

AN EXPERIMENTAL STUDY OF PHOSPHORAN OLIVINE AND ITS SIGNIFICANCE IN MAIN GROUP PALLASITES. J. S. Boesenberg^{1, 2}, D. S. Ebel² and R. H. Hewins¹, ¹Geological Sciences, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, ²Earth and Planetary Sciences, American Museum of Natural History, Central Park West, New York, NY 10024 (boesbrg@amnh.org, debel@amnh.org, hewins@rci.rutgers.edu)

Introduction: Experiments were conducted to investigate the occurrence and stability of phosphoran olivine. Phosphoran olivine is rare in nature, but has been found in four Main Group pallasites: Springwater, Brahin, Rawlinna and Zaisho [1, 2]. Some olivine crystals within these pallasites contain regions of phosphoran olivine that have between 3 and 5 wt% P₂O₅ [1, 2], where phosphorus substitutes for silicon in the tetrahedral site of the olivine structure. The formation of phosphoran olivine has been interpreted as subsolidus reaction between olivine and phosphorus-bearing metal [1]. However, subsolidus growth of phosphoran olivine is not consistent with existing phase diagrams [3] or experimentally determined partitioning, which shows that phosphorus in olivine typically is present only at the level of tens to a few hundreds parts per million [4, 5]. The distribution coefficient for phosphorus in olivine in equilibrium with a melt is only 0.02-0.04 [6]. Texturally, phosphoran olivine in pallasites appears as a rim along the edge of a normal olivine crystal, however sharp contacts always exist between phosphoran and “normal” regions. Phosphoran regions as large as 200 microns wide and several millimeters long have been noted [1].

Only two other natural occurrences of phosphoran olivine are described in the petrologic literature. They are the Disko Island silicate inclusions in an iron-carbon alloy [7], and a syenitic intrusion into an early Tertiary volcanic country rock in Pine Canyon, Utah [8]. These occurrences however are quite different from pallasites. Dendritic phosphoran olivines (and pyroxenes) were found by [7], while the olivine found in nepheline- and spinel-rich “skarn” assemblages of the Pine Canyon breccia pipe appear as irregular crystals whose phosphorus composition varies widely (up to 6.1 % wt. P₂O₅) both between and within crystals [8]. Both [7] and [8] have argued that the formation of phosphoran olivine by melting and crystallization is only possible under the restricted conditions of rapid crystallization from a melt, the presence of high P (and correspondingly low calcium), and an oxygen fugacity near or below the IW buffer curve. These observations have prompted us to investigate the oxygen fugacity, temperature and compositional stability fields of phosphoran olivine, determine whether the formation of the phosphoran olivine is consistent with current models for pallasite formation, and determine a charge balance substitution for this unusual mineral variety.

Experimental Procedure: Experimental charges of FeP or Mg₂PO₇ were mixed with San Carlos olivine (Fo₉₂) and placed inside dunite crucibles made from the Twin Sisters Range, Washington dunite. The crucibles were placed in a vertical muffle tube Deltech furnace and oxygen fugacity was controlled using a mixture of CO and CO₂. The experiments were run for durations of one day to three weeks.

Experimental Results: The experiments using FeP/San Carlos olivine were run in the range of 900 to 1200°C at a fugacity of IW-1 log units. The four experiments between 975 and 1075°C and durations between one day and one week produced phosphoran olivine. Equilibrium was NOT achieved in these experiments due to the sluggish kinetics. The charges contained fayalitic (Fo₂₀₋₂₅) cores of olivine surrounded by a wide rim (up to 30 microns) of phosphoran olivine, which was then surrounded by a phosphate-rich melt (Fig. 1). Silica was often present. However, when durations were extended to two weeks or more in the same temperature range and equilibrium was closely approached, no phosphoran olivine was present, only fayalite, iron rich pyroxene, and the phosphate-rich glass remained.

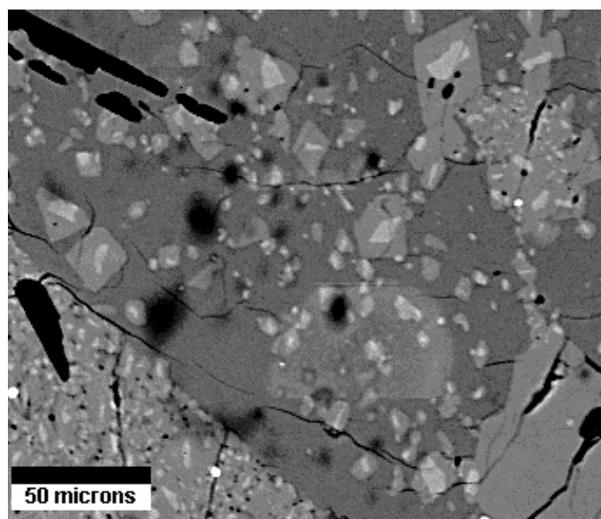


Fig. 1. Phosphoran olivine rims (med gray) surrounding fayalite cores (lt gray) in a phosphate-rich glass (dk gray) with silica (black).

Similar results were found when using Mg₂PO₇/San Carlos olivine at 1300°C and at a fugacity of FMQ-1. Experiments with durations of up to one week contained phosphoran olivine rims surrounding fosterite

(Fo₈₉₋₉₄) cores. Rims ranged from 3 to 15 microns and often tiny blebs of silica were adjacent to them. The single longer duration experiment of nearly two weeks showed no phosphoran olivine and silica was not found.

Discussion: Phosphoran olivine (and phosphoran pyroxene) is a disequilibrium phase. Its presence is indicative of rapid crystallization from a phosphorus-rich olivine normative melt which has not equilibrated with olivine or the other solids present. There are four requirements needed to produce phosphoran olivine: 1) enrichment of phosphorus in the melt, 2) depletion of SiO₂ in the melt, 3) rapid crystallization from a melt or rapid cooling in an unequilibrated system, and 4) olivine as the liquidus phase at the time of crystallization. The suggestion by [7] and [8] that low calcium correspond with phosphorus enrichment does not seem to be necessary to produce phosphoran olivine with greater than 1% P₂O₅. As long as olivine is the liquidus phase, calcium content should have a negligible effect. Furthermore, the oxygen fugacity controls phosphoran olivine formation only to the extent of influencing the composition of the melt. Fugacity will not have any direct effect on the phosphorus ion, as its charge will remain +5 throughout the olivine stability field. Phosphoran olivine was produced in these experiments from just below the FMQ buffer to IW-1.1 log units.

The occurrence of phosphoran olivine in a few pallasites suggests that it forms as a result of late stage crystallization (or recrystallization) from phosphorus-rich melt pockets (perhaps as a result of Ostwald ripening), and not as a result of subsolidus reaction between phosphorus-bearing metal and olivine. Its occurrence further suggests that the olivine cooled relatively quickly from high temperature, since slow cooling at high temperature would crystallize any remaining melt pockets into additional olivine and phosphate and equilibrate the system. The presence of phosphoran olivine is consistent with more recent minor and trace element research [9, 10] which suggests fast cooling through high temperatures, but slow cooling through lower temperatures.

The question of charge balance of phosphorus in olivine has been addressed by every researcher who has written on phosphoran olivine [1, 2, 7, 8, 11]. [1] left charge balance an open question suggesting interstitial anions, cation site vacancies, or substituting ions. [2] initially suggested charge balance by the addition of lithium, but ion probe work showed negative results. They then suggested "charge balance by having vacant octahedral sites". [7] agreed with [2] that octahedral site vacancies charge balance the P in the tetrahedral site, because octahedral cation totals were consistently low for the structural formula. [11] did high resolution structure determination and confirmed the negative correlation between Si and P, but had no convincing evidence

for the octahedral site vacancy. [11] suggested that in addition to $M + 2Si \leftrightarrow 2P$ substitution, that a tetrahedral vacancy involving $5Si \leftrightarrow 4P$ may occur. The difficulty faced by [2], [7] and [11] mainly hinges on the relatively low P₂O₅ content in natural samples. Our experimentally produced phosphoran olivine (Fo₂₀) contains up to 27% P₂O₅, the maximum amount possible in an olivine structure, with 70% of the tetrahedral sites being replaced by P. These experimental data confirm the vacancy of the octahedral site and its correlation with the tetrahedral deficiency (Fig. 2). The latter $5Si \leftrightarrow 4P$ scheme is not present. The charge balancing scheme for phosphoran olivine is (more formally written): $4^{VI}M^{2+} + 2Si^{+4} \leftrightarrow 3^{VI}M^{+2} + 2P^{+5} + {}^{VI}[]$.

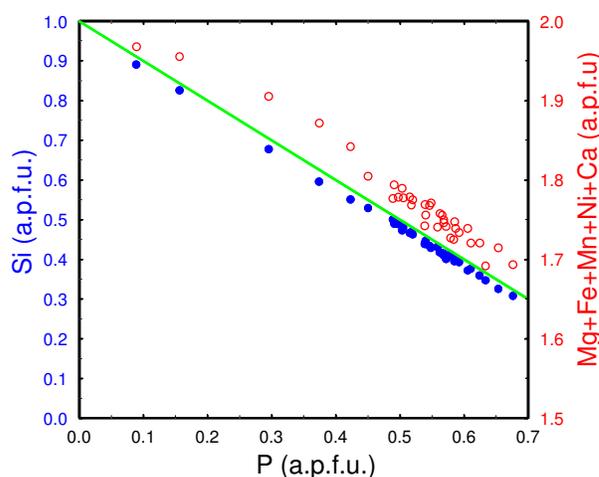


Fig. 2. Overlapping graphs of P vs Si (blue) and P vs. M cations (red) in phosphoran olivine in atoms per formula unit (a.p.f.u.). P vs. Si shows the depletion from full tetrahedral site occupancy where $P + Si = 1$ (green line). P vs. M cations show increasing depletion of the octahedral sites with increased P. One M must be removed (along with two Si) for every two P added to the olivine (complete removal of one M is shown by the green line).

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