

**LATE HIGH TEMPERATURE EVENTS INTERPRETED FROM FLUORINE DETECTIONS IN GALE CRATER SULPHATE UNIT.** O. Forni<sup>1</sup>, E. B. Hughes<sup>2</sup>, K. Rammelkamp<sup>3</sup>, F. Rivera-Hernández<sup>2</sup>, W. Rapin<sup>1</sup>, J. R. Johnson<sup>4</sup>, P. Gasda<sup>5</sup>, O. Gasnault<sup>1</sup>, N. L. Lanza<sup>5</sup>. <sup>1</sup>Institut de Recherche en Astrophysique et Planétologie (olivier.forni@cnsr.fr), <sup>2</sup>Georgia Institute of Technology, <sup>3</sup>Deutsches Zentrum für Luft- und Raumfahrt, <sup>4</sup>Johns Hopkins University, Applied Physics Laboratory, <sup>5</sup>Los Alamos National Laboratory

**Introduction:** The *Curiosity* rover is currently exploring the Sulphate Unit of Gale crater, Mars, in which a sequence of alternating light-toned and dark-toned bands is identifiable from orbit. These bands may have formed due to changes in depositional conditions, climate, brine fluid composition, or diagenesis, following a drying-out period after extensive clay deposition [1]—yet the formation history of such material is unknown. Here, we suggest that a likely explanation for the darker materials is post-depositional, possibly differently sourced fluids infiltrating the bedrock after the formation of primary crystalline evaporite phases. We identify the presence of moderately elevated fluorine uniquely associated with a highly hydrated Na-Mg-sulphate phase nearly exclusive to darker materials in this region (Fig. 1). Such chemistry suggests complex brine infiltration into this unit from a possibly felsic source.

From sol ~3600 to the time of writing, the *Curiosity* rover has encountered flaky dark-toned laminated material, in addition to lighter-toned materials in the Sulphate Unit. [2].

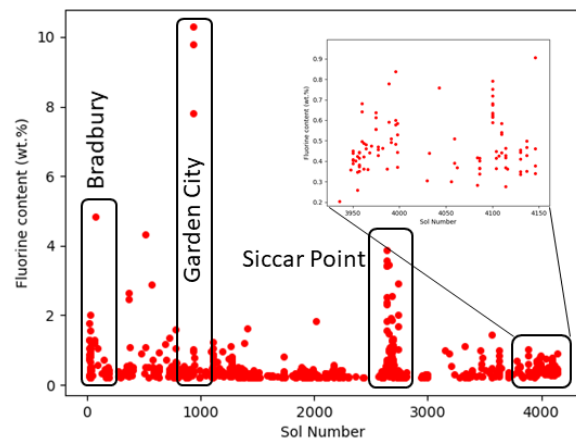


**Figure 1:** ChemCam RMI image of target Thor\_Peak acquired on Sol 3958 exhibiting the characteristic dark-toned slabby structure.

These darker materials became particularly abundant as the rover encountered the Light-Dark sequence, and appear to be present throughout the

region but possibly in higher abundances in the dark bands observed from orbit [2].

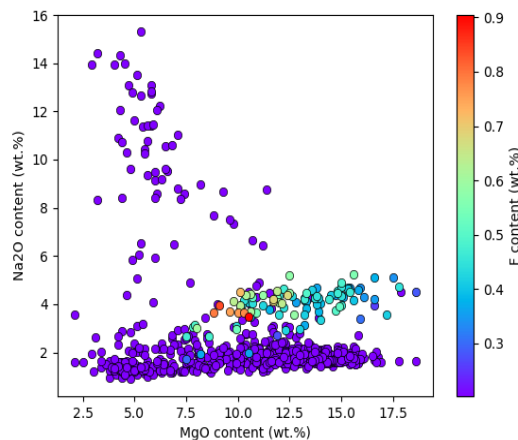
*Curiosity's* ChemCam instrument has obtained geochemical data from both the darker and lighter materials in this layered unit. ChemCam is an active remote sensing instrument that uses laser pulses to remove dust and analyze rocks up to 7 m away [3, 4]. Laser-induced breakdown spectroscopy (LIBS) obtains emission spectra of materials ablated from the samples in electronically excited states in a five-point raster. Thirty laser shots are taken at each LIBS point; the last 25 are averaged together to derive the chemistry. The “shot-to-shot” (STS) data—the chemistry derived from each of the 25 laser shots—provide information on how oxides correlate on a micron scale. LIBS is especially sensitive to halogens like chlorine and fluorine through the emission of molecular bands [5]. In this work, we report a background of numerous fluorine detections in the darker materials and try to propose some scenarios of formation in relationships with the unique composition of this material.



**Figure 2:** Fluorine content versus Sol number. High F contents were observed in the Bradbury formation, at the Murray-Stimson unconformity at Garden city and Siccar Point. The inset shows the occurrence of multiple detections in the Sulphate Unit, and a general moderate enrichment in this region.

**Observations:** Starting from approximately Sol 3940 and perhaps earlier, ChemCam detected a high density of fluorine points with values ranging from 0.3 wt.% F up to around 1.0 wt.% F with an average of about 0.45 wt.% F (Fig 2.). The shot-to-shot spectra

indicate a strong correlation between F and Ca, and no P can be identified at the ChemCam sensitivity. All these observations lead to the conclusion that the F-bearing phase is probably present in the form of fluorite ( $\text{CaF}_2$ ). However, some points are correlated with both  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , making cryolite ( $\text{Na}_3\text{AlF}_6$ ) a possible phase. Almost all of the 100 detections occur in a subset of dark-toned platy slabs as defined by the ChemCam passive relative reflectance spectra threshold defined by [2]. This subset is characterized by a very narrow range in the  $\text{Na}_2\text{O}$  composition of  $4.0 \pm 0.7$  wt.%  $\text{Na}_2\text{O}$  as well as by a relatively high MgO ( $> 8.0$  wt. % MgO) content (Fig. 3). This subset is also characterized by enhanced hydration and sulphur signatures and an absence of chlorine, excluding halite as a potential mineralogical phase contrary to the higher  $\text{Na}_2\text{O}$  ( $> 5.0$  wt. %  $\text{Na}_2\text{O}$ ) bearing targets. Additionally, fluorine is anti-correlated with MgO, H and S, making fluorite a probable distinct phase.



**Figure 3:**  $\text{Na}_2\text{O}$  versus MgO plot of the targets starting at Sol 3940. The high F-content targets are localized around 4.0 wt.%  $\text{Na}_2\text{O}$  and with MgO content larger than 8.0 wt. %. Note that the higher MgO, the lower F, suggesting these materials are in distinct phases.

**Discussion:** The cross-correlation between MgO- $\text{Na}_2\text{O}$ , H and S provides strong evidence of the presence of a hydrated Na-Mg-Sulphate phase in the dark-toned targets [2] contrarily to the light-toned targets. The same behaviour is observed for the presence of fluorine. The occurrence of fluorite and possible cryolite as a diffuse, perhaps amorphous component is different from what has been observed before, as fluorite has been generally observed in veins at the vicinity of the Stimson-Murray discontinuity [6, 7]. The fluorine we detect in these dark-toned targets is also not typically associated directly with Ca-sulphates; Ca is rather only moderately enriched for these detections and sulphur is associated

with the Na-Mg-Sulphate phase. This is in contrast with other fluorite detections on Mars, including recent detections by the Perseverance rover in which an association is observed between fluorite and Ca-/Mg-sulphates [8]. This suggests a unique event, with a unique brine chemistry, enriched both the Na, F and possibly S in these rocks, allowing for the formation of both fluorite, possible cryolite, and the hydrated Na-Mg-Sulphate phase. Such infiltration likely occurred along specific bedding horizons or surfaces as the signature is unique to the dark-toned platy, laminated materials. The complexity of the chemistry suggests a unique brine source, and possibly a relatively more felsic source rock, given high Na and F are rarer in more mafic igneous rocks. Indeed, fragments of feldspar-rich lithology (potentially anorthosites) have been documented by ChemCam at the beginning of the Curiosity traverse [9], suggesting the presence of a felsic source in the vicinity. In some rare cases, like in Greenland, the high concentration in F (and Na) leading to the cryolite could have formed during the continuous transition from a volatile-rich melt to a solute-rich fluid. Formation temperatures of minerals such as cryolite, rare fluorides, sulphides and siderite, which has been also identified by ChemCam [10], vary between 100 and 400 °C [11]. The presence of these new phases indicates complex brine systems and extended hydrologic activity were present in the Gale Crater Sulphate Unit, and may indicate fluid events occurred under possibly high temperature conditions.

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**References:** [1] Sheppard R.Y. et al. (2021) *JGR*, 126, 2 [2] Hughes E. B. et al. (2024) *LPSC LV*, Abstract #2288 [3] Maurice et al. (2012) *SSR*, 170, 95 [4] Wiens et al. (2012) *SSR*, 170, 167 [5] Forni et al. (2015) *GRL*, 42, 1020 [6] Nachon et al. (2017) *Icarus*, 281, 121 [7] Forni et al. (2021) *LPSC LII*, Abstract #1503 [8] Población et al. (2024) *LPSC LV*, Abstract #1464 [9] Sautter et al., (2014) *JGR*, 119, E1 [10] Tutolo et al. (2024) *LPSC LV*, Abstract #1546 [11] Köhler, J., Konnerup-Madsen, J., Markl, G., (2008) *Lithos* 103, 369