

LABORATORY ANALYSES FOR ADSORPTION EXPERIMENTS OF PHOSPHORIC ACID SPECIES AND PHOSPHATE ROCK STANDARDS FOR P CHARACTERIZATION ON MARS BY CHEMCAM. F. D. Dimitracopoulos¹, H. E. Newsom¹, P. J. Gasda², P. Y. Meslin³, J. M. Cerrato¹, L. J. Crossey¹, N. L. Lanza², B. M. Tutolo⁴, S. M. Clegg², O. Gasnault³, D. Delapp², ¹University of New Mexico, Albuquerque, New Mexico, USA, 87131 (fdimitra17@unm.edu), ²Los Alamos National Laboratory, USA, ³Institut de Recherche en Astrophysique et Planétologie, France, ⁴University of Calgary, Canada.

Introduction: Phosphorus is one of the biogenic elements (i.e., CHNOPS) that are essential for the development of life [1]. Phosphorus is especially crucial for the formation of nucleic acids and metabolic processes, and may have been a catalyst or pH buffer for prebiotic chemical reactions [1, 2]. As such, it is an element of particular importance in planetary science as it is relevant to potential habitability beyond Earth [3].

The ChemCam instrument on the NASA *Curiosity* rover in Gale crater has observed phosphorus in several diverse lithologies [4, 5, 6]. To make these observations, ChemCam uses Laser Induced Breakdown Spectroscopy (LIBS) which analyzes targets for chemistry [7, 8]. *Curiosity* has observed nodules in the Glen Torridon region of Gale crater that contain high amounts of Mn and associated P [9, 10, 13]. The darker, Fe-rich strata in this region are observed to contain high amounts of Cu adsorbed onto Fe, which is unusual as P more readily adsorbs onto Fe [9, 11, 12, 14]. Previous studies have determined that Gale crater lake waters were more neutral to alkaline in pH, which indicates that locations with diagenetic features containing more adsorbed P were likely formed episodically by lower pH fluids [9]. These observations indicate that at least one diagenetic process, perhaps redox reactions or carbonate exchange with the atmosphere, has taken place at this location.

One hypothesis to explain the presence of P suggests that it adsorbed onto oxide minerals in diagenetic features such as nodules (e.g., Fig. 1 [9, 10]). In order to test this hypothesis, we need to first, perform P adsorption experiments in the laboratory; second, measure these adsorbed oxides with the ChemCam laboratory instrument on Earth; and lastly, use the spectral data to quantify P to determine its abundance in nodules on Mars. Previous research has focused on the adsorption behavior of P on minerals such as goethite and MnO₂ and has shown that the concentration of adsorbed P₂O₅ can constrain aqueous conditions (i.e., pH, redox, temperature, etc.) in which these nodules formed [11, 12].

By studying adsorption processes in the context of the observations made by *Curiosity* in Gale crater, it will be possible to better characterize P on Mars and improve our understanding of how phosphorus was mobilized to these locations.

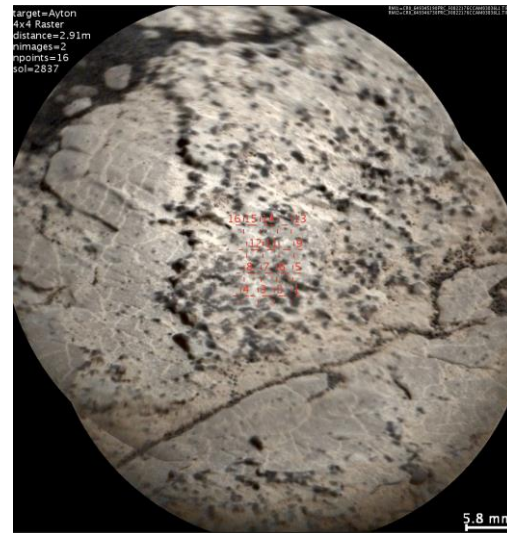


Fig. 1. Image from ChemCam target Ayton (sol 2837) depicting LIBS targets that hit nodules containing high Mn with adsorbed P.

A thorough investigation of phosphorus also has implications for its role as a biogenic element. Recent studies have discussed the potential of microbial life on Mars and how it might be detected if present [15]. Certain bacteria are capable of surviving the harsh conditions on Mars, such as *Deinococcus radiodurans*, which can survive ionizing radiation, desiccation, and freezing [15]. As a defense, *D. radiodurans* uses Mn²⁺-bearing antioxidants which can be detected as Mn-phosphates [15]; finding these materials on Mars could be a potential biosignature for these types of bacteria.

Methods: We will perform a series of phosphoric acid species adsorption experiments on Fe and Mn-oxides, and analyze the resulting materials for composition and mineralogy, and with ChemCam LIBS at Los Alamos National Laboratory (LANL) to provide Mars-like measurements.

First, we will produce four metal oxides in the laboratory: goethite (Fe(II) and Fe(III)), hematite, and MnO₂, using published methods [16, 17, 18]. A phosphoric acid stock solution will be added to each of the metal oxides, as well as NaCl to control salinity. The adsorption reaction will run for 24 hours under pH levels of 5, 8, and 10, which bracket the changes in oxidation state of P in the fluid. The pH levels of the lower pH solutions will be adjusted with NaOH. For

solutions of higher pH levels, a NaPO_4 salt will be used in lieu of phosphoric acid to create the stock solution that will be added to the oxides. At the end of the experiment runtime, the sediment and liquid will be separated via centrifuge and analyzed with X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) for the sediment, and Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for the liquid. The XRD and XRF analyses will identify the crystal structure and elemental composition, respectively. The ICPMS and ICP-OES analyses will determine the chemical composition and chemical concentration, respectively, and will identify how much phosphorus is still in solution. A portion of the solid produced by each experiment will be sent for further analysis with the ChemCam laboratory instrument at LANL. The LIBS spectra of the experimental materials and additional phosphate rock samples and mixtures (Brammer Standards), and natural hydroxyphosphate (from whiteite [19]) will be used to produce a univariate calibration similar to Meslin et al., (2016) [20].

Expected Results and Implications: The experiments are expected to produce approximately 10 g of solid for each experiment that have a minimum of 3 wt. % P. We expect that the adsorption rate behavior of phosphorus will follow similar trends as those that were observed in previous studies [11, 12].

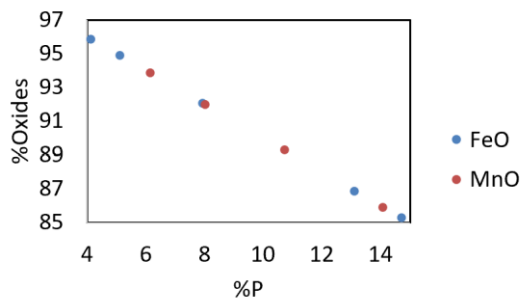


Fig. 2. Expected results for sediments produced by adsorption experiments; we assume a 1:1 adsorption rate of P to the oxides.

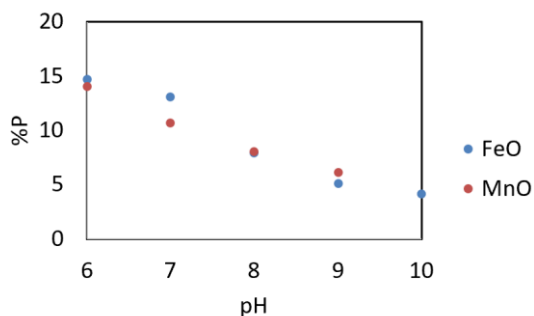


Fig. 3. Expected results for sediments produced by adsorption experiments; more P will adsorb to the oxides in lower pH solutions.

Figures 2 and 3 depict our expected results for phosphorus adsorption, assuming a 1:1 adsorption rate; we expect that the phosphorus will adsorb more to the metal oxides at lower pH levels than at higher pH levels. In addition, we plan to conduct P sorption modeling based on the results of the experiments, and we expect to see that there will be a greater adsorption rate of P where the pH is lower than the point of zero charge (PZC) of the oxides. Lastly, by measuring these P and oxide abundances, we will be able to identify deviations from the expected ratio shown in Figure 2 and determine how the deviations may have occurred according to oxide type and pH level. This requires a high level of precision, which further supports our need for a dedicated calibration.

Perspectives: This research will improve upon our understanding of how the nodular diagenetic features in Gale crater could have formed. These data will also provide a basis for quantifying P abundance in ChemCam LIBS data and potentially SuperCam LIBS data. Investigating the formation of these P-bearing materials will provide a better understanding of the past habitability of the surface of Mars by shedding light on the processes that transport and deposit phosphorus. Preliminary results for this research may be available by the time of this conference.

Acknowledgements: Thanks to Matthew Nellessen and Sean Czarnecki; NASA Mars Exploration Program; JPL; CNES.

References: [1] Bartlett, C. L., et al., (2018) *Astrobiology*, 18 [2] McKelvey, V. E., (1967) *USGS* [3] Weckwerth, G., and Schidlowski, M., (1995) *ADR*, 15 [4] Meslin, P. Y., et al., (2022) *EGU, Abstract EGU22-6613* [5] Meslin, P. Y., et al., (2022), *53rd LPSC, Abstract #2492* [6] Meslin, P. Y., et al., (2018) *49th LPSC, Abstract #1447* [7] Wiens, R. C., et al., (2012) *SSR*, 170 [8] Maurice, S., et al., (2012) *SSR*, 170 [9] Gasda, P. J., et al., (2022) *JGR Planets*, 127 [10] Lanza, N. L., et al., (2022) *53rd LPSC, Abstract #2689* [11] Yao, W., and Millero, F. J., (1996) *ES:T*, 30 [12] Hawke, D., et al., (1989) *ES:T*, 23 [13] Lanza, N. L., et al., (2017) *48th LPSC, Abstract #2913* [14] Dehouck, E., et al., (2022) *JGR Planets*, 127 [15] Horne, W. H., et al., (2022) *Astrobiology*, 22 [16] Schwertmann, U., and Cornell, R. M., (2000) *Wiley-VCH* [17] Murray, J. W., (1974) *JCIS*, 46 [18] Manickavasagam, S., et al., (2004) *JCIS*, 280 [19] Collection ENSMP, sample #53887, from Musée de Minéralogie Mines Paris Tech. [20] Meslin, P. Y., (2016) *47th LPSC, Abstract #1703*.