PHYLLOSILICATE IDENTIFICATION THROUGH CHEMCAM ELEMENTAL CORRELATION. O. Forni[1], G. David[1], A. Cousin[1], E. Dehouck[2], N. Mangold[3], O. Gasnault[1], R. C. Wiens[4], P.-Y. Meslin[1], S. Maurice[1], V. Payré[5], J. Frydenvang[6], A. M. Ollila[4], J. Lasue[1], D. L. Blaney[7]. [1]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, [2]LGL-TPE, Lyon, France, [3]LPGN, Nantes, France, [4]LANL, Los Alamos, USA, [5]GeoRessources, Nancy, France, [6]NHMD, Copenhagen, Denmark, [7]JPL, Pasadena, USA; [olivier.forni@irap.omp.eu]

Introduction: ChemCam is an active remote sensing instrument suite that has operated successfully on MSL since its landing the Aug. 6th, 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 are proportional to the amount 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 Li, Sr, Ba, and Rb. Qualitative and quantitative relationships between elements can be identified using univariate and multivariate techniques [3, 4]. The aim of this work is to investigate the possible identification of phyllosilicates (micas, illites, smectites) with ChemCam with the help of traces elements and their correlations. This is an important question since the Curiosity rover is approaching the phyllosilicate-rich region detected from orbit by the infrared CRISM instrument [5, 6]. However phyllosilicates have already been identified by the CheMin instrument in Yellowknife Bay (YKB) in the John Klein (Sol 163) and Cumberland drill samples (Sol 277) [7] as trioctahedral smectites representing ~20 wt% of the rock.. Lower amounts of phyllosilicates (<10 wt%), interpreted as a collapsed smectite or illite, were found in the lower section of the Pahrump outcrop, in the Confidence Hill and Mojave drill samples [8]. Finally, in the drill samples named Marimba, Quela and Sebina that were acquired in the Murray Buttes region of lower Mt. Sharp, up to ~25 wt% of Fe-bearing dioctahedral 2:1 clay minerals interpreted as nontronite or Fe-illite were identified [9]. The ChemCam data are in good agreement with these detections since Si-Al-F correlations have been identified at the same location [10]. Additionally, the ChemCam data show a relatively high concentration of Li correlated with Cr [11]. Smectites are good canditates as they can incorporate all these elements : for example, Cr can substitute for Al or Fe in the octahedral sites (Hisingerite, Bedeilite), Li can substitute for Mg and F for OH (Hectorite). Accordingly, the aim of this paper is to look into shot to shot correlations between those elements in the ChemCam spectra to figure out if any correspondances arise between the CheMin detections and some of these correlations.

Data Processing: We have analyzed the ChemCam shot to shot data up to Sol 1882. We discard the five first shots to avoid a contamination by dust and all spectra with high calcium content to avoid Ca-sulphate veins. To compute the shot to shot correlation between elements we rely on their ICA scores for the major elements and to univariate matchfilter score for the minor and traces elements. In this exercise we do not need to work with absolute quantitative contents since these correlations are relative. We assume in this study that the correlations we are reporting are relevant to a single phase, but this might of course not be true. Additionally, the nature of the rock may induce a bias in the correlations, that may appear less significant in fine grain mudstones with respect to coarser sandstones.

As an example, we performed the shot to shot correlation between Cr and Fe and between Cr and Ti. We selected the spectra having a correlation larger than 0.80 for both criteria.

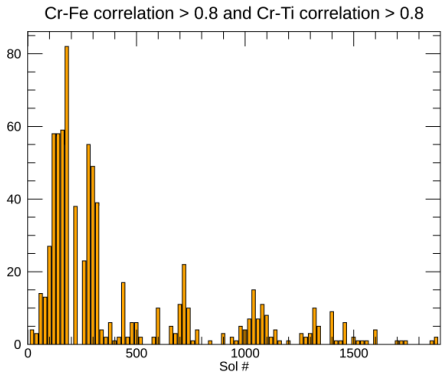

Figure 1.: Histogram of targets having both Cr-Fe and Cr-Ti corelations larger than 0.8

We clearly identify in the combined selection (Fig. 1) a large number of occurrences around the Rocknest outcrop that may be a clue to the presence of oxides or mafic silicates, the latter being less probable since samples only 40 among the 760 selected have also Cr correlated with Si.

Tentative Phyllosilicates Identification: In an attempt to identify phyllosilicates, we have computed several shot to shot correlations involving traces especially lithium and chromium. We correlate Li with Si, Al, Mg and K and Cr with Al. Regarding the Li-Mg (Fig. 2), we observe more detections around Sol 300, 500, 600, 750 which corresponds to the Cumberland

drill hole, the Jum-Jum conglomerates [12], the Kylie-Kimberley outcrop and the Pahrump outcrop. However the majority of the detections occur after Sol 1300 in the Murray formation.

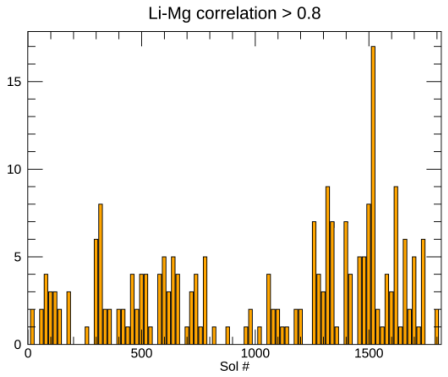

Figure 2.: Histogram of targets having Li-Mg correlation larger than 0.8

There are about 500 targets selected and, among them about 100 have Li correlated with Al and Si making those targets good candidates for illites. Among those 100; more than 20 have F correlated with these elements making those targets good candidates for illites or micas like in the Heath-1 target on Sol 1115.

The high Cr-Al correlation (Fig. 3) coefficient are mainly located in the John Klein and Cumberland areas in the YKB formation. However there are also numerous detections in the Murray formation around Sol 1350 but also in the Stimson Formation at the Lubango and Okoruso drill hole locations.

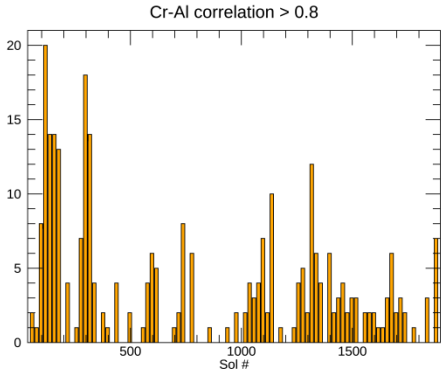

Figure 3.: Histogram of targets having Cr-Al correlation larger than 0.8

If we focus on the Cr-Al high correlations in the drill holes and their tailings (Table 1), we can observe two very different behaviours : in the YKB formation including the John Klein and Cumberland drill holes, Cr is also very highly correlated with Fe in good agreement with the CheMin Fe-smectite detection [7]. This is consistent with other detections up to Sol 300 with some of them corresponding to targets already identified by [13] as possible candidates for Fe-smectites in raised ridges like the McGrath or Lady-Nye targets. The behaviour is different in the other drill holes: the correlation with Fe is much weaker although it remains generally positive. This suggests that the pure Fe-smectite may be in some way mixed with other phases like illites as suggested by the generally high correlation with K.

John_Klein_RP2-6	165	0.86	0.8	0.84	0.8	0.18	47.3
John_Klein_RP2-6	165	0.86	0.8	0.84	0.8	0.18	47.3
Cumberland-3	187	0.94	0.91	0.91	0.89	0.06	46.3
Cumberland-5	187	0.98	0.95	0.67	0.74	0.64	45.2
Drillhole-10	227	0.9	0.82	0.71	0.82	0.36	45.4
Cumberland_CCAM-4	274	0.95	0.88	0.8	0.87	0.66	46.2
CumberlandNew_RP-3	277	0.88	0.86	0.2	0.3	0.53	43.8
CumberlandNew_RP-3	277	0.88	0.86	0.2	0.3	0.53	43.8
CumberlandNew_RP-2	281	0.94	0.85	0.57	0.74	0.13	46.9
CumberlandNew_RP-3	281	0.95	0.8	0.75	0.86	0.45	45.9
CumberlandNew_RP-10	281	0.98	0.8	0.75	0.76	0.05	45.1
CumberlandNew_RP-2	281	0.94	0.85	0.57	0.74	0.13	46.9
CumberlandNew_RP-3	281	0.95	0.8	0.75	0.86	0.45	45.9
CumberlandNew_RP-10	281	0.98	0.8	0.75	0.76	0.05	45.1
CumberlandA_LL-4	284	0.97	0.84	0.88	0.82	0.66	46.7
Windjana_drill_tailings-10	622	0.53	0.81	0.65	0.75	0.37	41.1
Mojave_Mini_Drill_Bottom-1	869	0.59	0.8	0.68	0.69	0.23	50
Buckskin_Full_Drill_Hole_ccam-2	1064	0.84	0.91	0.36	0.72	-0.23	44.3
Big_Sky_Drill_Hole_ccam-3	1123	-0.01	0.82	0.93	0.8	0.64	50.2
Lubango_Tailings_LIBS-5	1325	0.74	0.8	0.35	-0.38	-0.52	53.8
Okoruso_tailings_LIBS-5	1337	0.34	0.92	0.72	0.83	0.44	42.5
Okoruso_tailings_LIBS-6	1337	-0.46	0.83	0.54	0.85	0.73	42.5
Marimba_Drill_Hole_1420_ccam-9	1421	0.8	0.84	0.78	0.7	-0.48	48.4
Quela_Drill_Hole_CCAM-2	1466	0.78	0.87	0.84	0.64	0.38	40.4
Quela_Drill_Hole_CCAM-6	1466	0.76	0.81	0.87	0.85	0.43	40
Quela_Drill_Hole_CCAM_1-7	1467	0.08	0.8	0.8	0.69	0.24	48.5
Sebina_tailings_ccam_2-4	1497	0.61	0.83	0.8	0.54	0.75	53.2

Table 1. Drill and tailings targets having a Cr-Al correlation larger than 0.8

In contrast there is no clear correlation of Li with Mg in these observations making them difficult to interpret, although the interlayer spacing measured CheMin is more consistent with Na and K than Mg [7] whit also may explain the elevated correlation with K and Na. Finally, the different behaviour in the Cr-Fe correlation may simply indicate the higher abundances in Fe-oxides in the YKB unit.

Further work, including other traces and major elements correlations may potentially help to better constrain the contribution of phyllosillicates to the ChemCam data

References : [1] Maurice S. et al. (2012) *SSR, 170*, 95 [2] Wiens R.C. et al. (2012) *SSR, 170*, 167 [3] Clegg S.M. et al., (2017) *SCAB, 129*, 64. [4] Payré V. et al.. (2017) *JGR, 122*, 650 [5] Milliken R. E. et al. (2010) *GRL, 37*, L16202 [6] Fraeman A. et al. (2013) *Geology, 41*, 1103 [7] Vaniman D.T. et al. (2014) *Science, 343*, 6169 [8] Rampe E.B. et al., (2017) *EPSL, 471*, 172 [9] Bristow, T. et al, (2017), *LPS XLVIII*, 2462. [10] Forni O. et al. (2016) *LPS XLVII*, 1990. [11] Forni O. et al.(2015), *LPS XLVI*, 2099. [12] Mangold N. et al., (2016) *JGR, 121*, 353. [13] Leveillé et al. (2014) *JGR, 119*, 2398