

EFFECTS OF PHOSPHORUS ON MARTIAN MAGMA GENESIS: AN EXPERIMENTAL STUDY. V. Payre^{1,2}, and R. Dasgupta², ¹Northern Arizona University, Flagstaff, AZ (valerie.payre@nau.edu), ²Department of Earth, Environmental and Planetary Sciences, Rice University, Houston, TX.

Introduction: Martian magma compositions are distinct from those of terrestrial analogs like mid-ocean ridge or intraplate basalts, with for example lower SiO₂ contents [1]. One key difference between the martian and terrestrial mantle is the phosphorus content of the latter (P₂O₅ = 0.17 wt.%), which is ten times higher than that of the terrestrial mantle (P₂O₅ = 0.04 wt.%) [2]. In terrestrial basaltic melts, phosphorus is known to significantly affect the liquidus field of polymerized minerals like pyroxene, promoting its expansion over less polymerized ones like olivine [3]. With the formation of metal (M) -phosphorus complexes, the composition of melts is in turn affected as observed with the depletion of SiO₂ with the addition of P₂O₅ in terrestrial basaltic liquids [4]. With ten times higher P₂O₅ contents in Mars' mantle, one may expect its effects on martian melt composition and melting phase relation, as suggested by thermodynamical modeling [5], to be significant. Here, we explore the effects of phosphorus on partial melting of the martian mantle through piston-cylinder experiments.

Methods: Nominally anhydrous experiments have been performed on a primitive mantle composition [6] at 2 GPa, with variable P₂O₅ concentrations (0 wt.% and 0.5 wt.%). The experiments were performed using a half-inch piston-cylinder apparatus in the experimental petrology lab at Rice University. All experiments were conducted at temperatures between 1210 and 1450 °C for 72 to 24 hours with lower temperature experiments run longer. The texture, spot compositional analyses, and wavelength dispersive spectroscopy (WDS) elemental maps of the experimental samples were obtained using an electron probe micro-analyzer at Rice University.

The experimental procedure is similar to [7], which ran partial melting experiments on the same mantle composition [6] with a mantle-like P₂O₅ concentration (0.2 wt.%), at the same pressure (2 GPa), in the same lab. Therefore, we combined our results with those of [7] to assess the role of phosphorus in affecting martian mantle melting.

Approach to Equilibrium: As observed in backscattered electron images, boundaries between grains are well defined, supporting an approach to textural equilibrium. The sum of squared residuals obtained from mass balance calculations is low (<0.2), suggesting that experiments represent close systems. For each sample, the exchange coefficient between Fe and Mg between olivine and liquid is between 0.30 and

0.40, consistent with the accepted value of ~0.35 for the martian magmatic system [1]. The phase proportions and compositions of each bulk composition follow a systematic trend as a function of temperature. For all these reasons, the experiments are thought to approach thermodynamic equilibrium closely.

Phase Proportions: The proportion of each equilibrium phase was estimated through mass balance calculations. At temperature >1260 °C, mixtures of glass and dendritic pyroxene form melt pools. Regardless of phosphorus content, the extent of melting for P-free and P-bearing sample is similar for a given temperature. From backscattered images, experiments with bulk P₂O₅ of 0.5 wt.% present a larger quenched melt pool compared to P-free samples that shows a larger proportion of dendritic pyroxene, at similar extent of melting. This supports that phosphorus facilitates polymerization of (SiO₄)⁴⁻ tetrahedra as suggested by [3-4].

Regardless of phosphorus content, all experiments contain olivine and orthopyroxene. Pigeonite melts out at 11-18 wt.% and 10-19 wt.% of melting for P-free and P-bearing samples, respectively, and spinel melts out at 18-23 wt.% and 10-19 wt.% of melting for P-free and P-bearing samples, respectively. As shown on Fig.1, the addition of phosphorus leads to an increase of residual orthopyroxene and a decrease of olivine, regardless of the extent of melting, illustrating an expansion of the liquidus field of orthopyroxene over olivine.

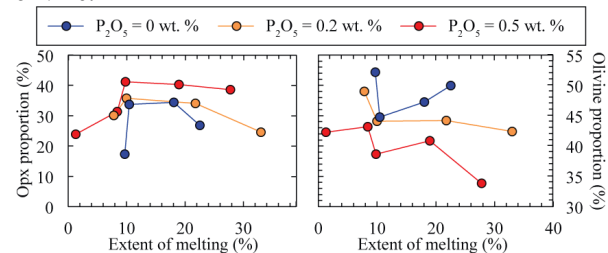


Fig.1. Proportion (in wt.%) of orthopyroxene (left) and olivine (right) in the mantle residue as a function of extent of melting (in %).

Mass balance calculations suggest the occurrence of residual apatite in low melting degree samples (<10%), which was confirmed by WDS elemental maps revealing SiO₂- FeO- depleted and CaO- P₂O₅-rich μm-size grains.

Liquid Compositions: Liquid composition is measured using defocused e-beam, integrating both

quenched glass and dendritic pyroxene. The addition of phosphorus lowers SiO_2 up to 13 wt.%, especially at low extent of melting (Fig. 2), which is likely related to the increased stability of orthopyroxene over olivine. At <18 wt.% of melting, FeO^* and $\text{CaO}/\text{Al}_2\text{O}_3$ increase with the increase of phosphorus in the bulk composition.

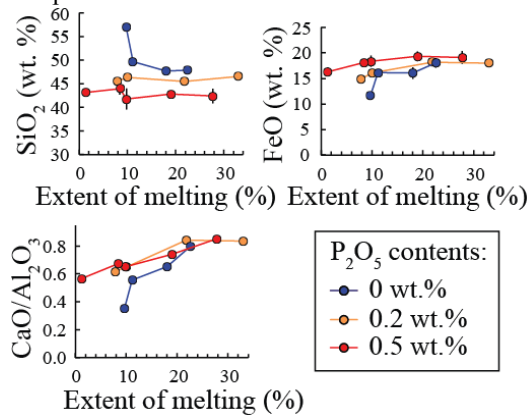


Fig.2. SiO_2 and FeO^* (in wt.%) contents and $\text{CaO}/\text{Al}_2\text{O}_3$ wt. ratio of experimental partial melts as a function of extent of melting (wt.%) from our study and ref. [7].

Effects of Phosphorus: As suggested by [3], the formation of M-O-P complexes in the silicate melt favor the polymerization of Si tetrahedral network according to the following equation: $2\text{Si-O}^- \text{M} + \text{O-P-O} = \text{Si-O-Si-O}^- \text{M} + \text{O-P-O}^- \text{M}$. As illustrated by our partial melting experiments, silicate glass proportion over dendritic, quench pyroxene-bearing domains, and residual orthopyroxene over olivine increase with the presence of phosphorus. Such mineralogical effects impact the composition of the liquids, with the dramatic decrease of SiO_2 up to 10-13 wt.% in primary melts, and the increase of FeO^* concentrations, potentially related to the formation of P-O-Fe complexes. The occurrence of twice FeO^* contents in the martian mantle relative to the terrestrial mantle likely amplify the silicate network polymerization in martian magmatic system.

Phosphorus Contents in the Martian Mantle: P_2O_5 concentration in the martian primitive mantle has been modeled at 0.16-0.18 wt.% based on geochemical, cosmochemical isotopic and/or geophysical data (e.g., [6,2]). Our experiments can be used to refine or reassess the P_2O_5 concentration in the mantle by comparing our melt compositions with the martian rocks thought to be representative of primary, mantle-derived melts (a few shergottites and basalts analyzed by the *Spirit* rover). Because shergottites and Gusev basalts have been formed at various pressures, we extrapolated our results obtained at 2 GPa using

experimental data from [7] and [8] obtained at pressures between 0.5 and 5 GPa (Fig.3) with bulk P_2O_5 content of 0.2 wt.%.

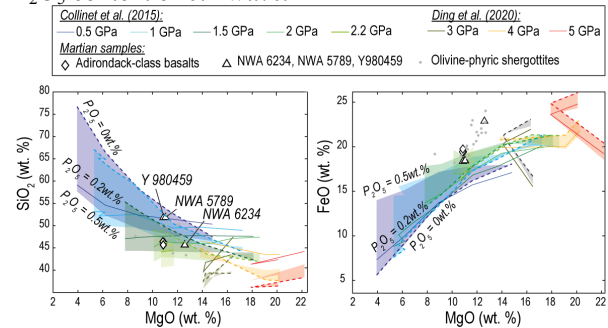


Fig.3. Composition of fractionation-corrected martian rocks representative of primary melts compared to experimental results from [7] and [8] (solid lines) combined with an extrapolation of our P-free (dashed lines) and 0.5 wt.% (no line) experimental data. Fractionation-corrected olivine shergottite compositions are plotted for reference [9].

Although melt SiO_2 concentrations present ambiguous results, no experimental sample reproduces the elevated FeO^* concentrations of martian rocks. High formation pressures (>3 GPa) might partly explain high FeO^* but are inconsistent with reproducing melt SiO_2 concentrations. P_2O_5 might yet contribute to the enhancement of FeO^* content in martian mantle-derived melts. Although a precise P_2O_5 concentration in the martian mantle cannot be estimated from our experiments, these results overall support that martian basalts were produced from a mantle containing P_2O_5 of 0.2-0.5wt.%.

Conclusions: Concentration of P_2O_5 as low as 0.2 wt.% in the mantle is sufficient to significantly affect both the composition of martian, mantle-derived melts, and the residual mineralogy. The enhancement of orthopyroxene over olivine in the presence of elevated P may facilitate the occurrence of orthopyroxene cumulates within the martian interior. If P_2O_5 heterogeneities exist within the martian mantle, apatite maybe expected as an equilibrium mantle accessory phase, as observed in spinel-peridotite xenoliths on Earth [9].

References: [1] Filiberto, J., & Dasgupta, R. (2011) *Earth and Planetary Science Letters*, 304(3-4), 527-537; [2] Dreibus, J., & Wanke, H. (1985) *Meteoritics*, 20, 367-381; [3] Kushiro, I. (1996) *Earth Proc.:Read. Is. Code*, 109-122. [4] Toplis, M.J., et al (1994) *GCA*, 58,2, 797-810; [5] Toplis, M.J., et al. (2008) *LPSC XXXIX Abst. #1282*; [6] Lodders, K., & Fegley Jr,B. (1997) *Icarus*, 126(2), 373-394; [7] Ding, S. and Dasgupta, R. (2020) *JGR*, 125(4), e2019JE006078; [8] Collinet, M., et al. (2015) *EPSL*, 427, 83-94; [9] Udry, A., et al. (2020) *JGR: Planets*, e2020JE006523 ; [10] Frey, F.A., & Green, D.H. (1974) *GCA*, 38(7), 1023-1059.