PHOSPHORUS IN JEZERO CRATER, MARS: DETECTIONS MADE WITH THE SUPERCAM INSTRUMENT ONBOARD THE PERSEVERANCE ROVER IN THE FIRST 1000 SOLS. Z. U. Wolf[1*], S. Clegg[1], P.-Y. Meslin[2], O. Gasnault[2], O. Forni[2], S. Schröder[3], A. Cousin[2], C. Legett[1], R. C. Wiens[4], M. Rock[1], E. Clave[3], A. M. Ollila[1], E. Cloutis[5], S. Maurice[2]; [1]LANL; [2]IRAP; [3]DLR; [4]Purdue; [5]U of Winnipeg; [*]wolf@lanl.gov

Introduction: Phosphorus, in the form of phosphate, is an essential element that played an important role in the origin and evolution of life. Much research on the development of life on Earth suggests that P was an early precursor of RNA, where it worked as a catalyst in the formation of life [1,2]. Understanding the formation conditions of phosphate minerals on Mars is therefore essential from an astrobiological standpoint, but it is also important for us to understand the P cycle in a presumably abiotic world [1].

P detections in Gale crater by ChemCam indicate the presence of nano-crystalline or amorphous hydrous (Mn,Mg)-phosphates as well as hydrous (Fe,Mn,Mg)-phosphates and apatites. The P/Mn ratio was too large in ChemCam detections to be associated with Fe or Mn oxides [1]. Here we report on the observations of P by SuperCam along with the presence of Fe, Mn, and Mg.

SuperCam is a remote sensing instrument suite currently operating on the Perseverance rover since landing on Mars in February of 2021 [3]. The suite contains a Laser-Induced Breakdown Spectroscopy (LIBS) instrument that is frequently used on Mars, as it has the ability of removing dust from the surface of rocks and to penetrate the coatings on rocks up to ~7 meters away [3,4]. The LIBS spectrometer obtains emission spectra of materials ablated from the targets covering the wavelength range from ~240-850 nm (with gaps from ~340-380 and 464-537 nm). The LIBS instrument can detect major elements such as Si, Ti, Al, Fe, Mg, Ca, Na, and K [5] and minor elements such as P, Mn, H, Cr, Ni, S, Cl, and C [4].

Jezero Crater P Observations: The first clear P detection made in Jezero crater by SuperCam was on sol 51 in the target Tselhbahih, which was on a float rock with a shiny coating and dusty pockets. There have since been 26 unambiguous detections made by SuperCam in float rocks, bedrocks, regolith, abrasion patches, and boreholes.

Máaz: Máaz, a succession of lava flows, and the first geologic unit in the crater floor analyzed provided our first SuperCam P detections. There was a total of 13 detections with 6 being bedrock (2 on natural surfaces,

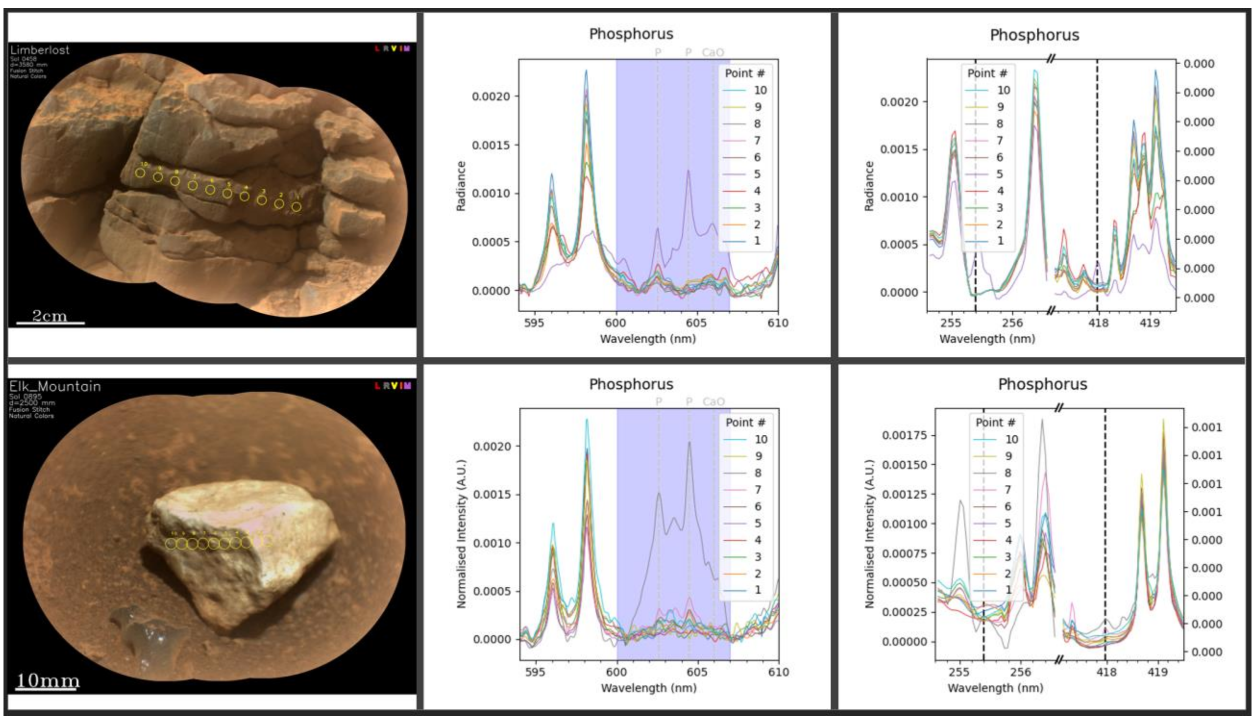

Figure 1: Remote Micro Images (RMI) and P spectral bands of two observations made by SuperCam. P exhibits 3 main peaks: a broad, prominent peak between 600 – 607 with noticable peaks at 602.6 and 604.5, and two weaker peaks at 417.8 and 255.4 nm. In each specctrum, the broad, triple-humped peak in the highlighted area is due mostly to P, indicating the presense of P. (Top) Target Limberlost on sol 458 in a layered bedrock with point 5 showing a strong P detection. (Bottom) Target Elk_Mountain on sol 895 on a light-toned floatrock with point 8 having the strongest P detection and weaker in points 7, 6, and 2, respectively.

1 on a borehole wall and 3 on abrasion patches), 6 float rocks, and 1 regolith. All 3 abrasion patches have detections that are indicative of Cl-rich Ca-phosphates [10].

Séitah: The second unit analyzed along the traverse was Séitah, an olivine cumulate in the crater floor, where we had 4 detections of P. Of these observations, 3 were bedrock and 1 was an abrasion patch (in bedrock).

Delta: Within the delta, we had another 5 P detections. Of these detections, 1 was bedrock, 3 were float rocks, and 1 was a regolith detection.

Upper Fan: In the Upper Fan, we had 3 P detections all of which are in float rocks.

Margin Unit: The most recent unit Perseverance is exploring in Jezero Crater is the Margin Unit [6], where we have seen only one P detection on bedrock.

Discussion: SuperCam P detections are most common in float rocks. The few bedrock detections that we have are generally not on a natural surface, rather, they are in abrasion patches, with one P detection in a borehole wall. An example of a natural surface P observation in bedrock is Limberlost, targeted on sol 458 on the delta. A significant number of the P detections in float rocks are in the light toned float rocks that we occasionally see [7,8]. An example of a P detection in a light-toned float rock in the upper fan is shown above in Figure 1, Elk_Mountain. Almost all recent P detections are in light-toned float rocks.

Most P detections were made earlier in the mission in Máaz and Séitah and are very rarely detected with only 7 detections in the past 500 sols. In addition, detections of P are often associated with elevated amounts of Ca, Sr, Mn, Fe, and Li. Only 12 of the 26 detections are associated with elevated Mg, and 14 are associated with high Fe. This is different from the more common (Fe,Mn,Mg)-phosphates detected in Gale. P quantification is important to better constrain the mineralogy of the P-bearing phases detected.

Lab Work: The experiments carried out at Los Alamos National Laboratory will allow us to derive a calibration curve for the P content and determine a detection limit for P by SuperCam. Univariate and multivariate analyses will be explored to identify the most robust model for quantifying P.

A suite of 20 mixing ratios were prepared from calcium phosphate ($Ca(H_2PO_4)_2$, Sigma-Aldrich) mixed with certified Japanese Basalt Standard JB-1b with a known P_2O_5 concentration of 0.256wt%. This basalt standard was selected due to the known composition of P being low as to not contribute significantly to the amount of P present in each mixture ratio. In addition to the prepared mixture suite, several geological samples and P bearing standards were included (Table 1).

Mixtures of these minerals with rock and mineral powders similar to those associated with the P Mars observations (e.g., basalts) were prepared and shot with SuperCam under Martian pressure conditions. Compositional data was obtained from Activation Laboratories, LTD. XRD measurements were conducted with Bruker D8 Discover or Advance diffractometers using Cu-Kα radiation. Data were collected from 2 to 70° 2θ with a 0.02° 2θ step-size and count times of 2 to 10 seconds per step. Phase analyses (XRD) was performed using Jade© 9.5 X-ray data evaluation software with the ICDD PDF-4 database.

Several geological samples were selected due to their contents of both P and F at varying ratios. This will enable us to differentiate between these two elements in the LIBS spectra as they both have peaks overlapping in the 600 – 607 nm region.

Mitridatite and carbonate-fluorapatite monazite listed in Table 1 are Mn bearing phosphate samples that will be used to explore the relationship between the presence of Mn with P as we see in the Mars data. Mitridatite contains high Fe and P and will be used as an example of a Fe-phosphate. All the P-bearing geological samples contain highly elevated concentrations of Sr, once again relevant to the Mars data collected in Jezero.

Table 1: P-bearing samples for the calibration of the data collected by the SuperCam LIBS spectrometer.

Phosphorous samples used for the calibration of SuperCam:
Apatite calibration sample suite from ChemCam study [9]
Sample suite of P mixed with basalt standard JB-1b
Apatite from Perth, Ontario, Canada
Blue apatite from unknown location
Chloroapatite from Bamble, Telemark, Norway
Chloroapatite from Bjordam, Telemark, Norway
Carbonate-fluoroapatite monazite from Zomba, Malawi
Vivianite from Blackbird Mine, Idaho
Lipscombite from Silver Coin Mine, Nevada
Mitridatite from Bull Mosse Mine, South Dakota
Tinticite from Gold Quarry Mine, Nevada
7 Certified Reference Material samples containing phosphorous

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