bearing molten metal during fast cooling through high temperature regions [13]: olivine + P (in metal) = P-olivine + pyroxene + Fe (metal). This must be a very unique non-equilibrium process.

P-olivines in Ningqiang OAs are similar to those in pallasites, in that olivine coexisted with Fe metal [6]. Therefore, P-olivine in OAs could have formed by a similar process that produced pallasitic P-olivine. We suggest the following process responsible for the formation of P-olivines found in Ningqiang OAs. During chondrule formation, olivine first crystallized from the silicate melt. Some of olivine grains were trapped in molten metal separated from a silicate melt due to immiscibility. P-olivine subsequently formed by redox reaction of pre-existing olivine with P-bearing molten metal during the fast cooling chondrule formation process. The occurrence of P-olivine in Ningqiang OAs provides important clues to the origin of OAs.

It is now generally believed that OAs of CV3 chondrites were produced by secondary alteration of pre-existing metal grains in CAIs, chondrules, and matrix [2-5]. At a lower temperature, the OA precursors exsolved into immiscible metallic phases (such as Pt,Os-rich nuggets and Ni-rich metal) as Fe
was removed from them by oxidization and sulphidization to form magnetite and associated phases during slow cooling at much higher $f_{O_2}$ and $f_{S_2}$ than solar fugacities [2,5]. However, there are two different views on the origin of OA precursors: one is endogenic, which holds that the metal alloy crystallized from immiscible droplets suspended in the silicate melt during CAI and chondrule formation [2]; the other is epigenic, which believes that the metal grains condensed directly from the solar nebula and then incorporated into CAIs and chondrules [5].

It was noted that individual OAs in a single CAI can vary largely in mineral assemblages and the abundances of Pt-group elements. If the precursors to these OAs were produced from the same melt, they should have very similar siderophile abundances [5]. However, the chemical variations of OAs in a single CAI can be explained by processes that occurred during melting and equilibrium of the CAIs rather than a process that sampled diverse grains formed under variable conditions in the nebula [2]. Elemental redistributions during secondary alteration processes could also cause the chemical variations of OAs [14]. The occurrence of P-olivine in Ningqiang OAs provides strong evidence that OA precursors were locally produced during chondrule formation.

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**Table 1**: Mineral chemistry of olivines in Ningqiang

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O</td>
<td>0.70</td>
<td>0.70</td>
<td>1.09</td>
<td>0.14</td>
<td>n.d.</td>
</tr>
<tr>
<td>SiO2</td>
<td>31.8</td>
<td>31.2</td>
<td>30.8</td>
<td>35.0</td>
<td>40.6</td>
</tr>
<tr>
<td>FeO</td>
<td>45.8</td>
<td>37.6</td>
<td>37.3</td>
<td>41.5</td>
<td>1.83</td>
</tr>
<tr>
<td>MgO</td>
<td>17.6</td>
<td>24.8</td>
<td>25.2</td>
<td>22.0</td>
<td>56.3</td>
</tr>
<tr>
<td>CaO</td>
<td>0.98</td>
<td>0.43</td>
<td>0.45</td>
<td>0.09</td>
<td>0.37</td>
</tr>
<tr>
<td>V2O3</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.04</td>
<td>0.31</td>
<td>0.20</td>
<td>59.3</td>
<td>1.60</td>
</tr>
<tr>
<td>MnO</td>
<td>0.36</td>
<td>0.19</td>
<td>0.23</td>
<td>0.37</td>
<td>0.16</td>
</tr>
<tr>
<td>P2O5</td>
<td>2.68</td>
<td>3.04</td>
<td>3.94</td>
<td>0.19</td>
<td>n.d.</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>98.8</td>
<td>99.5</td>
<td>99.5</td>
<td>99.3</td>
</tr>
</tbody>
</table>

Note: 1-3, P-olivines in OAs; 4, olivine at the chondrule-OA boundary; 5, olivine in the chondrule host. n.d.: not detected.