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EVIDENCE FOR PERCHLORATE AND SULFATE SALTS IN JEZERO CRATER, MARS, FROM SUPERCAM OBSERVATIONS. P.-Y. Meslin¹, O. Forni¹, P. Beck², A. Cousin¹, O. Beyssac³, G. Lopez-Reyes⁴, K. Benzerara³, A. Ollila⁵, L. Mandon⁶, R.C. Wiens⁵, S. Clegg⁵, G. Montagnac⁷, E. Clavé⁸, J.-A. Manrique⁴, B. Chide^{1,5}, S. Maurice¹, O. Gasnault¹, J. Lasue¹, C. Quantin-Nataf⁷, E. Dehouck⁷, S.K. Sharma⁹, G. Arana¹⁰, J.M. Madariaga¹⁰, K. Castro¹⁰, S. Schröder¹¹, N. Mangold¹², F. Poulet¹³, J. Johnson¹⁴, S. Le Mouélic¹², M.-P. Zorzano¹⁵, and the SuperCam Team. ¹IRAP, Université Paul Sabatier, CNRS, CNES, Toulouse (pmeslin@irap.omp.eu). ²IPAG, Univ. Grenoble Alpes, Grenoble. ³IMPMC, MNHN, Paris. ⁴Univ. Valladolid, Spain. ⁵LANL, Los Alamos. ⁶LESIA, Obs. Paris, Meudon. ⁷Univ. Lyon 1, ENSL, LGL-TPE, Lyon. ⁸CELIA, Bordeaux. ⁹Univ. Hawaii. ¹⁰Univ. Basque Country, Spain. ¹¹DLR, Berlin. ¹²LPG, Nantes. ¹³IAS, Orsay. ¹⁴APL/JHU. ¹⁵Centro de Astrobiología, INTA, Spain.

Context: Over the first 300 sols of the mission, *Perseverance* has explored two geological units within the Jezero crater called *Maaz* and *Séitah*, which are delimited by the *Artuby* ridge. Both were found to be of igneous origin: the *Maaz* rocks have a basaltic composition dominated by varying proportions of plagioclase and pyroxenes [1], while the underlying *Seitah* unit is interpreted to be an olivine cumulate [1]. These two units are believed to pre-date the lacustrine period that formed the western delta and have been exhumed by erosion of the latter. The exploration of Jezero crater therefore provides a unique opportunity to access the basal units of an ancient lake on Mars. Documenting the presence of secondary minerals is important to assess the intensity and conditions of aqueous alteration that these igneous rocks have undergone, and to constrain, for instance, the possible influence of lake waters and the time span of their interaction with pre-existing geological units. It is also important to disentangle multiple events of aqueous activity to track the evolution of environmental conditions.

Up to now, only limited aqueous alteration has been observed, most notably associated with the presence of (Fe,Mg)-carbonates in the *Seitah* unit, but also, to a lower extent, in *Maaz* [2]. This probably resulted from limited carbonation of olivines. IR observations also indicate the presence of Fe³⁺ and Mg-phyllsilicates, and oxyhydroxides [3,4]. Here, we report on the presence of highly soluble salts found along the traverse either in the interior of abraded rocks or at the surface of rocks, which may have resulted from a different, subsequent aqueous event.

Data and Method: This study is based on data acquired by the SuperCam instrument over the first 300 sols of the mission and corresponding to ~1560 LIBS analysis points (30 shots/point). VISIR spectra [0.4-0.85; 1.3-2.6 μm] were most of the time acquired at the same location, with a larger FOV. Raman spectra were occasionally collected at the surface of coarse-grained rocks or in abraded patches, where the S/N ratio was expected to be optimal. Finally, microphone recordings of the laser ablation and context color images (RMI) systematically accompanied LIBS analyses. All these techniques were deployed in the *Guillaumes*, *Bellegarde*, and *Quartier* abraded rocks (among others), where a comparison to SHERLOC and PIXL analyses was also possible and found to be consistent [5,6]. The abrasion tool was designed to produce abraded surfaces from 2 to 16 mm deep.

In addition to their direct detection by Raman spectroscopy, salts can also be detected by the LIBS technique. We looked more specifically at the distribution of sulfur and chlorine and at possible correlations with major elements. Hydrogen is also a key element for the identification and characterization of secondary minerals and is discussed in [7]. Finally, the oxygen line can be used to distinguish chlorates or perchlorates from chlorides, or sulfates from sulfides, for instance.

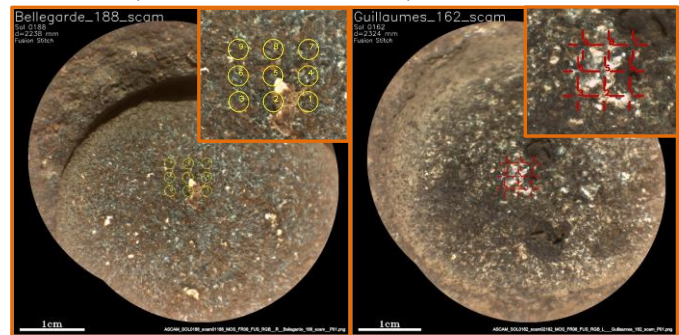


Fig. 1: RMI images of the Bellegarde and Guillaumes abraded patches. Left: FOV of the Raman analyses (notice the white patch in point #5). Right: location of LIBS analyses (notice the mixture of dark and white grains in point #5).

Observations: The first Raman signatures obtained by SuperCam were acquired on the *Guillaumes* and *Bellegarde* abraded patches (Fig. 1), where a narrow peak at ~954 cm⁻¹ was observed. The Raman spectrum of *Bellegarde* point #5 also exhibits peaks at 625, 1090 and 1140 cm⁻¹ (Fig. 2), but no OH/H₂O peaks. These peaks indicate the presence of anhydrous Na-perchlorate. A shot-to-shot analysis of the LIBS spectra collected on *Guillaumes_162* #5, where a fainter Na-perchlorate signature was also detected, shows a correlation between Na and Cl, together with a strong oxygen peak, which corroborates the Raman analysis.

The LIBS analysis also reveals that the presence of Na-perchlorate is accompanied by the presence of Mg-sulfate and Cl-rich Ca-phosphate, mixed with a clinopyroxene-rich igneous substrate. The chemical transitions observed in the LIBS shot-to-shot data are consistent with differences in mineral hardness recorded by the microphone recordings. Finally, IR spectra seem to be consistent with a mixture of hydrated Mg- and Ca-sulfates. The presence of these secondary phases is only patchy in the rock and seems to be associated with the presence of bright white patches disseminated in the interior of these vuggy rocks.

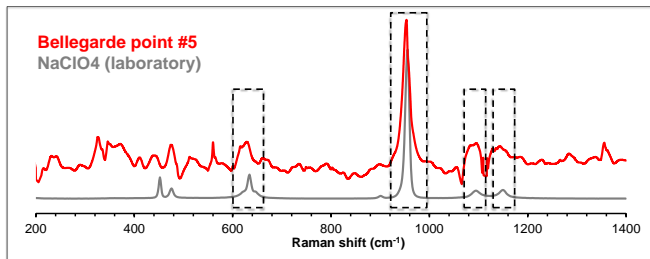


Fig. 2: Raman spectrum obtained on Bellegarde #5 and comparison to a reference spectrum of NaClO₄ obtained in the laboratory.

Apart from regolith targets, which represent the largest group of sulfur-rich targets observed so far (addressed in [8,9]), a few dozens of points were found to be sulfur-rich. Two categories stand out when considering their Ca-Mg-Fe composition (Fig. 3, dashed contours).

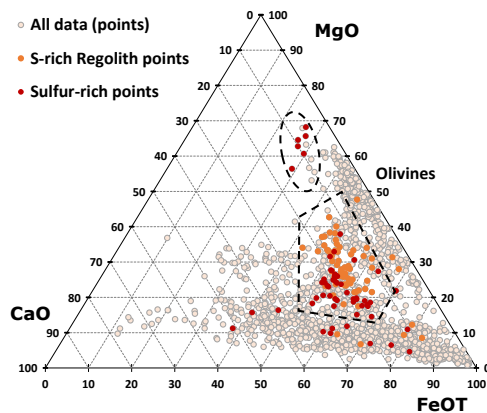


Fig. 3: CaO-MgO-FeO composition of sulfur-rich targets (regolith in orange, rocks in red). Olivines are shown for ref.

A first cluster trends towards the Mg apex, indicating the presence of Mg-sulfates. It does not appear to be linked to the olivine cluster (detections are in different targets). The second cluster falls outside of local igneous minerals' composition, in a portion of the ternary diagram that most resembles soil and dust composition [7,10]. Dust is likely to contain Mg-sulfates [11], and could be present as thick indurated coatings [7]. This cluster could also be explained as a mixture between Ca- and Mg-sulfates and primary minerals. Their hydration level indicates the presence of hydrated sulfates [7]. These detections are either found as isolated points at the surface or interior of rocks or as contiguous points associated with purplish coatings (e.g., Alk es disi, Grandes Tours du Lac, Naadiin_scam) (Fig. 4). They are distributed in both Maaz, Séítah and along Artuby ridge.

Discussion: The detection of perchlorates in Jezero crater confirms that oxychlorine species are widely distributed at the surface of Mars. Previous occurrences of perchlorates were identified in the martian regolith in polar regions (Mg- and Ca-perchlorates detected



Fig. 4: Sulfate-rich coatings on targets Grandes Tours du Lac and Alk es disi.

by Phoenix [12,13]) and in Gale crater [14], in proportions far exceeding those of terrestrial soils, and oxychlorine species (chlorates and/or perchlorates of uncertain composition) were detected in many sedimentary rock samples in Gale [15]. Perchlorate IR spectral signatures were also detected by CRISM [16]. The present direct identification of Na-perchlorate on Mars completes this global inventory. Although the processes leading to the formation of perchlorates on Mars are not well-established yet, heterogeneous photocatalytic or radiation-induced surface reactions involving chlorine-bearing phases were suggested to be involved [17], rather than atmospheric gas-phase oxidation of volcanically-derived chlorine [18]. These processes are thus likely to be surficial. The presence of perchlorate in the interior of vuggy rocks, mixed with Mg-sulfate, thus suggests that brines percolated through these rocks. Given the very high solubility of these salts, they were probably deposited by one of the last episodes of aqueous activity these rocks have encountered. A possible link to chlorides deposited during Jezero's lake evaporation, or to Na leached from feldspars observed in the same rocks should be investigated. But the sensitivity of perchlorates to radiolytic decomposition argues for a geologically young formation or exhumation age [19].

The detection of patches of hydrated Mg-sulfates at the surface of rocks also suggests contact with briny waters during a late-stage aqueous event, and their preservation against aeolian abrasion also supports a young formation or exhumation age. The absence of a link between olivines and most Mg-sulfates detections argues against the formation of these sulfates by very local alteration of the former.

The presence of perchlorates close to cached samples raises the question of the possible decomposition of putative organic molecules, although organic matter was found to be preserved in chlorate/perchlorate-rich rocks in Gale [15].

References: [1] Wiens et al., (*). [2] Clavé et al., (*). [3] Mandon et al., (*). [4] Poulet et al., (*). [5] Murphy et al., (*). [6] Allwood et al., (*). [7] Beck et al., (*). [8] Cousin et al., (*) [9] Hausrath et al., (*) [10] Lasue et al., (*) [11] David et al., 2022, submitted. [12] Hecht et al., 2009, Science. [13] Kounaves, 2014, Icarus. [14] Leshin et al., 2013, Science. [15] Clark et al., 2021, Minerals. [16] Massé et al., 2010, Icarus. [17] Jackson et al., 2015, EPSL. [18] Smith et al., 2014, Icarus. [19] Martin et al. 2020, JGR Planets. (*) this meeting.