NEW QUANTIFICATION OF BA AND SR IN CHEMCAM LIBS DATA AND IMPLICATIONS FOR GEOLOGICAL INTERPRETATIONS. A. Cousin[1], O. Forni[1], P.-Y. Meslin[1], S. Clegg[2], A. Ollila[2], O. Gasnault[1], S. Maurice[1], R.C. Wiens[2] and ChemCam Team. [1]IRAP, Toulouse, France (agnes.cousin@irap.omp.eu), [2]LANL, Los Alamos, NM, USA.

Introduction: The detection and quantification of minor and trace elements in geological settings is of great help to understand the different geological processes (formation and weathering) they have been through. This is of particular importance when the geological context of the rocks is unknown, or not well constrained. This is the case with planetary missions, such as on Mars with the Mars Science Laboratory (MSL)/Curiosity rover. Curiosity landed at Gale crater, Mars, during August 2012. The ChemCam instrument, onboard the rover, uses the Laser-Induced Breakdown Spectroscopy (LIBS) technique in order to assess the chemistry of the analyzed targets [1,2]. ChemCam can detect several minor and trace elements: H, Li, C, N, F, P, S, Cl, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Ba, and Pb. Nevertheless only a few of them are routinely quantified: Mn, Ba, Li, Rb, Sr. H, S, Ni and Cu have also been quantified in [3-7].

This study focuses on revisited Ba and Sr quantifications. Minor element quantifications with ChemCam are performed using univariate techniques [8], where the Ba line used is located at 455.53 nm. This ionized Ba line is the most intense in the range 240-900 nm, from the NIST database [9]. Nevertheless, it is strongly overlapped by Si and Ti lines, which makes the peak fitting harder and tends to bias the result when the target is enriched in SiO_2 [8,10]. However, Ba substitutes easily with K and therefore is found in K-feldspars. It is found as well in Ca-rich minerals (plagioclase, pyroxenes and amphiboles) but also in apatite and calcite, as it substitutes with Ca too. Ba is also found in high amounts in clays and in Fe and Mn oxides, onto which it is adsorbed. Its quantification is therefore of great importance, as Curiosity has sampled several kinds of Fe and Mn oxides during its traverse [11-14] and is now exploring the clay-bearing unit [15,16]. Recently, we found another ionized Ba line that shows almost no overlap with other element lines, located at 614.3 nm.

The Sr line used for quantification is located at 421.67 nm. This is the least overlapped line, even though another nice one is at 460.86 nm but that is at the end of the VIO spectrometer range with ChemCam. Sr can easily substitute with Ca and K. In igneous rocks, Sr is found preferentially in intermediate rocks, where the Sr/Ca ratio is helpful to determine the petrogenesis. In sedimentary rocks, there is a strong substitution between Ca and Sr in carbonates, and a strong adsorption on clay minerals. Sr can also substitute with Ba in sulphate materials.

Objectives of the work: Sr and Ba elements have already been quantified using the ChemCam data, by testing some multivariate tools [10] but also univariate techniques [8,10]. For these quantifications, the clean and calibrated spectra are used [17] and therefore the spectra are well calibrated in wavelength, which is important for such univariate techniques. This wavelength calibration is maintained and checked every few months, to make sure there is no shift in time. Nevertheless, last year, a few refinements implied a change in the Sr peak fitting output. We decided to update the automatic peak fitting in order to make sure this new calibration wavelength was not impacting the Sr estimations. Concerning the Ba line, the objective was to investigate a new elemental line in order to avoid the bias due to the Si lines.

Methodology: To check or investigate new quantification curves for Sr and Ba, we have used the calibration dataset acquired with the ChemCam replica in Los Alamos. This corresponds to more than 400 samples [18], that have been shot at 5 different point locations with 50 shots each.

For the univariate calibration, we have used the average spectrum obtained from the 50 shots. The selected emission line (for Ba and Sr) is then fitted using a Voigt function, after normalizing the spectrum to the total intensity of the VIO or VNIR range depending on the line.

More details about the calibration dataset can be found in [18] whereas more details about the peak fitting can be found in [8].

Results: *Sr quantification.* Compared to the method used in [8], only the parameters concerning the baseline have changed. In the previous work, the baseline was not constrained, and was a parabola most of the time. We have found that forcing the baseline to be linear was a better choice for maximizing the fitting results. The peak areas obtained with this new fitting routine are really close to the ones obtained with the previous methodology [8]. Two models were tested, linear or polynomial, but with similar results. Therefore, the linear model was chosen, with a Limit Of Detection (LOD) of 96 ppm, and a Root Mean Square Error (RMSE) at 138 ppm (were 87 ppm and 150 ppm resp. in [8]).

Ba quantification The line @ 614.3nm is the least overlapped compared to the others that are sufficiently intense with our setup, and in our spectrometer range. The best model is linear (Fig. 1), giving a LOD at 180 ppm and a RMSE at 388 ppm in average. Even though there can be an overlap with a Fe line located at 613.8

nm, we have found, that there is no correlation between the Ba predictions and the known Fe content. A bias due to a high Fe content would imply some overestimation of the Ba content, which has not been observed in the calibration dataset (Fig. 2).

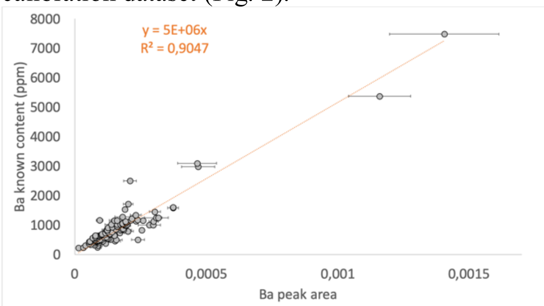

Figure 1: Ba content (ppm) from database versus Ba peak area. The standard deviations obtained from the 5 spectra for the peak areas are shown in the X error bars.

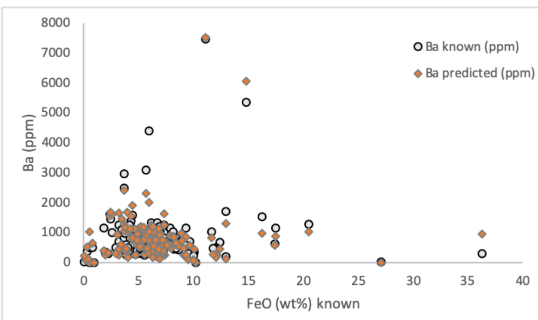

Figure 2: Ba content (ppm) versus FeO content (wt %). Ba content from database is in grey and predicted Ba content from model in orange.

Mars Observations. Curiosity has driven more than 21 km in total since its landing, and has traversed several types of deposits. ChemCam has performed more than 700000 laser shots in 7 years, corresponding to roughly 3000 Mars targets. Only the Ba predictions are investigated here.

The Ba signal is below the LOD (180 ppm) most of the time, as 98 % of the data do not show any Ba line. Among the data with a clear Ba signature, 75.6 % of them contain less than 500 ppm of Ba, whereas 19,5 % have a content between 500 and 1000 ppm. However, 4.9 % of the data contain more than 0.1 wt % of Ba and up to 0.3 wt %. Fig. 3 shows the abundances (ppm) for Ba over the elevation. At the beginning of the traverse, intermediate to high Ba contents (>500 ppm) are mainly observed in evolved rocks [19-21]. One of the most enriched point in Ba is located at the Kimberley outcrop, which corresponds to sedimentary rock enriched in sanidine [22]. In Pahrump Hills, more points are showing an intermediate Ba content (between 500 and 1000 ppm), probably due to the presence of mudstones [23].

Then, at higher elevation but still in the Murray Formation, in the Sutton Island and in Blunts Point members, Ba is overall observed at lower concentrations, and is mainly below the LOD. A few points have a high Ba content though, probably related to the presence of some clays. In the Vera Rubin Ridge, Ba is more abundant, up to 1 wt%, whereas at the beginning of the Clay Unit we can observe more Ba-rich points, up to 2 wt %. This might be due to a clay content that is higher in these deposits [24]. An important point to note is that no enrichment in Ba has been observed in VRR, even in the hematite grains observed [13-14]. The same observation can be made at the Blunts Point member, where several nodules enriched in Fe and sometimes in Mn have been observed [11].

Conclusions: The new Ba quantification is consistent with the work done previously, and easier to apply for Si-rich targets, which was the objective, as the Ba tends to be elevated in evolved magmatic rocks. Some higher Ba content has been observed in the Clay-rich unit, reflecting the enrichment of clays in that area. However, no Ba enrichment has been noticed in Fe-rich points, such as in the nodules observed at Blunts Point or in the hematite grains observed in the bedrock of VRR.

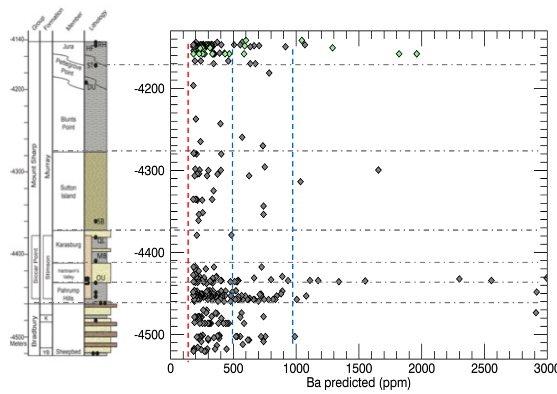

Figure 3: Log scale (left) from the sed. group with the distribution of the Ba abundances over the elevation. Green points correspond to Glen Torridon area (up to sol 2100).

References: [1]Wiens et al., SSR, 2012; [2]Maurice et al., SSR, 2012; [3]Payré et al., Icarus 321, 2019; [4]Meslin et al., LPSC 48, 2017; [5]Schröder et al., Icarus 249, 2015; [6]Clegg et al., this meeting; [7]Rapin et al. Spect. Chem. Acta B, 2017; [8]Payré et al, JGR Planets 122, 2017; [9]https://physics.nist.gov/asd; [10]Ollila et al. JGR Planets 119, 2014; [11]Meslin et al., LPSC 47 #1903, 2016; [12]Lanza et al, GRL 41, 2014 ; [13]L'haridon et al., submitted;[14]David et al., submitted; [15]Fox et al., LPSC 50, 2019 ; [16]Dehouck et al, this meeting ; [17]Wiens et al., Spect. Chem. Acta B, 2013 ; [18]Clegg et al., Spect. Chem. Acta B., 2017; [19]Sautter et al., Nature Geo., 2015; [20] Sautter et al., Lithos, 2016; [21]Cousin et al., Icarus, 2017; [22]Le Deit et al., JGR Planets, 2017; [23]Grotzinger et al., Science, 2015; [24]Rampe et al., 2019, submitted.