

**QUANTIFICATION OF FLUORINE IN JEZERO CRATER, MARS: DETECTIONS MADE WITH THE SUPERCAM INSTRUMENT ONBOARD THE PERSEVERANCE ROVER.** Z. U. Wolf<sup>1\*</sup>, S. Clegg<sup>1</sup>, C. Legett<sup>1</sup>, P.-Y. Meslin<sup>2</sup>, T. S. J. Gabriel<sup>3</sup>, O. Forni<sup>2</sup>, R. K. Martinez<sup>1</sup>, S. Schröder<sup>4</sup>, J. M. Madariaga<sup>5</sup>, J. Aramendia<sup>5</sup>, I. Poblacion<sup>5</sup>, A. M. Ollila<sup>1</sup>, A. Cousin<sup>2</sup>, R. C. Wiens<sup>6</sup>; <sup>1</sup>Los Alamos National Laboratory, Los Alamos, NM, USA; <sup>2</sup>Institut de Recherches en Astrophysique et Planétologie, Toulouse, France; <sup>3</sup>U.S. Geological Survey, Astrogeology Science Center, Flagstaff, AZ, USA; <sup>4</sup>German Aerospace Center (DLR), Cologne, Germany; <sup>5</sup>Univ. Basque Country UPV/EHU, Leioa, Spain; <sup>6</sup>Purdue University, West Lafayette, IN, USA; \*[wolf@lanl.gov](mailto:wolf@lanl.gov)

**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 Mars meteorites found that Mars contains volatile elements such as fluorine in concentrations greater than those of Earth [2]. The first in-situ 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]. Here we report on the observations of fluorine by SuperCam in Jezero crater, which represents a very different geological setting [3] than that of Gale crater.

SuperCam is a remote sensing instrument suite currently operating on the Perseverance rover since landing on Mars in February of 2021 [4, 10]. The suite contains a Laser Induced Breakdown Spectroscopy (LIBS) instrument that is frequently used on Mars. Each laser shot of a single point removes dust from the surface of rocks and penetrates the coatings on rocks up to ~7 meters away [4, 10]. 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 photons directly or recombine in the plasma and then emit photons, producing a molecular feature in the spectra.

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]. However, fluorine can combine with other elements in the plasma, mainly alkali species, which produces an easily identifiable feature. Gaft et al., [5, 8] found that the molecular emission of CaF has a temporally broader decay time than ionic or atomic fluorine. The 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].

**Lab Work:** Our experiments were carried out at Los Alamos National Laboratory in order to derive a calibration curve for the CaF content from LIBS spectra and determine SuperCam detection limits for CaF.

These limits can be converted to F. We used univariate analysis in our quantification of CaF.

A suite of 14 mixing ratios (0.04-75.67 wt% CaF) were prepared with pure calcium fluoride (CaF<sub>2</sub>, Fisher Scientific Company, LLC) mixed with certified Japanese Basalt Standard JB-1b with a known F concentration of 0.0374 wt%. This basalt standard was selected due to the known composition of F being low, minimally contributing F to the mixtures, allowing for better control. In addition to the prepared mixture suite, we included several geological samples (Table 1).

**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 CaF <sub>2</sub> mixed with basalt standard JB-1b
Apatite calibration sample suite from ChemCam study [9]
Apatite: Perth, Ontario, Canada
Blue apatite: Unknown location
Chloroapatite: Bamble, Telemark, Norway
Chloroapatite: Bjordam, Telemark, Norway
Carbonate-fluoroapatite monazite: Zomba, Malawi
Fluorite: Durham, England
Fluorite: Xiang Fang Lin Mine, Hunan Province, China
Biotite: Unknown location
Topaz: Mexico
Apophyllite: Maharashtra, India
7 Certified Reference Material containing F and P

Mixtures of these minerals with rock and mineral powders similar to those associated with the F 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-K $\alpha$  radiation. Data were collected from 2 to 70° 2 $\theta$  with a 0.02° 2 $\theta$  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 that contained both F and P at varying ratios. This will enable us to differentiate between these two elements in the LIBS spectra. Both elements have peaks overlapping in the 600 – 607 nm region of interest.

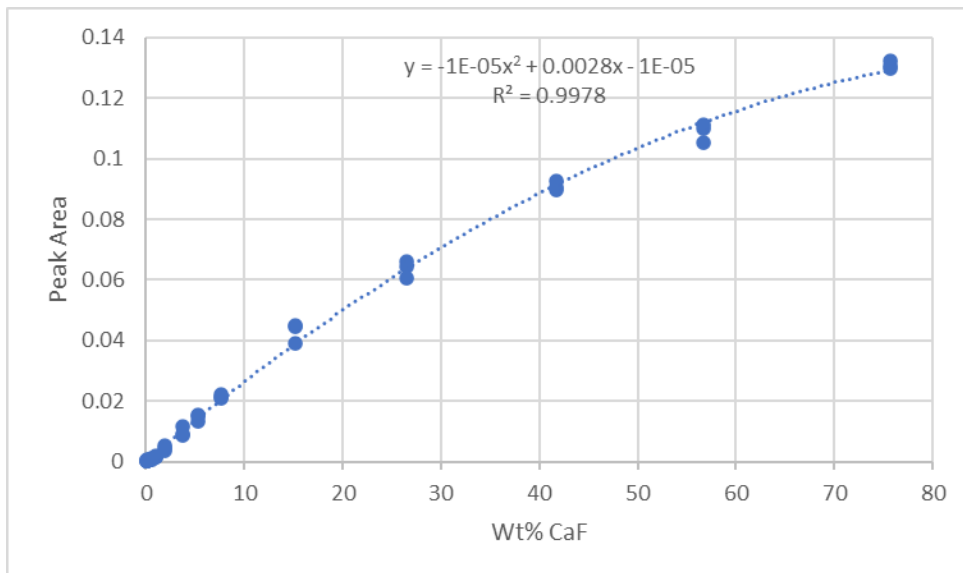


Figure 1: Initial univariate calibration curve for CaF based on CaF<sub>2</sub> mixture suite ranging from 0.04 wt% CaF to 75.67 wt% CaF. We normalized spectra by the intensity across all SuperCam spectrometers for each observation. The calibration model is represented for the 600 – 607.5nm molecular CaF feature.

**Univariate Model:** An initial draft of the calibration work in progress is shown in Figure 1. The final calibration model will be used to quantify our detections made by SuperCam on Mars.

An example of a CaF detection on Mars is target Point\_Cloates, targeted on sol 931. Based on our initial estimates, point 1 is 10.48 wt% CaF, point 2 has 13.86 wt%, point 3 has 15.96 wt% CaF, and point 4 has 5 wt% CaF. More work is being done to refine this calibration.

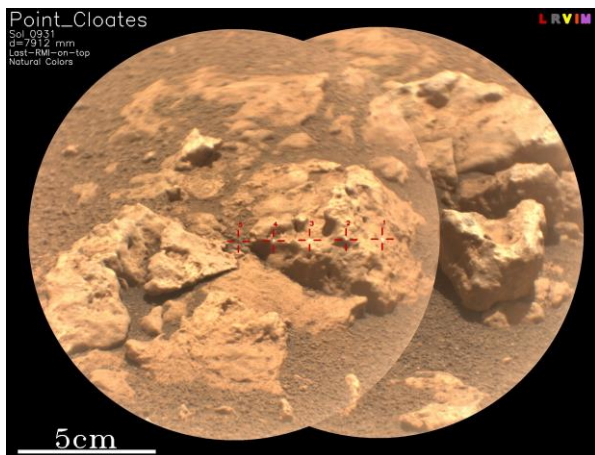


Figure 2: RMI of target Point\_Cloates, targeted by SuperCam on sol 931.

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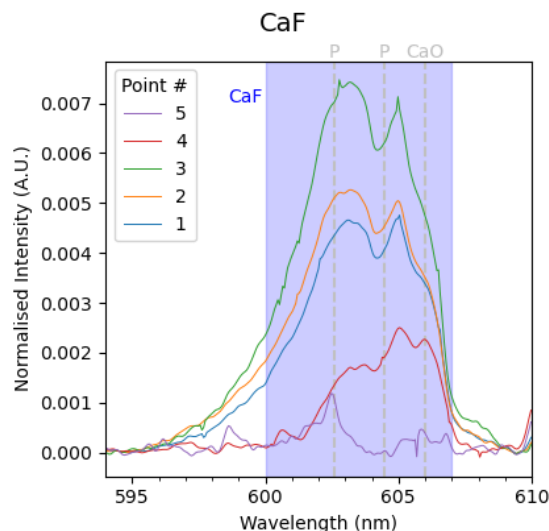


Figure 3: LIBS spectra collected on Point\_Cloates in Jezero crater, Mars which shows a CaF detection on points 1-4.

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