

**Thermal Phosphide Mineral Oxidation Chemistry** T. Feng and M. A. Pasek<sup>1</sup>, <sup>1</sup>Department of Geoscience, University of South Florida, 4202 E. Fowler Ave, Tampa, FL, 33620, USA, tianfeng1@usf.edu, mpasek@usf.edu.

**Summary:** Reduced oxidation state inorganic phosphorus species have been viewed as key source of phosphorus for the development of life. Previous studies reported that these organophosphates—such as those found in life—may be produced as the aqueous corrosion products of siderophilic phosphide minerals (e.g., schreibersite). Here, we demonstrate that siderophilic phosphides are able to oxidize into lithophilic calcium phosphates with the support of silicate minerals in meteorites under high temperatures and anhydrous conditions. Reduced P oxyanions are formed in this phosphide oxidation process. The intermediate  $P^{4+}$  species may be abundant if oxygen fugacity is sufficiently low in this reaction, and these radical  $P^{4+}$  species may oxidize or reduce into phosphate and phosphite with support of  $FeO/Fe_2O_3$  in meteorites.

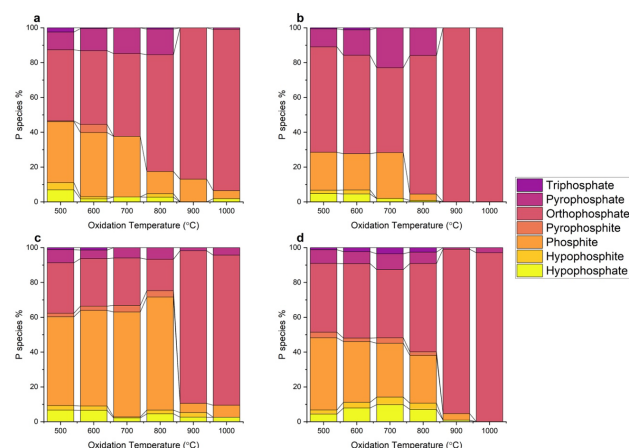
**Introduction:** Phosphorus (P) is a minor element in solar system samples but plays a significant role in modern biochemistry [1,2]. Phosphate minerals are the major P-bearing materials in the Earth's crust and presumably also the solar system. However, there is a “phosphorus problem” with prebiotic phosphorylation, where phosphate minerals are far too inert to transform into organophosphate species and exhibit low solubility in aqueous solvents [3].

Prior work has demonstrated that P in phosphide minerals may have been a source of P for prebiotic phosphorylation, due to the reactions these minerals can undergo. When added to water, the phosphide mineral schreibersite generates P oxyanions including hypophosphite, hypophosphate, phosphite and polyphosphates[4] and these rare phosphorus species are over 1,000 times more soluble than orthophosphate in water with divalent cations [5].

Furthermore, the oxidation of phosphides to phosphate is presumed to be a key step in phosphorus cosmochemistry[6]. Specifically, phosphide minerals oxidize into phosphate species as seen in the stony meteorites under high temperatures conditions. This reaction is a solid phase reaction in meteorite parent bodies, which occurs between common silicate minerals and phosphide metals. However, the exact process and rate at which such a reaction occurs is unclear. This work attempts to fill in the blank about the transformation of phosphide under different temperature conditions into phosphate, which may buttress phosphide's significance in the origins of life [7].

**Methods and Results:** We examined iron phosphide oxidation with forsterite and diopside by placing the mineral mixing inside a glass tube furnace and heating to various temperatures (500-1000°C) for 6,

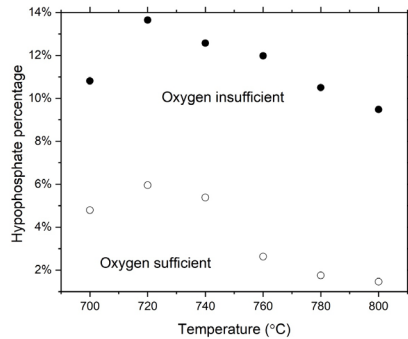
12, 24 and 120 hours. Sample products were analyzed by Raman Spectroscopy, XRD (X-Ray Diffraction), XPS (X-ray Photoelectron Spectroscopy), SEM (Scanning Electron Microscope) and NMR (Nuclear Magnetic Resonance). These results indicate that after heating, the majority of phosphide transformed into phosphate minerals, specifically calcium phosphate. Moreover, the species include not just orthophosphates but also some rare P species, like hypophosphate, hypophosphite, phosphite, pyrophosphite, pyrophosphate and triphosphate. In addition, these intermediate P species are more abundant in systems with insufficiently oxidizing conditions, at the IM buffer (Fig 1).



**Fig 1.** Phosphorus species catalog and percent in phosphide thermal oxidation process under argon. a). Phosphide thermal oxidation with Magnetite-Hematite buffer in 6h. b). Phosphide thermal oxidation with Magnetite-Hematite buffer in 120h. c). Phosphide thermal oxidation with Iron-Magnetite buffer in 6h. d). Phosphide thermal oxidation with Iron-Magnetite buffer in 120h.

**Discussion:** Phosphide minerals can oxidize to form several P species under thermal conditions. Moreover, at low reaction temperature (under 900 °C), reduced P species have a high degree of diversity in all P products. On the other hand, when the experiment temperature was over 900 °C, over 90% P species in product distribution were orthophosphate. This sets a hard constraint on the transformation of schreibersite into calcium phosphate minerals in chondrites, of about 1 week at 900°C readily producing phosphate from phosphide.

Surprisingly the intermediate hypophosphate (with  $P^{4+}$ ) was shown to increase during phosphide oxidation process. In addition, in contrast with oxygen rich environment, low oxygen fugacity condition supported more  $P^{4+}$  (Fig 2).



**Fig 2.** Diagram for the relation between temperature and  $P^{4+}$  percentage in phosphide thermal oxidation with silicates.

This may indicate that  $P^{4+}$  could substitute for  $Si^{4+}$  in silicates. Previous studies indicated that these radical  $P^{4+}$  species could readily stabilize with metal ions (like  $Fe^{2+}$  and  $Fe^{3+}$ ) and water, and finally disproportionate forming into reduced phosphite ion or redox phosphate ions [8]. Hence, we believe that this disproportionation reaction is possible in meteorites (by  $FeO/Fe_2O_3$ ). This suggests a role for lower redox state P oxyanions in meteorite parent bodies.

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