

**EFFECTS OF PHOSPHORUS ON MARTIAN MAGMAS: AN EXPERIMENTAL STUDY.** V. Payre<sup>1</sup>, and R. Dasgupta<sup>1</sup>, <sup>1</sup>Rice University, Houston, TX (vpayre@rice.edu).

**Introduction:** Mars' primitive mantle is 3 times more enriched in iron concentration than that of Earth, and 10 times more enriched in phosphorus [1]. Preliminary thermodynamical partial melting models based on a martian mantle composition using pMELTS software [2] showed that such differences likely have implications in terms of resulting magma compositions. Moreover, crystallization experiments on Fe-rich terrestrial evolved basalts demonstrated significant impacts of addition of phosphorus, including an increase of SiO<sub>2</sub> activity, stabilization of low-Ca pyroxene in favor of olivine, especially at low fugacity [3]. Lower silica contents and superchondritic Ca/Al ratio of martian mafic rocks in comparison with terrestrial basalts are still enigmatic, and may be related to higher P<sub>2</sub>O<sub>5</sub> in martian primitive mantle than that of Earth. Such effects have not been experimentally investigated on martian systems, which contain more elevated Fe concentrations contents than those from Earth. Here we explore these questions through partial melting experiments on one primitive, martian mantle composition.

**Methods:** Phosphorus concentrations within the martian primitive mantle has been estimated within the range P<sub>2</sub>O<sub>5</sub> = ~0.15-0.2 wt.% [1,4-6]. Because partial melting experiments have been run based on mantle composition from [4] with P<sub>2</sub>O<sub>5</sub> = 0.2 wt.% using the same piston-cylinder apparatus and conditions as this study [7], we chose composition from [4] with P<sub>2</sub>O<sub>5</sub> = 0 wt.% and P<sub>2</sub>O<sub>5</sub> = 0.5 wt.%. All our results are compared with those obtained from [7] with P<sub>2</sub>O<sub>5</sub> = 0.2 wt. % .

Similar to [7], experiments were performed using a piston-cylinder apparatus at Rice University at a pressure of 2 GPa and temperatures from 1210 to 1450 °C. Experimental duration varied from 48 to 72 h. The homogeneous starting material was placed within a graphite capsule inside a platinum outer capsule in order to reach an oxygen fugacity below the fayalite-magnetite-quartz buffer, and preventing any water contamination during the experiment, respectively. The cell assembly consists of BaCO<sub>3</sub> pressure sleeves, cylindrical graphite furnaces, and spacers of crushable

MgO, the whole assembly being wrapped within a Pb-foil. Before welding shut the platinum capsule, the graphite capsule, the starting material, and the platinum capsule are kept at 300 °C for 24 h, and the graphite furnaces and BaCO<sub>3</sub> sleeves are kept at 110 °C at least overnight in order to minimize any water contamination.

The composition of glasses, quenched melt matrix, and residual minerals have been analyzed with the field emission electron probe JEOL JXA 8530F at Rice University. Phase proportions of each experiments have been calculated by mass balance calculations from the chemical composition of each phase.

**Effects of Phosphorus on Melt Compositions:** At 2 GPa and without any phosphorus, low-degree melts are enriched in SiO<sub>2</sub>, which decreases at higher melting degree as long as pigeonite is present in the system (Figure 1a).

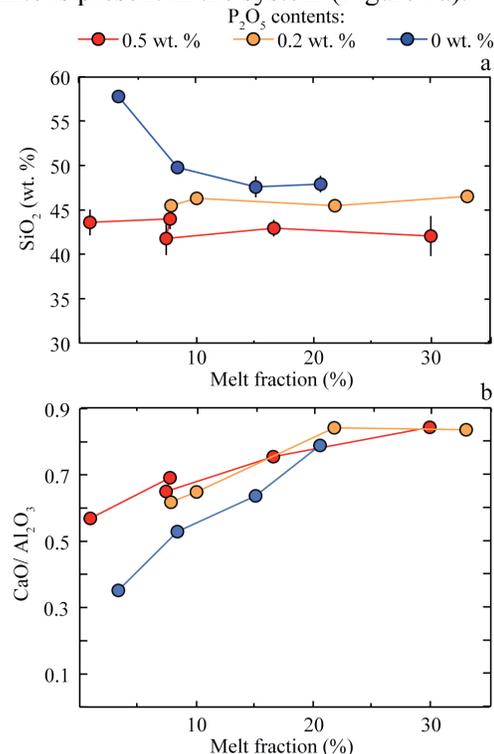


Figure 1. SiO<sub>2</sub> concentration of experimental melts versus degree of partial melting of primitive mantle composition with P<sub>2</sub>O<sub>5</sub> = 0 - 0.5 wt. %. P<sub>2</sub>O<sub>5</sub> = 0.2 wt. % is from [7].

Although this behavior is well-known for terrestrial magmas, the addition of phosphorus leads to a decrease of  $\text{SiO}_2$  at low melting degrees, effect being enhanced at the smallest melting degrees (Figure 1a). The presence of only 0.2 wt.% bulk  $\text{P}_2\text{O}_5$ , leads to a significant  $\text{SiO}_2$  decrease in the lowest degree melts, by up to 5-10 wt.%. Evidenced with pMELTS modeling, this effect can be explained by the enhancement of Si-O-Si polymerization leading to a decrease of  $\text{SiO}_2$  concentration in the liquid with the addition of polyvalent phosphorus [8].

Moreover,  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio is also affected by the addition of phosphorus (Figure 1b). Indeed, the increase of  $\text{P}_2\text{O}_5$  leads to a slight enhancement of  $\text{CaO}$  and a depletion of  $\text{Al}_2\text{O}_3$  in low-degree melts implying an enhancement of  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio by  $\sim 2$ .

**Effects of Phosphorus on Mineral Assemblage:** In addition to significant impacts on partial melt compositions, phosphorus influences the phase proportions of residual minerals (Fig.2).

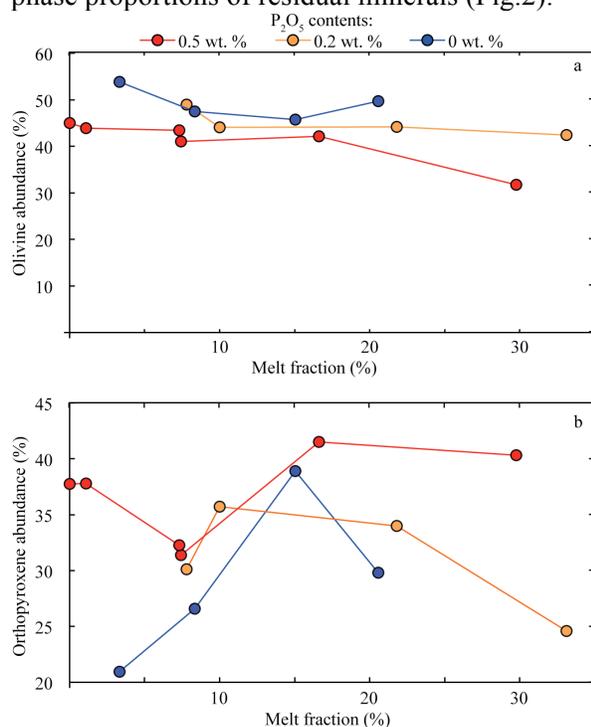


Figure 2. Residual (a) olivine and (b) orthopyroxene abundances at various melt fractions.

The increasing abundance of phosphorus in the bulk stabilizes orthopyroxene and tends to lower the abundance of residual olivine. The increase of polymerization related to the enhance-

ment of silica activity explains the increased stabilization of orthopyroxene in favor of olivine as also demonstrated during crystallization experiments on basaltic composition [3].

Mass balance calculations revealed an excess of phosphorus and calcium content in low-degree melts (melt fraction  $< 7\%$ ). Although not observed with scanning electron microprobe, the consideration of small amounts of apatite ( $< 1\%$ ) resolves this issue, implying subsolidus or the near solidus assemblage potentially includes a residual P-bearing phase such as apatite.

**Discussion:** The occurrence of 10 times more phosphorus in the martian mantle relative to the terrestrial mantle has dramatic effects on the composition and crystallization sequence of magmas. The increase of Si-O-Si polymerization related to phosphorus results in the depletion of silica contents and the stabilization of residual polymerized silicate minerals (orthopyroxene) in favor of less polymerized phases (likely olivine) in low-degree melts. The depletion of silica contents in low-degree magmas likely have a straightforward effect on their viscosity. In addition, stabilization of low-Ca pyroxene may lead to an enhancement of orthopyroxene cumulates within the martian crust. Finally, partial melting of a mantle composition with  $\text{P}_2\text{O}_5 = 0.2$  wt. % leads to the formation of P-rich liquids at low melting degrees ( $\text{P}_2\text{O}_5 > 1$  wt. % [7]), likely explaining the elevated  $\text{P}_2\text{O}_5$  concentrations of martian basalts including those analyzed by Mars Exploration Rover (MER) at Columbia Hills, and the large amount of apatite likely detected by the ChemCam instrument onboard the *Curiosity* rover in Gale crater [9-10]. At the end, although low in concentration within the martian primitive mantle, phosphorus has first order impacts on the petrology of martian magmas.

**References:** [1] Dreibus G. and Wänke H. (1985) *Meteoritics*, 20, 267-381. [2] Toplis, M. J., et al. (2008) *LPSC XXXIX Abst. #1282*. [3] Toplis, M. J., et al (1994) *GCA*, 58, 2, 797-810. [4] Lodders, K., & Fegley Jr, B. (1997) *Icarus*, 126(2), 373-394. [5] Wänke, H. and Dreibus, G. (1988) *Phil. Trans. Royal Soc. London A349*, 285-93. [6] Taylor, G. J. (2013) *Chemie der Erde 73 (2013) 401-420*. [7] Ding, S. and Dasgupta, R. (2015) *LPSC 48 abst. 2079*. [8] Kushiro, I. (1996) *Earth Process: Reading the Isotopic Code*, 109-122. [9] McSween, H. Y. et al. (2006) *JGR : Planets*, VOL. 111, E09S91. [10] Forni, O. et al. (2015) *GRL*, 42.