doi:10.1017/S1431927622010145
Microsc. Microanal. 28 (Suppl 1), 2022

Correlative Analysis of P-bearing Assemblages in the QUE 97008 and Orgueil Chondrites.

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As a part of the backbone of DNA and RNA, and a key component in the cell energy cycle and in cell membranes, phosphorus is a biocritical element. Yet, whereas P is the 5th-most biologically abundant element [1], it does not rank in the top 10 most-abundant elements in the solar system [2], raising questions on its origins, delivery, and subsequent fate. It is thought to have formed via s-process nucleosynthesis in massive stars ($\geqslant 8\ M_\odot$) and in the carbon- and neon-burning layers of supernovae [3]. [4] first reported molecular PN in several molecular clouds, and more recently, discovered that PO and PN are common constituents of oxygen-rich circumstellar environments [5]. In comparison, P has been reported in meteorites as schreibersite $(Fe, Ni)_3P$), apatite ($Ca_5(PO_4)_3(Cl, F, OH)$), merrillite ($Ca_9NaMg(PO_4)_7$) [6] and as a solute in Fe-Ni sulfides [7]. Thermodynamic calculations that model a cooling gas of solar composition indicate that P condensed from the nebular vapor phase into schreibersite at 1225 K (10^{-4} atm) [8]. Using a correlative microscopy approach, here we report on the carrier phases of P and its spatial relationships with surrounding materials in the QUE 97008 L3.05 and Orgueil CI 1.0 chondrites. This study is a part of a larger effort to understand P chemistry from its origins in stars to its fate in planetary materials.

P-bearing assemblages were identified in petrographic thin sections of the QUE 97008 L3.05 and Orgueil CI 1.0 (USNM 388) chondrites obtained from the Antarctic meteorite and Smithsonian collections, respectively. The thin sections were initially mapped for P, O, Fe, S, and C using the Cameca SX100 electron microprobe (EMPA) in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the Lunar and Planetary Laboratory, University of Arizona. We identified >45 P-bearing regions of interest (ROI) in the samples and down selected a total of 11 for more detailed analysis based on the location (matrix assemblages were prioritized for this work), size ($\geqslant$10 μm), and to obtain representative microstructures. Next, we acquired higher spatial resolution energy dispersive X-ray spectrometer (EDS) maps of the selected ROIs using the Hitachi S4800 cold-field emission scanning electron microscope (SEM) in KMICF to identify qualitatively the mineral phases. From these data sets, we selected two ROIs for more detailed crystal-chemical and structural analysis using transmission electron microscopy (TEM). Each of these ROIs were cross sectioned, extracted, and thinned to electron transparency (<100 nm) using previously described methods [9] with a ThermoFisher (formerly FEI) Helios NanoLab 660 G^3 focused-ion-beam scanning-electron microscope (FIB-SEM) located at KMICF. The FIB sections were analyzed using a 200 keV Hitachi HF5000 scanning transmission electron microscope (S/TEM) located at KMICF. The HF5000 is equipped with a cold-field emission gun, 3rd-order spherical-aberration corrector for STEM imaging, and an Oxford Instruments X-Max^N 100 TLE EDS system with dual 100 mm^2 windowless silicon-drift detectors (Ω =

2.0 sr). Selected-area electron-diffraction (SAED) patterns and EDS maps were acquired for determination of crystallinity and phase.

ROI 36 of QUE 97008 (Fig. 1a) contains two Fe-sulfide assemblages measuring ∼40 µm × 30 µm and 20 µm × 30 µm with a euhedral P-bearing assemblage between them that measures ∼10 µm × 30 µm. We extracted a FIB section transecting the interface between the P-bearing phase and the Fe-S phase. High-angle annular dark field (HAADF) and bright field (BF) imaging in the TEM reveal that the assemblages are polycrystalline. STEM-EDS maps and SAED patterns confirm the phosphate is merrillite and the sulfide is pyrrhotite. STEM and SAED analysis also show that an amorphous interfacial layer composed of Si, Fe, Mg, Na, and O occurs between the merrillite and the pyrrhotite. In comparison, ROI 7 of Orgueil (Fig. 1b) contains coarse (≤10 µm) P-bearing grains surrounded by minor magnetite framboids and plaquettes. We extracted a FIB section of a large (20 µm × 10 µm) P-bearing phase along its interface with the surrounding matrix. STEM-HAADF and -BF images of the FIB section and EDS maps show that the section is polyphasic containing Fe-and P-bearing domains. SAED patterns reveal that the P-bearing phase is a single crystal of hydroxyapatite, and the Fe-bearing domain is a single crystal of magnetite. The matrix that surrounds the hydroxyapatite and magnetite is composed of serpentine.

The chemical pathways for the origins of P-bearing material in the early solar system are diverse. P occurs in type 3 chondrites in P-bearing Fe-Ni metal [10] and merrillite-troilite assemblages [7] hypothesized to form via condensation and transient heating, respectively, in the solar nebula. In addition, [10] suggested that P can diffuse outward from Fe-Ni metal and oxidize into secondary minerals on meteorite parent bodies as a result of thermal metamorphism. The hydroxyapatite and magnetite that we find in Orgueil, which is embedded in a hydrated matrix, is consistent with formation by secondary aqueous alteration on the parent body [11-12]. In comparison, QUE 97008 is a petrologic type 3.05 chondrite that shows minimal evidence of secondary alteration [13]. We do not observe local evidence of aqueous processing, which suggests a possible nebular origin for the merrillite-pyrrhotite assemblage [14].

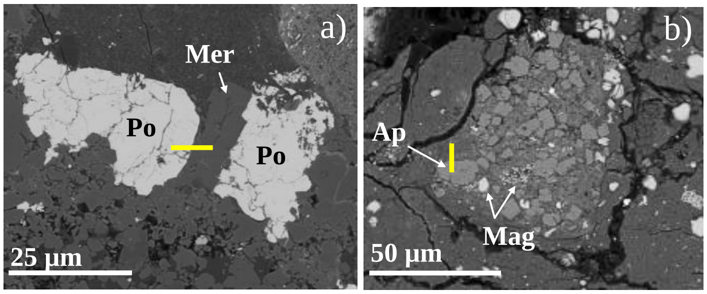

Figure 1. BSE images of a) ROI 36 in QUE 97008 and b) ROI 7 in Orgueil. The yellow lines indicate locations of FIB transects. Po= pyrrhotite, Mag= magnetite, Mer= merrillite, Ap=apatite.

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[14] This work was supported by NASA Emerging Worlds grant # 80NSSC18K0584.