FLUORINE ON MARS: SEVEN YEARS OF DETECTION WITH CHEMCAM ON-BOARD MSL. *O. Forni[1], P.-Y. Meslin[1], A. Cousin[1], S. M. Clegg[2], N. Mangold[3], Le Deit[3], O. Gasnault[1], G. David[1], M. Nachon[4], D. Blaney[5], H. Newsom[6], S. Maurice[1], R. C. Wiens[2], M. Gaft[7],* [1]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, [2]LANL, Los Alamos, USA, [3]LPGN, Nantes, France, [4]Texas A&M University College Station, USA, [5]Jet Propulsion Laboratory, Pasadena, USA, UNM, [6]Albuquerque, USA, [7]Ariel University Ariel, Israel; [olivier.forni@irap.omp.eu]

Introduction: ChemCam is an active remote sensing instrument suite running successfully on MSL since 2912[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. Additionally when the plasma cools down, elements can recombine and molecular emission lines are observed. Recent experiments [3] have shown that, when occurring, these molecular emissions can be much brighter than the associated atomic lines especially when halogens and REE are concerned. These molecular emissions have been observed in several ChemCam spectra and allowed the first ever detection of fluorine on the surface of Mars [4].

Experimental Data: Experiments under martian conditions conducted at LANL with various mixing ratios of CaF_2 exhibit bands at 532.1, 584.5, 603.1 and 623.6 nm assigned to CaF molecular emissions. The band at 603.1 nm is the strongest while the other bands are less intense. Those experiments allowed us to derive a calibration curve for the F content and confirmed a detection limit for fluorine of 0.2 wt.%.

Observations: Over the seven years of observations, ChemCam detected over 1000 points containing fluorine. This represents 0.5 % of all the observations. Two types of relationships between the fluorine and the others elements can be identified: the first one relates fluorine with calcium. In this case the F-bearing phases are either apatite, $Ca_5(PO_4)_3(H, Cl, F)$ or fluorite, CaF_2. Often it is not clear to disentangle between the two unless phosphorus is detected which is not easy given the detection limit of about 3.0 wt% P with ChemCam. The second type relates fluorine with silicon and aluminium. In this case, the F-bearing phase could be mica (muscovite or biotite) or more broadly phyllosilicates. Fluorine has been detected in very different geological settings (fig..1). We will describe some of them.

Conglomerates: Fluorine was detected on the conglomerates at several locations and as early as Sol 14 in the Goulburn conglomerates. Fluorine detections are observed as points distributed across a single clast (Harrison), on conglomerates distributed along the rover traverse (Goulburn, Link, Deloro, Bald Mountain) and in specific outcrops (Lamboo at Kimberley and Platypus Ridge at Darwin) [5]. Fluorine detection is not restricted to one conglomerate type. Localized Fluorine abundances of 0.5 to 1.9% were only found in isolated points and as such would not translate to average bulk rock compositions of this magnitude, with the exception of Goulburn and Link where a bulk content of 1.2% can be estimated because all points contain fluorine. At those two locations the low Ca emission lines as well as the correlation of fluorine with silicon, aluminium and potassium favours the occurrence of micas like muscovite. Note the presence of H in varying proportions in these F-bearing points suggest that some of these minerals are also hydrous, which is a possibility for mica.

Kimberley: Curiosity spent sols 572-632 analyzing outcrops of sandstone, siltstone, and conglomerate in a region of Aeolis Palus informally named the Kimberley formation. The exposed strata contained three informal members: the lowermost "Square Top" member, an overlying "Dillinger" member, and the uppermost "Mt. Remarkable" member [6]. A range of sediment transport directions, reconstructed from crossbed dip directions, suggests complex paleoflow hydraulics with a primarily southwesterly flow in an ancient fluvial (or possibly mixed fluvial-aeolian) system [6]. 36 observations contain fluorine with concentrations ranging from 0.2 wt.% up to 0.8 wt.%. It is notable that these fluorine observations are spread throughout all units of the Kimberley outcrop. Interestingly, all 9 points of the Dillinger target (Sol 628) contain fluorine at a level of about 0.5 wt.%, indicating that fluorine is present in one of the major phases and not as accessory phases.. Among the Kimberley observations, fluorine is generally correlated with K, Al, Si and Mg in that decreasing order [7]. These correlations suggest that the F-bearing phase may be compatible with a silicate phase. Of the phases determined by CheMin in the Windjana drill sample the likeliest hosts are clay minerals or the amorphous component [8] or else a component that was not observed in that drill hole, as no F was observed by ChemCam in the hole.

Pahrump Hills--Stimson units: Based on orbital mapping, Pahrump Hills is the first stratigraphic unit of Mt. Sharp that Curiosity explored. Curiosity reached Pahrump Hills ca. sol 750. At Pahrump Hills, the Lower Murray formation consists of finely laminated mudstones, with interstratified cross-bedded basaltic sandstones [9]. ChemCam performed extensive analyses of the material within this Pahrump section, providing chemical compositions both on the host rock/sediment

[10, 11] and on post-depositional features. On sol 923, Curiosity left the primary Pahrump Hills locality and encountered a network of prominent veins, termed Garden City, protruding above the host rock. The majority of the detections occurred in the basal Pahrump Hills outcrop, correlated with silicon probably in phyllosilicates [10] in good agreement with CheMin [11]. In the upper part of the outcrop, fluorine is detected as secondary calcium correlated phases because found in dentritic features and veins. In the Garden city location in the uppermost part of Pahrump Hills, very high fluorine contents were detected in association with Ca (and no other element), thus likely associated with fluorite [12]. Its formation can be structure-related including mineralization in breccia and veins or unconformity-related and may require hot (200°C) hydrothermal and/or acidic fluids [10]. Leaving this area on sol 949, the rover proceeded toward a contact between the Murray Formation and an unconformably overlying eolian deposit, named the Stimson Formation. 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. The majority of the detections was made very close the unconformity between the Murray mudstone and the Stimson sandstone and is mainly located in the Stimson unit. The fluorine is generally found in a calcium-correlated phase, either apatites or fluorite. Theses phases are probably indicating fluid circulation at the unconformity [13]. Finally from Sol 1500 on, the rover entered the Murray buttes region, which belongs to the Murray formation. The rate of detection notably increases after Marias Pass especially on the Naukluft Plateau and Murray Buttes area. It is worth noting that all the detections occur in the Murray formation. More than 200 detections were made in the Naukluft Plateau and Murray Buttes. These detections are related to calcium bearing phases and mainly found in fractures fills, in the dark-toned veins or maybe in the interstitial space between these veins and the sulphate veins. However, there are some differences between the veins we observe in the Naukluft Plateau and Garden City: fluorine is in apatite and not in fluorite.

VRR: VRR is a topographic ridge on the central mound, Aeolis Mons (Mt. Sharp), in Gale crater that displays a strong hematite spectral signature from orbit [14]. The ridge is comprised of two stratigraphic members within the Murray formation, the Pettegrove Point member (lower) and the Jura member (upper) [15].The Pettegrove Point member overlies the Blunts Point member of the Murray formation [16]. The Jura member comprises bedrock showing areas of red and gray coloration. Red areas show steep ferric absorptions near 550 nm and also contain an ~860 nm absorption feature attributed to red hematite. Gray regions show weak to absent 860 nm absorption and have a weak to no ferric edge near 550 nm [17]. Generally, gray Jura rocks are found in local topographic depressions, but contacts between red and gray Jura are observed to crosscut stratigraphy. Overall, in-situ observations show that VRR is comprised of planar-laminated mudstones similar to lithologies observed in the underlying membersof the Murray formation. Sedimentary facies characteristics suggest that these mudstones were primarily deposited in an ancient lake environment. An increase of fluorine detections is observed in VRR with about 230 detections. The detections are equivalently distributed between the Pettegrove unit and Jura. Very few belong to the Gray Jura unit. Generally the fluorine bearing phase is mainly correlated with apatite which is often associated with iron rich deposits indicating hydrothermal alteration similar to what is observed with the Durango apatite [18].

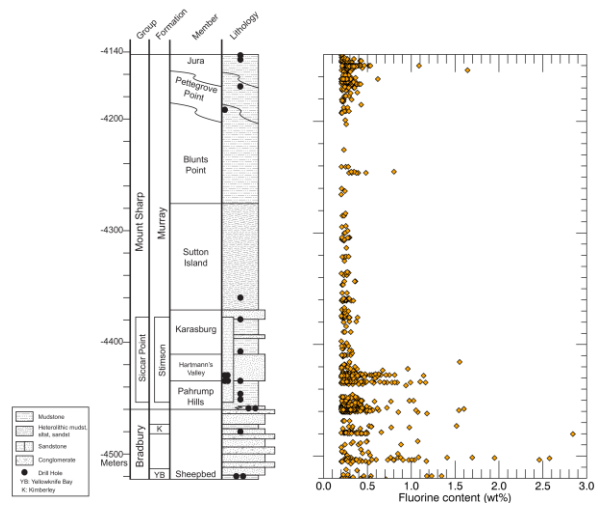

Figure 1: Stratigraphic distribution of the fluorine detections. Only detections less than 3 wt% F are displayed.

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