1 Copper calibration and quantification using LIBS

1.1 Experimental set-up

We used a laboratory spectral database obtained from more than 400 homogeneous pressed powder samples with grain size generally varying between 20 and 60 μm that were analyzed with the ChemCam laboratory testbed from Los Alamos National Laboratory (LANL, NM, USA) (Clegg et al., 2017). This database, which contains natural and synthetic geological standards, was used to quantify major and several trace elements and is largely detailed in Cleg et al. (2017) and Payré et al. (2017) papers. The standard compositions were analyzed by spectrometry including X-ray fluorescence (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Clegg et al., 2017). The LANL LIBS setup consists of the ChemCam engineering model Mast Unit and flight spare parts for the Body Unit: a ChemCam-like instrument is thus used to sample each standard with a spot size ~350 μm at a distance of 1.6 m from the telescope. All the standards have been analyzed in a simulated Mars atmosphere (P_{CO_2} ~ 6.9 mbar), and each of them has been sampled at five LIBS points with fifty LIBS shots in each point. The obtained LIBS spectra are processed following the ChemCam data pipeline, removing the continuum and the background, denoising the spectrum and calibrating for the wavelength and instrumental response (Maurice et al., 2016; Wiens et al., 2013). Then, spectra are normalized to each of the three spectrometers spectral range by dividing each pixel intensity by the sum of the intensities of each spectrometer separately. For each LIBS point, the five first spectra (out of 30 per point) are removed to avoid any surface dust contamination and the remaining spectra are averaged. For each standard, the five resulting averaged spectra are themselves averaged and a standard deviation is calculated.

1.2 Univariate calibration of copper

Trace element concentrations are usually calibrated by univariate models with the ChemCam instrument since they are mostly low in concentration (< 0.1 wt. %) and LIBS signal intensity of these elements is low (Li, Rb, Sr and Ba, (Fabre et al., 2014; Ollila et al., 2014; Payré et al., 2017), Zn (Lasue et al., 2016), F (Forni et al., 2015; Meslin et al., 2016), B (Gasda et al., 2017), Mn (Lanza et al., 2014, 2016); H (Rapin et al., 2017; Thomas et al., 2016); and Cl (Anderson et al., 2017; Meslin et al., 2016)): their emission line can be neglected in favor of higher-intensity lines in multivariate models such as the partial least squares analysis models. In this study, as used in terrestrial LIBS studies, copper is also calibrated by a univariate model (e.g., (Rosenwasser et al., 2001)).

Among the 400 standards, 167 diverse samples--natural and synthetic sedimentary, igneous and Mn-ore powders--contain more than 50 ppm and up to 11,132 ppm of copper. The strongest and the least interfered copper emission lines detected by the testbed and the ChemCam suite are located at 324.789 nm and 327.428 nm (Goetz et al., 2017). Each spectrum is normalized to the total intensity of the UV range (240-342.2 nm). The Cu I emission line at 324.789 nm appears as a bump on the left shoulder of titanium lines (Ti II at 324.831 nm, Ti II at 324.876 nm and Ti I at 324.951 nm; Figure S1a), and may be observed at concentrations > 100 ppm. The Cu I emission line at 327.428 nm can be observed at lower concentrations (> 30 ppm) and is surrounded by Ti II at 327.21 nm, Ti I at 327.31 nm, an unknown line at 327.34 nm, and Na II at 327.519 nm (Figure S1b). This Cu line is yet largely interfered by the 327.34 nm emission line when present. Indeed, calculating the area under the Cu I at 327.428 nm with a Lorentzian function, the deconvolution of all the lines previously listed is not sufficient to reduce the intereference with the Cu I at 327.428 nm line. Indeed, the area under Cu I at 327.428 nm is largely over-estimated when the 327.34 nm emission line is present (Figure S1c-d): for instance, the Cu reference concentration of the standard 221138 is

25 ppm while the calculated area corresponds to that of a standard K919 with Cu = 130 ppm (2.04E-6 and 2.05E-6 respectively, Figure S1d). Therefore, to assess the abundance of copper, the area under the Cu I line at 324.789 nm is preferred and is calculated using a Lorentzian function as shown in Figure S1a. The Ti doublets are deconvolved to minimize interference with the Cu line as shown on Figure S1 a and c. To be conservative and to strengthen a calibration model based on a single line, the Cu peak is fitted only when an actual Cu I 327.428 nm bump or peak is observed (i.e., when the intensity of the pixel corresponding to the 327.428 nm line is 0.97 times higher than the intensity of the previous pixel, corresponding to the 327.382 nm line - this threshold being empirical and based on the ability to see a clear bump corresponding to the Cu I at 327.428 nm line as shown for Yulleroo #9 in Figure S2).

In the laboratory database, the two highest Cu concentrations are 1.1 wt. % in JMN1 standard and 1850 ppm in IGS29. Since all martian Cu data have peak areas lower than those in the 1850-ppm-standard, we prefer to remove these two standards. Only laboratory standards displaying a peak area four times higher than their standard deviation, i.e. < 0.25 times the mean, are considered for calibration. Elevated peak-area standard deviations are related to large spectral intensity variations that are mainly due to heterogeneity within the samples - most of them have been also removed from other trace element calibrations (e.g., G3MT with Cu = 253 ppm has been removed from Sr calibration (Payré et al., 2017)). In the end, twenty-one diverse standards with Cu concentrations ranging from 50 to 1230 ppm are used for copper calibration (Table 1). The calibration curve of copper is shown in Figure S3 a.

We assess the accuracy of the resulting model, i.e. the calibration error between the reference concentrations of the laboratory standards used for calibration and the calculated predictions, with the Root-Mean-Squared Error (RMSE, (Wiens et al., 2013)). It is the square root of the summed squares of the differences between the reference value and the estimated content

divided by the number of standards used in the model, and is equal to 41 ppm - a slipping RMSE over all the standards used for this calibration with a width of three points does not change up to 400 ppm. The limit of detection (LOD) of this model calculated with the method LOD3 of (Lasue et al., 2012) is ~ 50 ppm. The limit of quantification (LOQ) estimated by ~3.3 times the LOD is 165 ppm. As shown in Figures S3 b-c, notice that the area of the Cu I peak at 324.789 nm is not correlated with the sum of the peak areas of Ti II at 324.831 nm, Ti II at 324.876 nm and Ti I at 324.951 nm, and no correlation exists between Cu signals and reference concentrations of TiO_2: the titanium lines therefore do not interfere significantly with the area of the Cu I peak at 324.789 nm.

ChemCam Calibration Targets (CCCTs) are present onboard the Curiosity rover. Their compositions are given in (Fabre et al., 2011) and (Vaniman et al., 2012a, 2012b). Among them, a synthetic shergottite glass contains 43 ppm of copper. This CCCT is regularly analyzed by ChemCam. Although this amount of Cu is below the LOD of the model, we quantified it using the univariate regression for sanity check. The averaged Cu content is well predicted with 70 ppm and a standard deviation of 30 ppm. The prediction error is 25 ppm, i.e., well within the 41 ppm accuracy of our model, obtained by determining the RMSE, as described above.

In addition, APXS and ChemCam analyzed two common targets in the Kimberley formation: Liga on sol 601 and Stephen on sol 611. Since APXS' field of view is larger than ChemCam's with an analysis spot of 1.7 cm diameter, APXS observes a mineralogical assemblage or a bulk composition rather than pure minerals. ChemCam's laser beam size enables analysis of pure mineral grains when they are at scales of hundreds of microns or larger, or a mixture of grains and cement. For ChemCam targets, the whole rock composition can be approximately calculated for materials analyzed by at least 9 LIBS points: the bulk Cu concentration can

thus be calculated for Liga and Stephen targets that were analyzed by 9 and 30 points respectively. The Cu abundance of 580 ± 10 ppm measured by APXS for Liga compares favorably to that of ChemCam, with an average of 680 ppm (with a point-to-point standard deviation of 260 ppm), and 270 ppm vs an estimated ChemCam average of 280 ppm in Stephen (with a point-to-point standard deviation of 110 ppm) (Berger et al., 2017). Therefore, the estimations of copper contents from the Shergottite on-board calibration target (CCCT) and the APXS-ChemCam common targets are coherent.