POTASSIUM ENRICHMENTS AND MINOR ELEMENT ABUNDANCES MEASURED BY CHEMCAM AT GLEN TORRIDON, GALE CRATER, MARS . A. Cousin[1], E. Dehouck[2], O. Forni[1], G. David[1], G. Berger[1], P. Meslin[1], J. Lasue[1], A. Ollila[3], W. Rapin[4], S. Maurice[1], O. Gasnault[1], R. Wiens[3], [1]IRAP, Toulouse, France (agnes.cousin@irap.omp.eu), [2]Université de Lyon, [3]LANL, Los Alamos, NM, USA. [4]Caltech, CA, USA.

Introduction: The *Curiosity* rover reached the Glen Torridon (GT) area around sol 2300 (January 2019). GT is known to display relatively strong and extensive smectite signatures from orbit [1]. The year-long exploration by *Curiosity* has revealed several rock facies as well as variations in chemical compositions [2-4]. The dominant type of rock in the lowermost part of GT (now recognized as the lateral continuation of the Jura member) is described as the "rubbly" bedrock because it outcrops as small pieces of bedrock embedded in soil. The rubbly bedrock has shown a surprising enrichment in K_2O [3], whereas the slabs of coherent bedrock adjacent to it are low in K_2O but enriched in MgO [3]. The overlying Knockfarril Hill member is somewhat intermediate between these two groups, showing intermediate MgO content, an overall high K_2O content similar to the rubbly rocks, but a low Na_2O content compared to these two groups. More details about the distinction of these groups, concerning their major element compositions along with their facies can be found in [1,3]. X-ray diffraction (XRD) analyses performed by the CheMin instrument showed that the Jura coherent bedrock contains ~30 wt% of Fe-smectites [5]. However, concerning the GT rubbly bedrock, no XRD data is available, and the discussion below is thus based solely on elemental compositions measured by ChemCam [6,7].

Objectives of the work: The first objective of this work is to interpret the observed K_2O enrichment of the GT rubbly bedrock in terms of mineralogy and, in particular, to determine if it may be due to partial illitization of the clay minerals. Elevated K_2O abundances were previously observed in the Kimberley area [8-9], on the floor of Aeolis Palus [10], where CheMin results showed an associated enrichment in K-felspar (sanidine) [9].

The second objective of this work is to investigate the distribution of minor elements in GT rocks, including the rubbly (K-rich) and coherent (Mg-rich) facies of the Jura member, as well as sandstones from the Glen Etive area in the Knockfarril Hill member [3]. Minor elements could provide some insights into the origin of the rocks, and into the processes (e.g., alteration, burial) that they have undergone [11].

Methodology: ChemCam uses the LIBS technique to perform remote chemical analyzes [12]. The laser beam (300-500 µm, [13]) is large enough that it mostly samples mixtures of mineral phases (as opposed to pure phases), especially in mudstones. Therefore, we used trends in elemental ratios to interpret the mineralogy of the rocks. Compositions with a sum of oxides <90 % were discarded in order to minimize the contribution of the ubiquitous Ca-sulfate veins. Concerning minor elements, peak areas have been used, as described in [11].

Results and Discussion:

K_2O enrichment in the GT rubbly bedrock: Fig.1 shows the K/Al molar ratio for the Kimberley dataset (blue) along with the GT rubbly bedrock (orange).

The dispersion in the Kimberley points is likely due to the larger grain size of these sandstones, which favors the sampling of different phases. The points with the higher K abundances follow a K/Al trend consistent with sanidine (blue dashed line). The GT rubbly bedrock data (orange) is much more clustered, which could reflect the smaller grain size (these are mudstones), but also a single mineral source for both K and Al.

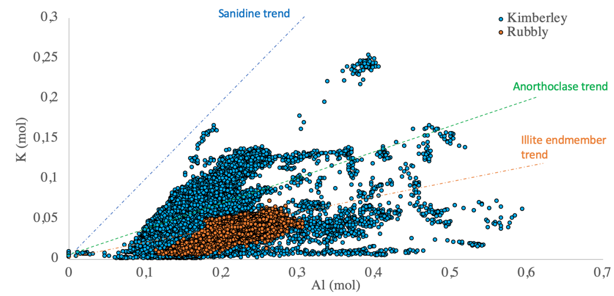

Fig.1: K vs Al (mol) for the Kimberley (sanidine-rich) bedrock in blue and the Rubbly bedrock encountered at GT (orange). Each data point corresponds to a single laser shot. The dashed lines correspond to the theoretical trend for a sanidine $K(AlSi_3O_8)$ (blue), anorthoclase $Na_{0.75}K_{0.25}AlSi_3O_8$ (green) and an end member illite $K_{0.85}Al_2(Si,Al)_4O_{10}(OH)_2$ (orange).

The K-Al relationship observed in the rubbly bedrock of the GT Jura member is different from that observed at Kimberley and could be consistent with the composition of the illite endmember. Alternatively, this trend may also correspond to an average composition between a K-felspar and another Al-rich, K-poor mineral such as plagioclase. However, if plagioclase was responsible for this lower K/Al ratio, we should observe a positive correlation between Sr and CaO [14], which is not the case. Also, when comparing the Kimberley sanidine-bearing rocks with the GT rubbly bedrock, the K/Rb average in the latter is lower, suggesting as well the presence of K-rich phyllosilicates instead of K-felspars. Indeed, the K/Rb is generally lower in K-rich clay minerals than in igneous materials [15].

The possible presence of illite in the GT rubbly bedrock raises the question of the source of potassium and the diagenetic reactions having affected these sediments. Taking Earth as a proxy, K-feldspar is the usual source of potassium, but this mineral is not as ubiquitous on Mars, although it was identified in several rocks along *Curiosity*'s traverse [8-9,16-18]. On Earth, the progressive conversion of detrital smectite to illite in terrestrial marine sediments (monitored by their swelling properties and not the bulk composition) is a slow process requiring time and temperature [19], making it unfavorable under present-day Martian conditions. However, a chemical balance in shales from several petroleum wells in the U.S. Gulf Coast reported in [20] discussed the K and Al abundance during illitization of the sediments. By reprocessing the data of this study, we found the same K/Al trend as for the GT rubbly bedrock (Fig. 1). Note that the sampling scale in [20] was centimeter, much higher that the ChemCam's micron scale, and the observed variations were correlated to depth, from 1 to 5 km. Nevertheless, the similitude between the GT and Gulf Coast chemistry pleads for an illitization reaction having affected the rubbly sediments, eventhough the Martian and terrestrial contexts are radically different.

Distribution of minor elements: Compared to previous rocks analyzed along the traverse, the GT bedrocks are enriched in Li, and to a less extent in Sr (Fig. 2).

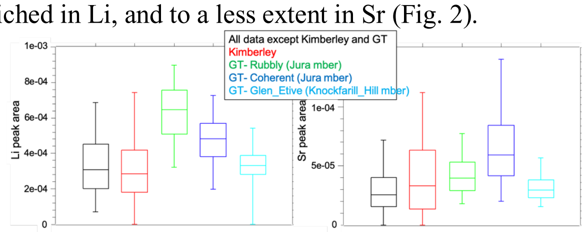

Fig.2: Boxplots for the Li and Sr peak areas for all the data along the traverse (black), Kimberley (red) and GT bedrock.

Similarly to their major elements differences, these three types of bedrock show clear differences in terms of minor elements. The Jura rubbly bedrock is enriched in Li, Rb, as well as Ni and Cr compared to other rocks of GT (Fig. 3). Rb and Li are slightly correlated with K_2O (they both substitute with K), but the Cr and Ni do not seem to correlate with any other major or minor elements. Cr and Ni enrichment could be linked to the slight FeO increase, or they might just be sorbed onto phyllosilicates [21].

The Jura coherent bedrock is enriched in Sr compared to the other GT bedrocks (Fig. 3). This type of bedrock shows more abundant Ca sulfates compared to the rubbly bedrock [22]. Nevertheless, Sr is not related to the high Ca contents linked to the sulfates. Therefore, more investigations will have to be made, target by target, to look for correlations, taking out any Ca sulfate component. In that way, correlations in bedrock with CaO, K_2O and other elements will be investigated.

The Knockfarril Hill member does not show any particular enrichment in the minor elements investigated here compared to other GT rocks. It is only slightly enriched in Rb, very similar to the rubbly bedrock, mainly due to its high K_2O content as well.

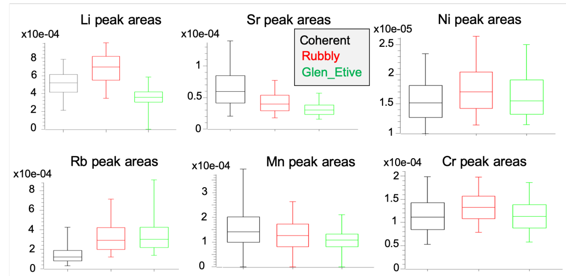

Fig.3: Boxplots for the Li, Sr, Ni, Rb, Mn and Cr peak areas for the rubbly, coherent and capping-types of bedrock in GT.

Conclusions: This is a preliminary study investigating the possible mineral phase(s) responsible for the K_2O enrichment observed in the rubbly bedrock of the GT Jura member, as well as the signature of the minor elements in the GT bedrock.

In conclusion, after an inventory of different possible mineral contributions to the K enrichment in the rubbly bedrock (amorphous component not discussed here), the most probable source for it is an illite endmember. The K/Al relationship suggests that the conversion of smectite to illite, in Gale crater or at the source of the sediments, was sufficient to produce regular (R1) interlayered smectite-illite, even though the past conditions at Gale seem to be very different from those on Earth to produce such mineralogy. In any case, the observation of K-rich bedrock so close to smectite rich ones [1-5] is very intriguing.

Rb, Sr, Li and Ni are commonly enriched in clay minerals, as they are easily adsorbed into such structures.

Even though all the rocks found in GT have shown to be enriched in Rb, Li and in less extent in Sr, we have observed that depending on the type of bedrock, the distribution of these minor elements is varying. Rb and Li are more enriched in the K-rich bedrock, as they both substitute with K. Also, the Jura rubbly bedrock has shown to be enriched in Ni and Cr. More investigations will have to be done to better understand to which phases these elements are related. Each of these minor elements have different mobility, under different conditions (pH, temperature, etc..). Investigations of their content in clay-rich rocks, along with the major elements composition of such rocks, can bring some clues about the past environment of these deposits.

References: [1]Grotzinger et al., 2012; [2]Fox et al., this meeting; [3]Dehouck et al., this meeting; [4]O'Connel-Cooper et al., this meeting; [5]Thorpe et al., this meeting; [6]Maurice et al., 2012; [7]Wiens et al., 2012; [8]Le Deit et al.,2016; [9]Treiman et al.2016; [10]Palucis et al., 2014; [11]Payré et al., 2017; [12]Clegg et al.,2017; [13]Maurice et al., LPSC 2012; [14]Simmons, 1999b; [15]Heier and Billings, 1970; [16]Sautter et al., 2015; [17]Cousin et al., 2017; [18]Mangold et al.,2016; [19]Velde & Vasseur, 1995; [20]Berger et al., 1999; [21]Short, 1961; [22]Gasda et al., this meeting.