FLUORINE IN THE PAHRUMP OUTCROP, GALE CRATER : IMPLICATIONS FOR FLUID CIRCULATION AND ALTERATION

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Introduction: ChemCam is an active remote sensing instrument suite that has operated successfully on MSL since landing Aug. 7th, 2012 [1,2]. It uses laser pulses to remove dust and to profile through weathering coatings of rocks up to 7 m away. Laser-induced breakdown spectroscopy (LIBS) obtains emission spectra of materials ablated from the samples in electronically excited states. The intensities of these lines scale with the abundances of the related element. ChemCam is sensitive to most chemical major elements as well as to a set of minor and trace elements such as F, Cl, Li, Sr, Ba, and Rb [3]. We report here a summary of the fluorine detections [4] occurring at the Pahrump outcrop and Murray formations from Sol 758 to Sol 1150. We identify the F-bearing phases, look at the chemical variation related to these phases in the various sub-units of the outcrop and place constraints on the fluid circulation and related alteration.

Geological unit description: Based on orbital mapping, Pahrump is the first stratigraphic unit of Mt. Sharp that Curiosity has explored. It has distinct albedo and textural appearance in HiRISE imaging. Curiosity reached Pahrump Hills ca. sol 750 (in September 2014). Orbital data suggests Pahrump Hills outcrop to be the northernmost exposures and stratigraphically lower part of the Murray formation. Lithologies of the Murray formation can be traced continuously in HiRISE data to the lowermost strata of Mount Sharp [5, 6]. At Pahrump Hills, the Lower Murray formation consists of finely laminated mudstones, with interstratified cross-bedded basaltic sandstones [6]. The Pahrump Hills section is ~13 m thick [6], and the primary sedimentary faciès observed include: (a) finely laminated fine-grained mudstone; (b) laminated mudstone/siltstone, which appear interbedded within the previous faciès; (c) resistant laminated to massive mudstone/siltstone, at Pink Cliffs, Book Cliffs, Alexander Hills, and Carnivore Canyon; (d) cross-stratified sandstone, at the Whale Rock outcrop [5, 6]. ChemCam performed extensive analyses of the material within this Pahrump section, providing chemical composition both on the host rock/sediment [7, 8] and on post-depositional features. The localization of these features within the stratigraphic column will be detailed in sections ahead.

On sol 923, Curiosity left the primary Pahrump Hills locality, through the Artist's Drive Valley, and encountered a network of prominent veins, termed Garden City, protruding above the host rock. These veins have different albedos and a complex history is suggested by their inter-relationships [9]. Leaving this area on Sol 949, the rover proceeded toward the contact between the Murray Formation and the unconformably overlying Stimson Formation. At the Maria's Pass area, on Sol 992 (May 21, 2015) ChemCam observed the "Elk" target, still in the Murray Formation, that has a very high SiO_2 content greater than 80 wt%, [10]. The rover continued to an area where the contact is fully exposed. ChemCam observations were acquired on the rocks and materials in this area of the contact during two visits, which ended with the departure of Curiosity from the Marias Pass area on Sol 1072.

Fluorine detection and chemical relationships: More than 200 fluorine detections have been identified (Fig. 1) during the mission so far. Up to the Garden City outcrop, fluorine has been very frequent. At Garden City, fluorine contents are very high (up to 12 wt.% for the highest point on the Alvord Mountain target). After Garden City and up to the departure from Marias Pass there are very few detections. The rate of detection notably increases after Marias Pass.

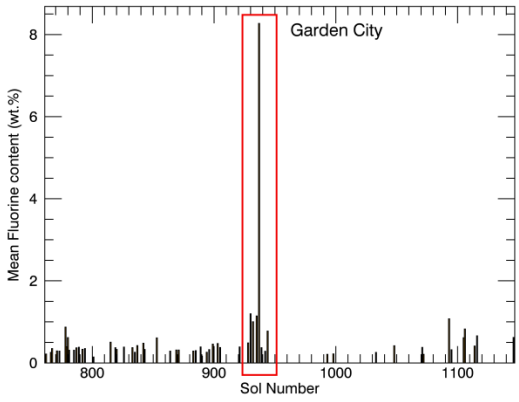

Figure 1: Mean fluorine content vs Sol number.The Garden City unit is characterized by high fluorine content

In figure 2, we display the characteristic signature of the CaF molecular emission feature starting from Sol 940 to Sol 1150. For this period 62 detections have been identified. The fluorine content varies from an estimated detection limit of 0.2 wt.% up to 1.3 wt.%.

Fluorine is detected in the Big Sky drill hole as well as in the surroundings targets but the highest fluorine content was located on the dark vein Alvord Mountain with value up to 12 wt.% [11].

To determine the possible fluorine bearing phases, we have performed a shot to shot correlation between the fluorine content and the major element composition (Fig. 3). Generally fluorine is best correlated with calcium which means that the most probable phase is apatite or fluorite. In the case of Alvord Mountain, fluorite is preferred since apatites is incompatible for such high level of fluorine. Otherwise, since it is difficult to detect phophorus with ChemCam, it is also difficult to distinguish between apatites or fluorite although the ratio of F to CaO is more compatible with apatites for targets with low F contents. Two targets have F that is not correlated with Ca: the Big Sky Drill Hole #10 and especially Heath #1. Those two observation are strongly correlated with Si, Mg, Al and alkalis, suggesting a phyllosilicate.

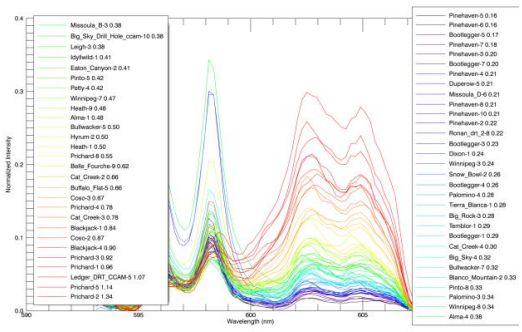

Figure 2: CaF emission feature for target from sol 940 to sol 1150

Discussion: Different geological environments show F-bearing mineralogies. Before Garden City apatites were found in the Pahrump sandstones but in close relationship with calcium sulphates. Apatites were also found at the contact between the Stimson and Murray formations which also exhibit calcium sulphate veins [12]. Finally they were observerd mainly after Marias Pass. These observations suggest some kind of hydrothermal fluid circulation. At Pahrump Hills, the SAM instrument also detected F as SiF_4 formed by the release of mineral F at >800°C and reaction with silicates. Fluorite is mainly found at the Garden City vein complex in dark-tone veins. The presence of this large amount of fluorite suggests acidic leaching or fluid circulation could have leached phosphates, minerals that are easily dissolved by acidic alteration. Mobility of fluorine in fluids due to dissolution of phosphates at low temperature may explain the observed veins, but it does not explain the unique observation of these fluorite veins at Garden City and not in the Pahrump Hills section below [11]. However, some preliminary simulations similar to those of [13], but including fluorine, suggest that fluorite may be the stable phase. No acid leaching is required mainly because species such as F and silica are enriched in alteration fluids and readily precipitate at any change of conditions. The formation of these dark-toned veins seem to preceed the formation of the Ca-sulphates veins. Finally some rare F-bearing observations related with silicates were generally found beyond Marias Pass. They trace the presence of phyllosilicates perhaps forecasting their nearby detection,from orbit [14].

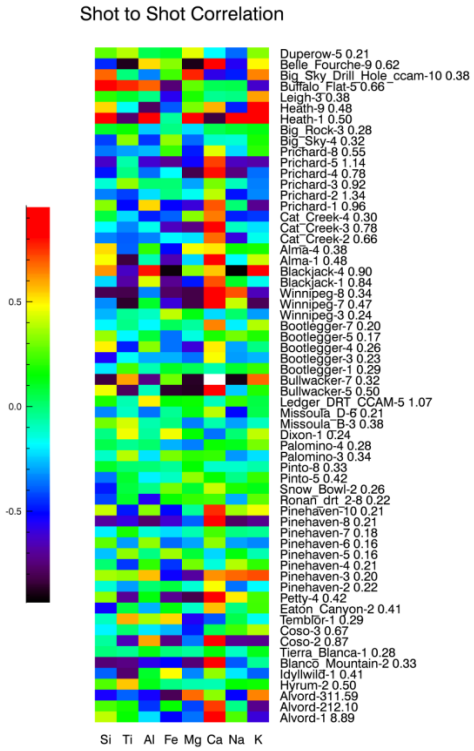

Figure 3: Correlation of fluorine with major elements

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References: : [1] Maurice S. et al. (2012) *SSR, 170,95-166* [2] Wiens R.C. et al. (2012) *SSR, 170, 167.* [3] Paryré V. *(this meeting)* [4] Forni O. et al. (2015) GRL, 42, 1020 [5] Stack K. et al. (2015) LPSC [6] Grotzinger et al. (2015) Science, 350, 6257 [7] Forni et al. (2015) LPSC XLVI, *2099* [8] Blaney et al. (2015), EPSC, *391* [9] Kronyak et al. (2015) LPSC XLVI, *1901* [10] Frydenvang et al. (2016) LPSC (this meeting) [11] Nachon et al. (2016) Icarus (submitted) [12] Newsom et al. (2016) LPSC *(this meeting)* [13] Bridges J.C. et al. (2014) *10.1002/2014JE004757* [14] Carter et al. (2016) LPSC *(this meeting)*