FLUORINE IN JEZERO CRATER, MARS: DETECTIONS MADE WITH THE SUPERCAM INSTRUMENT ONBOARD THE PERSEVERANCE ROVER IN THE FIRST 1000 SOLS.

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Introduction: Understanding the context of the presence of fluorine on Mars is important as halogens such as fluorine may play a key role in alteration processes on Mars [1]. Studies conducted on SNC-meteorites found that Mars contains volatile elements such as fluorine in concentrations greater than those of Earth [2]. The first detections of fluorine on Mars were made in Gale crater by the ChemCam LIBS instrument onboard the Curiosity rover [1, 3]. The detections were generally associated with either a calcium-rich phase, e.g., apatite, or fluorite [3]. The fluorine detections made by ChemCam in Gale crater have been found in very different geological settings [3] than the Perseverance rover has encountered in Jezero crater. Here we report on the observations of fluorine by SuperCam.

SuperCam is a remote sensing instrument suite currently operating on the Perseverance rover since landing on Mars in February of 2021 [4]. 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 [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). As the LIBS plasma cools down, elements in their electronically excited states can either emit directly or recombine in the plasma and then emit, producing a molecular band.

Halogens such as fluorine can be difficult to detect as fluorine does not produce an atomic line spectrum of sufficient intensity to be detected by LIBS except in high concentrations [1, 3, 5, 8].

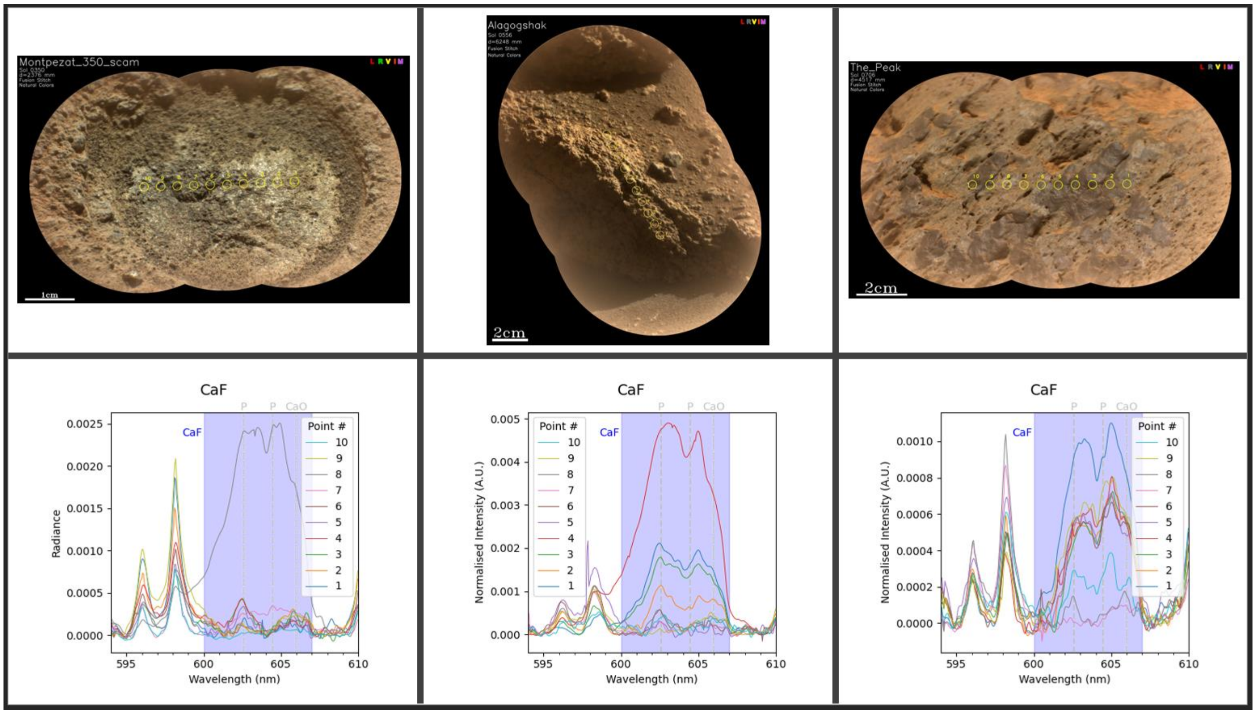

Figure 1: Remote Micro Images (RMI) and CaF spectral bands of three observations made by SuperCam. In each specctrum, the broad, double-humped peak in the highlighted area is due mostly to CaF, indicating the presense of F. (Left) Target Montpezat_350_scam on sol 350 in abraison patch with point 8 showing a strong CaF detection and point 7 showing a weak detection. (Middle) Target Alagogshak on sol 556 on bedrock with point 4 having the strongest CaF detection and weaker in points 1, 3, and 2, respectively. (Right) Target The_Peak on sol 706 on float rock with point 1 having the strongest CaF detection and all other points showing CaF to a lesser degree except point 7 and 8 where CaF is not detected.

However, fluorine can combine with other elements in the plasma, mainly alkali-earths, to form an easily identifiable feature. Gaft et al., [5, 8] found that the molecular emission of CaF is temporally broader than ionic or atomic fluorine and has a longer decay time. The duration of decay time corresponds to the lifetime of the CaF molecule present in the plasma. The longer the molecule exists in the plasma, the greater the detectability of that molecule [5, 8].

Jezero Crater Fluorine Observations: The first clear CaF detection made in Jezero crater was on sol 79 in the target Tsetah, which was on a float rock with a shiny coating and dusty pockets. There have since been 59 unambiguous detections made by SuperCam in float rocks, bedrock, regolith, abrasion patches, and boreholes. Similar to detections in Gale by ChemCam, the context of the following observations varies significantly.

Máaz: Máaz is the first geologic unit in the crater floor analyzed in Jezero with CaF detections. There was a total of 23 detections with 9 of those observations being bedrock, 8 float rocks, 2 regolith, 1 borehole, and 3 abrasion patches.

Séitah: The second unit analyzed along the traverse through Jezero was Séitah, also in the crater floor where we had 11 detections of CaF. Of these observations, 9 were bedrock and 2 were an abrasion patch (in bedrock).

Delta: Within the delta, we had another 17 CaF detections. Of these detections, 11 were bedrock, 4 were float rocks, and 2 were regolith detections.

Upper Fan: In the Upper Fan, we had 6 CaF detections. Of these, 3 are bedrock and 3 are float rock.

Margin: The most recent unit Perseverance is exploring in Jezero Crater is the Margin Unit. So far, we have had only two detections of CaF and that was target Point_Cloates (sol 931), a vein [6] and target Ballandarra (sol 945) on bedrock.

Most of the CaF detections have been on in-place bedrock, and, to a much lesser extent, float rocks.

Discussion: Most detections of CaF are associated with the presence of high or moderate Ca based on the LIBS data. In Figure 1, we can see three different examples of CaF detections made by SuperCam. The CaF feature is quite distinct in the spectral region due to its two humps in the peak. The shape of the double peak changes or shifts due to the presence of other elements. In the spectra shown in the lower left of Figure 1, the CaF peak for Montpezat_350_scam, the shape and position are affected by the presence of phosphorous (weak atomic peaks added to the large CaF molecular peaks). The other CaF peaks in Figure 1 are not being impacted by phosphorous and are truer to the CaF shape. Of the 52 detections of CaF, 12 of them appear to have the presence of P, indicating that the F is most likely associated with apatite [7]. Whereas the detections with no clear presence of P are most likely fluorite [7].

Lab Work: A sample suite of various fluorine rich rocks and minerals was selected for analysis by the SuperCam instrument located at Los Alamos National Laboratory. Forni et. al., [1] conducted a study calibrating ChemCam's detections of fluorine using 12 mixing ratios of fluorite with a certified basalt powder standard (BHVO-2). These exact same 12 mixtures will be included in the compositional modeling done using SuperCam spectra. Additionally, new F-bearing minerals have been obtained and analyzed to broaden the type of matrices included in the modeling (Table 1). Mixtures of these minerals with rock and mineral powders similar to those associated with the CaF Mars observations (e.g., basalts) will be prepared and shot with SuperCam under Martian pressure conditions.

The experiments carried out at LANL will allow us to derive a calibration curve similar to [*1*] for the fluorine content and determine a detection limit for fluorine by SuperCam. Multivariable and univariate analyses will be explored to identify the most robust model for quantifying CaF.

Table 1: Fluorine samples used for the calibration of the data collected by the LIBS spectrometer on SuperCam.

Fluorine samples used for the calibration of SuperCam:
Sample suite of apatites from the French team [9]
Sample suite of CaF_2 used in ChemCam calibration by Forni
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
Fluorite from Durham, England
Fluorite from Xiang Fang Lin Mine, Hunan Province, China
Biotite from unknown location
Topaz from Mexico
Apophylite from Maharashtra, India

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References: [1] Forni, O. et al., (2015) *Geophys. Res. Lett., 42*, 1020-1028. [2] Dreibus, G. and Wanke, H. (1985) *Meteoritics 20*(2), 367-381. [3] Forni. O. et al., (2019) *Nineth Int. Conf. on Mars*, LPI Contrib. No. 2089. [4] Wiens, R. et al., (2021) *Space Sci Rev* 217,4. [5] Gaft, M. et al., (2013) *SCAB 98*, 39. [6] Poblacion, I. et al., (2024) *55th LPSC* (this conference). [7] Forni, O. et al., (2016) 47th *LPSC*, Abstract #1990. [8] Vogt, D.S. et al., (2019) *Icarus*, 335. [9] Meslin, P.-Y., et al., (2016) *47th LPSC*, Abstract #1703.