Elevated Fluorine Abundances below the Siccar Point Unconformity: Implications for Fluid Circulation in Gale Crater. O. Forni (olivier.forni@irap.omp.eu)[1], E. Dehouck[2], A. Cousin[1], C. C. Bedford[3], G. David[1], S. P. Schwenzer[4], J. C. Bridges[5], O. Gasnault[1], P.-Y. Meslin[1], C. R. Webster[6], E. B. Rampe[7], S. M. Clegg[8], P. Gasda[8], J. Lasue[1], S. Maurice[1], R. C. Wiens[7]. [1]Institut de Recherche en Astrophysique et Planétologie, Toulouse, France, [2] LGL-TPE, Lyon, France, [3]LPI, USRA, JSC, Houston, USA, [4]The Open University, UK.[5]University of Leicester, UK, [6]JPL, Pasadena, USA, [7]JSC, Houston, USA, [8]LANL, Los Alamos, USA.

Introduction: ChemCam is an active remote sensing instrument suite that has been operating successfully on the *Curiosity* rover since landing on Aug. 6th, 2012 [1,2]. It uses laser pulses to remove dust and analyze rocks up to 7 m away. Laser-induced breakdown spectroscopy (LIBS) obtains emission spectra of materials ablated from the samples in electronically excited states. It is especially sensitive to halogens like chlorine and fluorine through the emission of molecular bands [3]. In this work, we report numerous detections of high concentration of F near the Siccar Point unconformity in the Glen Torridon (GT) region of Gale Crater.

Context: In late 2019/early 2020, *Curiosity* explored a section of the Murray formation, referred to as the "fractured Intermediate Unit" (fIU), located immediately below the basal Siccar Point unconformity. This erosional unconformity separates the mudstone-dominated Murray formation from the Stimson formation sandstone (which at this location forms the surface of the Greenheugh pediment (GP)). In orbital imagery, the Murray fm. located within ~15 m of horizontal distance of the contact is distinctively light-toned compared to the rest of the fIU, suggesting possible compositional differences [6].

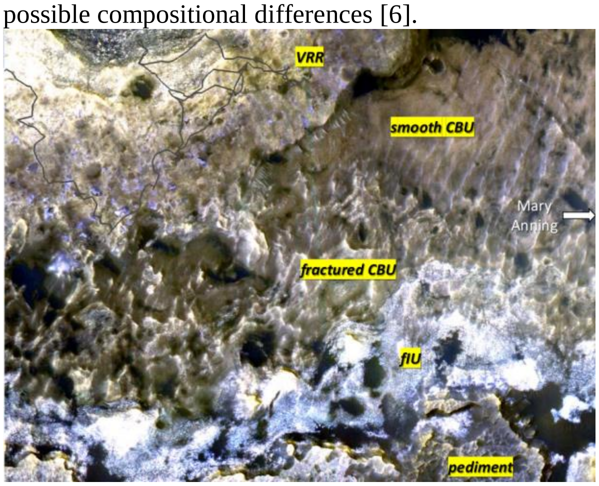

Figure 1: Context map of the fIU.

Three different buttes (Central Butte (CB), Western Butte (WB) and Tower Butte (TB) in chronologic order), have been investigated in this member, along with the Greenheugh Pediment (GP) Capping Unit sandstone, which unconformably overlies the Murray formation and is hypothesized to be part of the Stimson formation; the Hutton drilled sample was acquired within this light-toned band, on a small bench on the flank of Tower Butte.

Observations: During the ascent of Western Butte, we observed a sudden and strong increase of the fluorine detections made by the ChemCam. Since then, more than 200 points above 0.3 wt.% F were detected and the average content is above 0.7 wt.% F with a maximum of about 4 wt.% F. The F detections are located on all points of the ChemCam targets, indicating that the fluorine presence is pervasive in that area. ChemCam first detected this increase in F on sol 2634 in the Ben_Eighe target, which is located near the top of Western Butte. It was not until the rover traversed onto the GP on sol 2694 that F detections almost stopped. F detections reappeared immediately after leaving GP on sol 2737 with the Ben_Wyvis target, during the Tower Butte descent (Fig. 2).

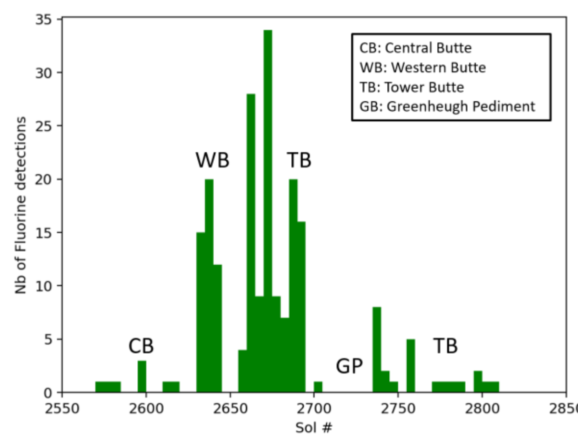

Figure 2: Fluorine detections in the fIU. Note the absence of detection in the Greenheugh Pediment

Several lithological and stratigraphic observations can be outlined. On Western Butte, 50 F detections have been identified with the majority of them located near the top. Among the F detections, about 3/4 are found in the bedrock and the remaining ones are found in diagenetic features like the Hascosay target on sol 2635. This target is located in what appears to be an alteration slab which seems to be cross-cut by a Ca-sulphate vein, indicating that this alteration process occurred prior to the episode that formed the veins. This target is characterized by a mean F of 2.5 wt. %. 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 (CaF_2) in the diagenetic features.The bedrock targets have less F, around 0.5 wt.% on average. In these targets, F is also correlated with Ca on a shot to shot basis, and sometimes P can be observed, making fluor-apatite the most likely F-bearing phase. In the Tower Butte section, where the rover was able to reach rocks located stratigraphically above those of Western Butte, even more F detections have been observed. Almost all of them occur in the bench. Half of the detections are located in the bedrock and a quarter of them can be found in diagenetic features. The remaining ones are distributed between float rocks and unidentified or unclear features. Generally, the F-bearing phases in the bench can been attributed to the presence of apatite since P is observed in the targets. The area is also characterized by several resistant and light-toned "fins", the spectra of which exhibit a strong F signature, with content up to 1.8 wt.%. The first target of this type was "Glen_Rosa", analyzed on sol 2686, and then again on sol 2690 with a depth profile (Fig. 2). The targets Glen_Cannish and Glen_Moriston acquired in the same area exhibit the same properties. Fluorine shows two types of chemical association in these features: 1) with Ca only, suggesting once again fluorite as the main F-bearing phase; 2) with K and Li, suggesting the presence of phyllosilicates and/or micas (Fig 3). This second type of association was also observed in the Kimberley outcrop, on Aeolis Palus [4,5].

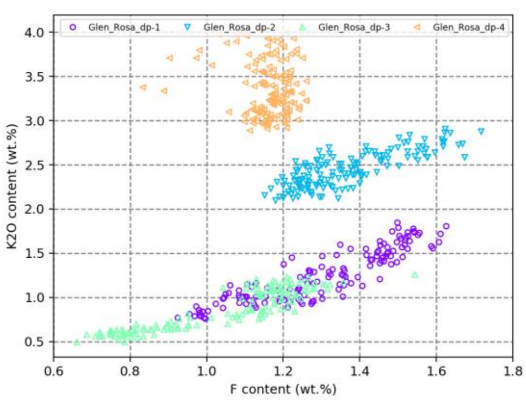

Figure 3: Shot to shot plot of K20 vs F in the Glen_Rosa depth profiles (dp 1 to 4 on the labels)

Interpretations and implications: ChemCam has identified several mineralogical phases that could bear the fluorine. At the Hutton drill site, many fluorine-bearing points are probably related to fluor-apatite, since P is also detected in those points. The presence of fluor-apatite was also confirmed by the CheMin instrument [6] and the ChemCam observations are consistent with SAM observations of HF in the Hutton drill hole. Away from the light-toned layers, the fIU bedrock has a composition broadly in line with the rest of GT. However, as the rover climbed up toward the unconformity, ChemCam measured significant changes, most notably a decrease in SiO_2 (from ~56 to ~49 wt%) and an increase in CaO (from ~2.4 to ~4.4 wt%). In addition, the ChemCam sum of oxides decreased from ~98 to ~94 wt%, and the Chemical Index of Alteration (CIA) dropped from ~54 to ~45 [7]. These trends were observed on both Western Butte and Tower Butte, i.e., where the majority of the F detections are located.

These observations confirm that the light-toned appearance of the Murray rocks near the contact is indeed associated with geochemical variations. The abundance of diagenetic features in these rocks compared to the rest of GT suggests that these variations are not simply due to a change in the sediment source. On the other hand, the decrease in CIA near the unconformity is not consistent with a weathering profile, because the top horizons of such profiles are typically depleted in mobile cations, resulting in increased CIA. Instead, it appears that the light-toned fIU rocks, if they were initially similar to those further away from the unconformity, have been recharged in some mobile cations (including Ca), along with other elements, including the F reported here, in order to explain the lower ChemCam sum of oxides [7]. It is difficult to determine the exact timing of formation of the F-bearing phases, but their presence is likely associated with fluid(s) circulation, and perhaps even hydrothermal activity late in the history of Gale crater, i.e., after the formation of the GP and the deposition of the Stimson formation on top of it. Apatite-bearing bedrock has also been observed in the Jura member on Vera Rubin ridge [8], but not on in the laterally-equivalent terrains in GT, which further suggests that the F-bearing phases are of diagenetic origin. Finally, the possibility of late-stage fluid circulation near the contact between the Murray and the Stimson formations is also supported by previous observations of similar F-bearing phases at Garden city [9] and Marias Pass [10].

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References: : [1] Maurice et al. (2012) SSR, *170,95-166* [2] Wiens et al. (2012) SSR, *170, 167.* [3] Forni et al. (2015) GRL, 42, 1020. [4] Le Deit at al. (2016), JGR 121, 784. [5] Forni et al. (2015) LPSC 46, 1989. [6] Dehouck et al. (2020) AGU Fall Meeting [7] Rampe et al. (2020) AGU Fall Meeting [8] Forni et al. (2020) LPSC 51, 172 [9] Nachon et al. (2017) *Icarus*, 281, 121 [10] Newsom et al. (2016), LPSC, *47, 2397*