ALTERATION OF P-BEARING PHASES IN ALLAN HILLS 77307 AND MURCHISON METEORITES

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Introduction: Despite its biological and geological importance, it is unclear in what form phosphorus is delivered to the early solar nebula and how it is subsequently transformed. P is synthesized by neutron capture on silicon in massive stars (≥ 8 $M_{\odot}$) and core-collapse supernovae (SNe) [1]. In the gas phase, P was reported in molecular form as PO, PN, CP, CCP, HCP, and PH_3 [2] in circumstellar envelopes. In the solid state, the most abundant P-bearing minerals in meteorites are schreibersite ($(Fe, Ni)_3P$), apatite ($Ca_5(PO_4)_3(Cl, F, OH)$), and merrillite ($Ca_9NaMg(PO_4)_7$) [3]. Equilibrium thermodynamic modeling of a cooling gas of solar composition predicts schreibersite to condense at ~1225 K and apatite/merrillite at ~700 K (10^{-4} bar) [4]. Here we report on the carrier phases of P in Allan Hills (ALHA) 77307 and Murchison, which represent pristine CO 3.0 and aqueously altered CM 2.0 chondrites, respectively. Our goal is to understand how P was delivered to the early solar nebula, in what forms it condensed into the solid state, how it subsequently evolved on meteorite parent bodies, and in what form it was delivered to the early Earth.

Samples and Methods: Petrographic thin sections of Murchison and ALHA 77307 from the UofA collection were analyzed in the Kuiper Materials Imaging and Characterization Facility located at the Lunar and planetary Laboratory, University of Arizona. We mapped each sample for P, O, C, Fe, and S using the Cameca SX-100 electron microprobe. P-bearing regions of interest (ROIs) were down selected based on location, representative microstructure, and element maps acquired using the energy dispersive X-ray spectrometer (EDS) on the Hitachi S4800 scanning electron microscope (SEM). Chosen ROIs were cross sectioned, extracted, and thinned to electron transparency (≤100 nm) using a ThermoFisher Helios NanoLab 660 G^3 focused-ion-beam scanning electron microscope (FIB-SEM) with methods previously described [5]. FIB sections were analyzed for crystal chemistry and structure using a 200 keV Hitachi HF5000 Scanning Transmission Electron Microscope (S/TEM) equipped with a 3rd-order spherical aberration corrector for S/TEM mode, bright field (BF)- and dark field (DF)- STEM detectors, and an Oxford Instruments X-Max^N 100 TLE EDS system with dual 100 mm^2 windowless silicon-drift detectors ($\Omega = 2.0$ sr).

Results and Discussion: We identified 29 P-bearing ROIs in ALHA 77307 and chose ROI 2 based on its isolated location in the matrix, making it a candidate for nebular dust. We extracted a FIB section measuring ~6.22 µm × 4.91 µm and thinned it to electron transparency. STEM-HAADF and BF images reveal a ~ 6 µm × 3 µm single crystal of schreibersite with a layered rim. The inner layer of the rim is composed of an Fe- and Na-bearing phosphate, whereas the outer layer is composed of Cr-bearing oxide, tentatively identified as ferroalluaudite ($NaFe_3PO_{12}$) and chromite ($FeCr_2O_4$), respectively. The matrix material of ALHA 77307 is heterogenous and largely consists of anhydrous minerals including olivine, pyroxene, and magnetite. In comparison, we identified 13 P-bearing ROIs in Murchison. ROI 3 of Murchison is ~170 µm long matrix grain that was selected based on SEM-EDS results maps, which reveal a P-bearing Fe-Ni sulfide phase. We extracted a FIB section from the interior of the grain. STEM-BF and HAADF imaging and STEM-EDS reveal that a Ca-phosphate phase occurs between grains of a P-bearing Fe-Ni sulfide. The P-bearing sulfide phase is nanocrystalline, as revealed by SAED patterns.

Thermodynamic calculations that model a cooling gas of solar composition predict that schreibersite, apatite, and merrillite form in the solar nebula from gas-solid reactions [4,6]. The model includes nine gas species: P, P_2, P_4O_6, PH, PH_2, PH_3, PN, PO, and PS [6]. The solid phases predicted in [4] are ideal solid solutions and represent endmember compositions. The single crystal of schreibersite located in the matrix of ALHA 77307 is generally consistent with equilibrium predictions. The presence of ferroalluaudite, chromite, and magnetite surrounding the schreibersite grain in ALHA 77307 is suggestive of a nebular metasomatic reaction of schreibersite. In comparison, P-bearing Fe-Ni sulfides were previously reported in CM 2.0 and CM 1/2 chondrites [9-11]. Such sulfides are not consistent with previous thermodynamic predictions [4,6], and are likely produced by secondary alteration on the parent body [10].

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