Phosphorus behaviour in pallasites: Experimental constraints

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Pallasites are stony-iron meteorites mainly composed of olivine (Fa_{11-20}) and iron-nickel metal in approximately equal weight proportions. They are believed to have formed at the core-mantle boundary of planetary bodies. An alternative model is that these meteorites represent pieces of metal pools or 'raisins' isolated within the silicate mantle of their parent body. The minor-element content of the pallasites metal suggest that pallasites are linked to the IIIAB iron-meteorite group (Scott, 1977). Trace and minor element variations within the IIIAB group has been successfully modelled considering that these iron meteorites are pieces of a single asteroidal core material which solidified according to a fractional crystallisation process (Haack and Scott, 1993). Following this model, the high Ni-content of the pallasites metal relative to IIIAB iron-meteorites and the presence of olivine crystals is consistent with a late crystallizing core-liquid, enriched in incompatible elements, which has intruded the asteroid olivine-mantle as already proposed by Scott (1977). A remarkable feature in pallasites is the occurrence of phosphates coexisting with schreibersite, $(Fe,Ni)_3P$. Whitlockite, $Ca_3(PO_4)_2$, farringtonite, $(Mg,Fe)_3(PO_4)_2$, and stanfieldite, $Ca_4(Mg,Fe)_5(PO_4)_6$, are the most widespread species. Phosphoran olivine, a forsterite-rich olivine containing up to 4–5 wt.% P_2O_5 , has also been reported in some pallasites. Phase equilibria involving both phosphates and phosphides have been used to infer oxygen fugacity in pallasites. If we assume that pallasites are composed of metal (either metal pools or core) and olivine of mantle origin and since phosphorus is a siderophile element, accordingly schreibersite phosphorus was dissolved in the metal. The origin of the phosphorus in phosphates, however, is not as obvious. Phosphates could be of mantle origin where they would coexist with olivine. This would rule out the core-mantle origin for pallasites since in terrestrial magmatic systems, phosphates are known to be late crystallizing phases unlikely to occur in magmatic cumulates. However, on the basis of *REE* pattern analyses, Davis and Olsen (1991) pointed out that some calcium-rich phosphates (whitlockite and stanfieldite) in Springwater and Santa Rosalia have crystallised from a chondritic melt. The *REE* pattern and content of some other phosphate crystals occurring in phosphate-pyroxene-troilite intergrowths between olivine and metal, is different and seem inherited from olivine. In that case, phosphates are supposed to have formed by subsolidus reaction between metal and olivine as suggested by the textural observations. Buseck and Holdsworth (1977) have described striking phosphate textures which rather suggest that phosphates where present as molten droplets attached onto the olivines surface.

Phosphates appear to be key minerals in order to decipher the pallasites origin. To our knowledge, no experimental data on the silicate-metal-phosphate system relevant to pallasite formation. Only thermodynamic calculations have been performed in that system in order to derive oxygen fugacity in pallasites (e.g. Righter *et al.*, 1990).

Run procedure

We have conducted a set of experiments at 1000°C and 1 GPa (10 days duration) in the olivine-iron metal-schreibersite-O_2 system. The initial idea was to test whether with increasing the oxygen amount in the starting material, phosphates would grow and what phosphates? At this stage, sulphur and nickel were ignored to start with a simple chemical system (i.e. Si-P-O-Fe-Mg ± Ca). The capsule was made of pure iron and the sample was sealed under pressure by friction-fitting lids in a piston-cylinder apparatus using NaCl-pyrex based pressure cells. This method which allows to insure a close system with respect to oxygen, requires, however, pressures that are definitely higher than that encountered in small planetary bodies.

The starting material is a mixture of FeP, Fe, San Carlos olivine (Fo_{90}) or synthetic forsterite and Fe_2O_3 (oxygen carrier). The olivine/metal weight ratio in the starting material is close to unity and the

Fe/P molar ratio although much higher than in pallasite to facilitate the phase observation, is kept below three. After the run, the capsule is cut into two pieces and polished under alcohol. Textures are characterized using SEM and phases are analysed using an electron microprobe (Cameca SX50).

Results

After several attempts, the best results were obtained mixing approximately 52 wt.% fine grain San Carlos olivine (8–20 μm) with 25 wt.% iron metal, 10 wt.% FeP and 13 wt.% Fe_2O_3.

In this run, schreibersite (Fe_3P) was recovered instead of FeP. All iron grains have compositions around $Fe_{95}P_5$ and $Fe_{96}P_4$ and are homogeneous across the sample. This phosphorus content is consistent with the phosphorus saturation concentration in αFe around 1000°C derived from the Fe-P one-atmosphere phase diagram.

Hematite is no longer present in the experimental product. Mg-bearing wuestite ($Wu_{83.5}$) has formed, again with a homogeneous composition across the whole sample. The larger olivine grains (above 10 μm) are zoned with a decreasing forsteritic content from core (Fo_{90}) to rim (Fo_{73}). Smaller olivine crystals are homogeneous and exhibit a Fo_{73} composition. Taking advantage of the temperature dependency of the Fe-Mg partioning between olivine and wuestite, we were able to calculate, at 1 GPa, an equilibrium temperature of ca. 1050°C, in good agreement with the run temperature. Furthermore, the composition of the wuestite in equilibrium with iron metal implies an oxygen fugacity of IW-O.25 $\text{Log}f_{O_2}$.

An interstitial phase is clearly observed which is interprated as a quenched liquid phase. This intergranular phase tends to assimilate the capsule material by penetrating along the iron crystals grain boundary. Microprobe analyses indicate this phase to be phosphatic with a $A_3(PO_4)_2$ stoichiometry (A = 0.78Mg + 0.20Fe + 0.02Ca). Calcium, although minor, is strongly partitioned into this phase. According to its stoichiometry, when crystallizing, this molten phase is likely to produce typical pallasite phosphates like whitlockite, farringtonite or stanfieldite.

Interestingly, no phosphoran olivine was detected even though our synthetic system has a much higher phosphorus content than natural pallasites.

Conclusions

Although preliminary, these results give an insight into possible reactions involving phophates and which may have occurred in pallasites. These reactions involving P°, P^{5+}, Fe°, Fe^{2+} are controlled by oxygen fugacity. In our synthetic system, olivine composition was modified via the following reaction: $[Fe]^{metal} + 1/2O_2 \rightarrow [FeO]^{olivine}$

The iron incorporation in olivine must, in turn, provide the phosphatic melt with magnesium. The Ni-content of pallasite olivines indicates that they equilibrated with the metal. On another hand, the Prior's rule implies that olivines have also equilibrated with metal in the presence of excess silica. However in pallasites, a part from olivine there is no other early silicate. Equilibrium between a phosphatic melt and olivine provides a way to modify the Fe/Mg content of olivine without involving an extra silicate phase. In any case, phosphate textures as those described by Buseck and Holdsworth (1977) strongly suggest that such a residual melt of phosphatic composition did effectively occur.

Clearly, further experiments need to be carried out, especially at lower oxygen fugacities. The oxygen fugacity calculated for the experiment described above is higher than that generally assumed for pallasites (e.g. Righter *et al.*, 1990). However, it should be noted that the composition of our synthetic olivine (Fo_{73}) approaches that of the Eagle Station meteorite ($Fo_{79.5}$). Furthermore, thanks to the experimental procedure described here, we should be able to extend this study to nickel- and sulphur-bearing systems relevant to pallasite mineralogy.

References

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