THE RELATIONSHIP BETWEEN LUNAR METAL PARTICLES AND PHOSPHATE MINERALS, J.J. Friel, and J.I. Goldstein, Metallurgy and Materials Science Dept., Lehigh University, Bethlehem, PA, 18015.

Lunar metal particles often contain phosphorus and are commonly associated with phosphate minerals. It has been suggested that phosphorus in lunar metal is derived from the reduction of calcium phosphate (1,2). However, it has also been suggested that the phosphate adjacent to metal grains may be the result of the reverse reaction in which phosphorus is oxidized out of the metal (3,4,5). It has been shown experimentally that this reaction may go either way depending on a number of factors; principally, oxygen fugacity, maximum temperature and cooling rate (6).

Figure 1 illustrates the effect of $f_{O_2}$ and temperature. As a material is heated within the region below the cpx-iron/whitlockite-opx equilibrium curve, phosphorus is reduced into metal. The amount of phosphorus dissolved is limited only by the diffusion of phosphorus in FeNi metal and the reaction rate at the interface until the equilibrium concentration is reached. During cooling, phosphorus will leave the metal if the $f_{O_2}$ becomes greater than the equilibrium curve. The highest P content would be expected in the metal grains of rocks which were heated to partial melting under reducing conditions and then cooled quickly enough to preserve the reducing environment. Previous experiments indicated that Fe could be saturated with P even below the solidus in 1 day at $10^{-20}$atm.$O_2$ and 950°C. Phosphorus loss by oxidation and the formation of whitlockite, however, is limited by diffusion rates in the surrounding silicates and is probably negligible below 750°C. If adjacent phosphates are oxidation products, they would, therefore, be expected in rocks heated hot enough to allow the reduction reaction to proceed and then cooled slowly under more oxidizing conditions.

In order to apply the knowledge gained from experimental work to lunar samples, the metal particles and the phosphates were analyzed in three Apollo 14 rocks: 14310, 14306, and 14321. The rocks were chosen because of their high bulk phosphorus contents, and because they have apparently been reheated to different temperatures and cooled at different rates. The phosphorus relationships in sections: 14310, 175; 14306, 60; and 14321, 215 were studied in detail, while other sections of these rocks were checked to confirm the observed trends.

Sample 14310 is a feldspathic basalt which has been interpreted as an impact melt (3). Axon and Goldstein (1) estimate that it cooled from the solidus to 700°C in a period of about a month. Sample 14306 is a strongly annealed breccia (7). Anderson et al. (8) observed three generations within this breccia; however, nearly all of the metal occurs in the predominant second generation. This second generation is a dark matrix polymict breccia with occasional clusters of plagioclase laths, which appear to indicate local melting. Sample 14321 is a moderately annealed dark matrix breccia (7). This sample and the second generation of 14306 have been interpreted as examples of the Fra Mauro formation (9); however, 14306 apparently cooled more quickly (8) than 14321. Actual values of maximum temperature of reheating and cooling rate depend on many factors which are not known for these samples. We may, however, infer a relative order of increasing temperature: 14321, 14306, 14310; and increasing cooling rate: 14310, 14321, 14306.
PHOSPHORUS RELATIONSHIPS

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The metal grains in these rocks were analyzed with the electron microprobe for Fe, Ni, and P using the crystal spectrometers in the beam scanning mode. The phosphates were analyzed for Ca, P, Fe, Na, Si, Mg, Cl, and F using the solid state detector. At least 25 metal particles from each of these rocks were analyzed, and the average phosphorus content of the particles is as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aver. P (wt.%)</th>
<th>Range of P Conc.</th>
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<tbody>
<tr>
<td>14310</td>
<td>0.163</td>
<td>0.01 - 0.36</td>
</tr>
<tr>
<td>14306</td>
<td>0.153</td>
<td>0.04 - 1.33</td>
</tr>
<tr>
<td>14321</td>
<td>0.029</td>
<td>0.01 - 0.09</td>
</tr>
</tbody>
</table>

No phosphides were observed optically in the grains of 14321. The averages for 14306 and 14310, however, are strongly dependent on the phosphide content of the grains analyzed. It is probable that 14321 was not reheated sufficiently to reduce much phosphorus into the metal. This result is based on the assumption that the fo2 during reheating was similar for all three rocks. Since 14306 and 14321 are from the same formation, this may be a reasonable assumption. However this has not been established. The metal of 14310 and 14306 acquired considerably more phosphorus probably due to a higher temperature of reheating. Sample 14310 may have contained more phosphorus in the metal at high temperature but lost some to oxidation on cooling. The texture of 14310 indicates that it must have spent considerably more time at high temperature than the breccias. Unless very reducing conditions were maintained during this cooling period, the intrinsic fo2 of the rock (10) would be sufficiently high to oxidize phosphorus out of the metal.

The phosphorus trends in these rocks are consistent with the observations of Gooley et al. (2); that is, phosphorus content in reheated metal particles increases with increasing temperature but decreases with slower cooling rate. The dependence on cooling rate, however, assumes that cooling is done under conditions more oxidizing than those required for phosphate reduction. Such a 2-step process is consistent with a transient reducing agent such as carbon or hydrogen, which would be present during the reheating event but then lost during cooling.

Analyses of numerous phosphate grains from these rocks revealed no significant difference in any of the elements analyzed between phosphates adjacent to metal and sulfide particles and the independent phosphates in the matrix. Apatite was the only phosphate mineral adjacent to metallic particles in 14306 and 14321. Both apatite and whitlockite were present in the matrix of these breccias, but apatite predominated. In 14310, whitlockite predominated over apatite away from the metal grains, but although apatite predominated around the metal, some whitlockite was also present. No significant phosphorus concentration gradients were observed from the metal grains to adjacent apatite crystals in any of the rocks studied. Further, many of these apatites had idiomorphic outlines as did both apatite and whitlockite crystals in the matrix. Concentration profiles of P were evident, however, from metal grains to peripheral whitlockites, all of which had irregular outlines in 14310. The highest phosphorus was found at the center of the metal grain decreasing toward the whitlockite. This gradient is typical of diffusion out of the metal and might be explained by oxidation of the phosphorus in the metal to form
whitlockite. It appears that the apatite commonly associated with lunar metal and sulfide particles merely adhered to the Fe-Ni-P-S liquid without reacting with it. On the other hand, whitlockite, when it occurs around metallic particles in 14310, is probably an oxidation product.

This type of "second generation" whitlockite was also observed in soil 14162,80 by Agrell et al. (4). They found greater FeO in the whitlockite adjacent to metal grains than in those in the matrix. However, the analysis of 14310,175 revealed no consistent difference with the exception of a greater abundance of rare earth elements in the independent whitlockites.

In summary, it appears that phosphorus in lunar metal particles is related to the phosphate minerals by a redox reaction. The independent phosphates probably formed over much of the cooling period of the rock with whitlockite favored at higher temperature. While the rock was at high temperature, however, P was free to diffuse and dissolve in the metal droplets providing conditions were sufficiently reducing. If the rock was partially molten, this process would take less than 1 hr. If cooling occurred slowly under less reducing conditions, some of the phosphorus in the metal particles would be oxidized to form whitlockite. Some apatite, however, persisted to lower temperatures in contact with the immiscible metallic liquid, but evidently did not react with it. A reheating event may be viewed in terms of the temperature and fO2 plot in Figure 1. Upon impact, a rock may be heated to an area in the vicinity of, or below, the open box determined for lunar breccias by Sato (10). This is below the cpx-I/whit-opx curve, thus phosphates should be reduced. Cooling may take place on a line extending from this box and intercepting the P equilibrium curve between about 700° and 850°C. If the fO2 is much above the curve at 850°, P will be lost by oxidation. If, however, the cooling path remains below that curve until about 750°C or below, diffusion will limit oxidation, and the P content of the metal will be preserved.