CHLORINE IN JEZERO CRATER, MARS: DETECTIONS MADE BY SUPERCAM. Z. U. Wolf[1*], J. M. Madariaga[2], S. Clegg[1], C. Legett[1], G. Arana[2], T. S. J. Gabriel[3], I. Poblacion[2], O. Forni[4], O. Gasnault[4], R. Anderson[3], E. Clavé[5], S. Schröder[5], A. Cousin[4], R. C. Wiens[6]; [1]Los Alamos National Laboratory, Los Alamos, NM, USA; [2]Univ. Basque Country UPV/EHU, Leioa, Spain; [3]U.S. Geological Survey, Astrogeology Science Center, Flagstaff, AZ; [4]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France; [5]German Aerospace Center (DLR), Cologne, Germany; [6]Purdue University, West Lafayette, IN, USA; [*]wolf@lanl.gov

Introduction: The Perseverance rover landed in Jezero crater, Mars in February of 2021, equipped with several instruments. Among them, SuperCam uses a Laser Induced Breakdown Spectroscopy (LIBS), which obtains emission spectra of ablated target materials in the wavelength range of ~240-850 nm and can detect major elements such as Si, Ti, Al, Fe, Mg, Ca, Na, and K [1,2,3] and minor elements, e.g. Li, Ba, Rb, Sr, P, Mn, H, Cr, Ni, S, Cl, and C [1,2,4].

Volatiles, such as chlorine (Cl), are important species that are mobilized by fluids and thus play a key role in alteration processes on Mars [e.g. 5].

The first detections of Cl were made in the 1970's by the X-ray fluorescence (XRF) spectrometers on Viking 1 & 2, followed by the α-proton x-ray spectrometer (APXS) instruments onboard the Mars Pathfinder (Sojourner), Mars Exploration rovers (Spirit & Opportunity), and the Curiosity rover, all of which documented Cl detections at their respective landing sites [6,7,8,9,10]. The Phoenix mission also detected Cl mainly in the form of perchlorates and chlorides in the soil at its landing site [11]. Studies conducted on martian meteorites found the concentration of volatiles such as chlorine to be higher on Mars than what we see on Earth [5]. Comparison of Cl in past landing sites and Mars meteorites with Cl in Jezero crater can help us understand how Cl varies across Mars and thus the variation in Mars environmental conditions.

Developing a Calibration Model: A suite of 14 mixed samples were prepared from anhydrous calcium chloride (($CaCl_2$), Sigma-Aldrich) and certified Japanese Basalt Standard JB-1b, the latter of which has a known Cl concentration of 50.6 ppm. The basalt standard was selected due to its low Cl composition. It minimally contributes to the amount of Cl present in each mixing ratio.

In addition to the prepared mixture suite, several geological samples including Na and K salts and chlorapatite were included. Compositional data were provided by Activation Laboratories, Ltd on all geologic samples to verify the exact amount Cl present in the samples.

X-ray diffraction data were collected on all of our geologic samples to confirm their mineralogy. 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 analysis (XRD) was performed using Jade© 9.5 X-ray evaluation software with the ICDD PDF-4 database.

All samples were then analyzed using the SuperCam testbed instrument at Los Alamos National Laboratory. The data collected by the SuperCam testbed was used to develop a univariate calibration model (Figure 1), allowing us to isolate signal from the Cl peak at 837.824 nm in the LIBS spectrum in the quantification model. The model's limit of detection for the model was calculated to be 0.6 wt.% Cl and the uncertainty to be ±0.6 wt.% Cl.

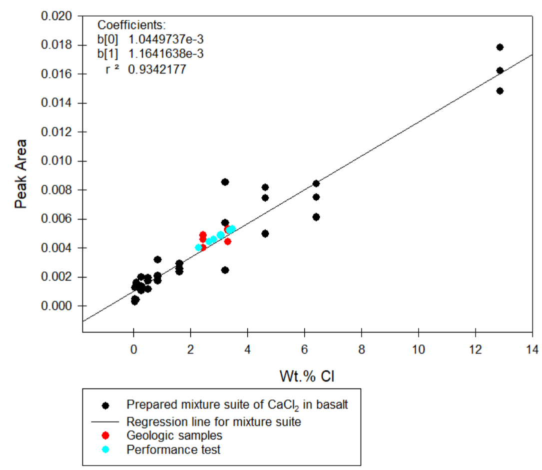

Figure 1: Calibration curve based on a univarite model with asymretric least square baseline correction applied to the data. Data is normalized to the total emission intensity of each of the SuperCam spectral windows.

Chlorine Detections in Jezero by SuperCam: We quantified Cl in all SuperCam data up to sol 1247 were quantified using the above model. Those Mars data were spilt into 5 groups, Máaz, Séitah, the Delta front, the Upper Fan, and the Margin unit. We summarize the distribution of Cl by geologic unit in Table 1. Most Cl detections are found to be in regolith, which is expected (e.g., Figures 2 and 3). The data for each unit was also compared to the data collected by Viking 1, Viking 2, Mars Pathfinder, Spirit, Opportunity, Phoenix, and Curiosity. The quantified LIBS data from SuperCam show that all 5 groups in Jezero crater are more Cl rich than all previous landing sites, which range from 0.35 to 1.12 wt.% Cl. The regolith Cl concentration in Jezero varies slightly between each group:

- Máaz ranging from 0.6 – 5.0 wt.%
- Séitah ranging from 0.9 – 3.9 wt.%
- The Delta front ranging from 0.6 – 5.0 wt.%
- The Upper Fan ranging from 0.6 – 4.7 wt.%
- The Margin unit ranging from 0.9 – 4.7 wt.%

Figure 2: Remote Micro Image (RMI) of a LIBS analysis by SuperCam on Lha tsaadah target (sol 110) covering coarse- and fine-grained regolith.

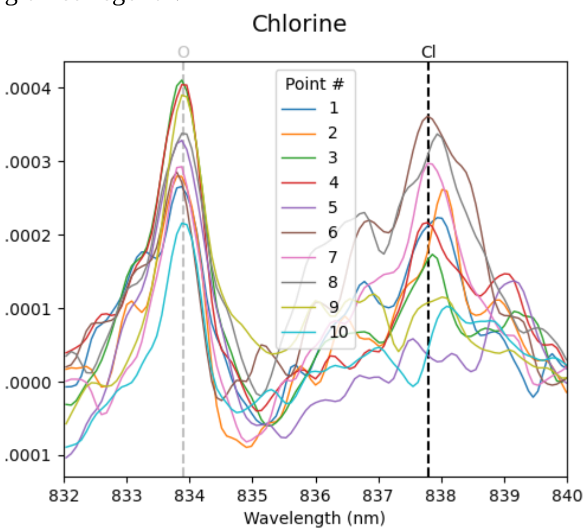

Figure 3: Corresponding LIBS spectra indicating the Cl lines detected for target Lha tsaadah with quantified values ranging from 0.9 – 3.6 ± 0.6 wt.% Cl.

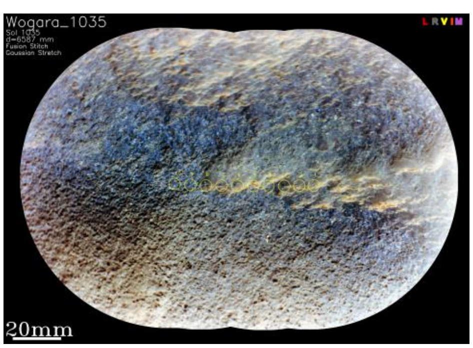

Figure 4: RMI of Wogara_1035.

Quantification of rocks in Jezero showed more variation than regolith with the strongest detection occurring in a float rock targeted on sol 1035 called Wogara (Figure 4). Point 8 hit a salt crystal (NaCl) that was quantified to have 9.4 ± 0.6 wt.% Cl.

The quantified data in targets collected in Table 1 show that the exterior of rocks have positive Cl detections above the 0.6 wt.% limit of detection less than 1% of the time.

Table 1: Summary of Cl detections from sol 0 to the end of the Margin Campaign (sol 1247). Total LIBS shots until sol 1274 is 7771.

Units/ Type	Regolith	Tailings from Boreholes	Abraded Patches	Bedrock	Float Rock
Máaz	49 points 11 targets	22 points 4 targets	11 points 2 targets	11 points 7 targets	1 point 1 target
Séitah	28 points 4 targets				
Delta	118 points 21 targets	21 points 3 targets		1 point 1 target	
Upper Fan	12 points 4 targets		2 points 2 targets	6 points 4 targets	
Margin Unit	61 points 12 targets			10 points 8 targets	2 points 2 targets
Total	**268 points 52 targets**	**43 points 7 targets**	**13 points 4 targets**	**28 points 20 targets**	**3 points 3 targets**

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