DETECTION OF COPPER BY THE CHEMCAM INSTRUMENT ONBOARD THE CURIOSITY ROVER AND SEARCH FOR COPPER-HOSTING MINERALS IN GALE CRATER, MARS.

W. Goetz[1], V. Payre[2], R. C. Wiens[3], S. M. Clegg[3], O. Gasnault[4], R. Gellert[5], H. Newsom[6], C. Fabre[2], O. Forni[4], J. Lasue[4], P.-Y. Meslin[4], S. Maurice[4], J. Frydenvang[3,7], B. Clark[8], and the MSL Science Team, [1]Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany (goetz@mps.mpg.de), [2]Univ. of Lorraine, Nancy, France; [3]LANL, Los Alamos, USA; [4]IRAP, Univ. Toulouse, France; [5]Univ. Guelph, ON, N1G 2W1, Canada; [6]Univ. New Mexico, Albuquerque, USA; [7]NBI, Univ. Copenhagen, Denmark; [8]SSI, Boulder, CO, USA.

Introduction: The ChemCam/LIBS and the APXS instruments onboard the MSL Curiosity rover have detected copper (Cu) along her traverse across Gale crater, Mars. This abstract follows up on earlier work [1-4] and focuses on ChemCam data up to sol 1906 (Dec 21, 2017).

Data analysis: Cu has two strong UV emission lines (324.8 & 327.5 nm, here also referred to as left & right emission line, respectively) that partly interfere with lines from Ti and another (unidentified) element. Therefore Cu lines can be easily recognized in spectra of Ti-poor samples (Figure 1), but appear as broad Cu/Ti bands in the case of average or Ti-enriched Martian samples. The current fit model (Table 1) describes each one of the two bands as a superposition of 4 lorentzian emission lines (Figure 2) so that fitting of any given spectrum returns one Cu peak area & several Ti peak areas from each band. Figure 3a plots the sum of 3 Ti peak areas (left band, y-axis) against the sum of 2 Ti peak areas (right band, x-axis) for 14073 average ChemCam spectra observation points. The linear correlation of all data points (except data of highly Ti-enriched samples or data of pure Ti that is part of the ChemCam Calibration Targets onboard the rover) lends credibility to the fit model. Figure 3b relates these 14073 three-peak-areas to absolute TiO_2 abundances (wt%) that in turn are provided by a PLS (Partial Least Squares) & ICA (Independent Component Analysis)-based data processing pipeline [5] that is run on a daily basis and whose results (referred to as *MOC data* [Major-element Oxide Compositions] below) are published at NASA's PDS Node (http://pds-geosciences.wustl.edu/msl/msl-m-chemcam-libs-4_5-rdr-v1/mslccm_1xxx/data/moc/).

fit parameter	*initial value*		*fit constraints*
Height	0.5*(y-value – background) Background: A + Bx		must be > 0
center [nm]	**324.80 (Cu)** 324.85 (Ti) 324.91 (Ti) 324.95 (Ti)	327.20 (Ti) 327.30 (Ti) **327.43 (Cu)** 327.519 (?)	+/- 0.015
HWHM [nm]	0.05		must be within [0.04, 0.06]

Table 1 *Model for Cu/Ti fitting of ChemCam spectra.*

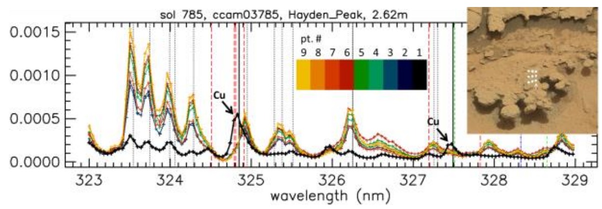

Figure 1 *ChemCam average spectra of 9 points on Hayden_Peak (sol 785). Point #1(arrow in the inset) is enriched in Cu, but poor in Ti, and therefore has a different spectrum. Vertical lines are NIST-tabulated spectral lines (Cu: thick black, Ti: dotted black, Fe: dashed red, Na: dashed green),* *https://physics.nist.gov/PhysRefData/ASD/lines_form.html*. *The spectra are shifted to the left due to calibration inaccuracy (~0.03 nm) near the spectral end of the detector.*

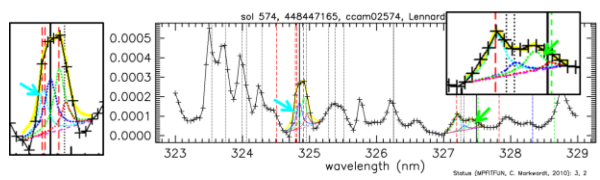

Figure 2 *Fit example according to model in Table 1. Cu lines are marked by teal (left band) and green arrow (right band). Vertical lines as in Figure 1. Fit codes use software by C. B. Markwardt, GSFC, USA (http://purl.com/net/mpfit).*

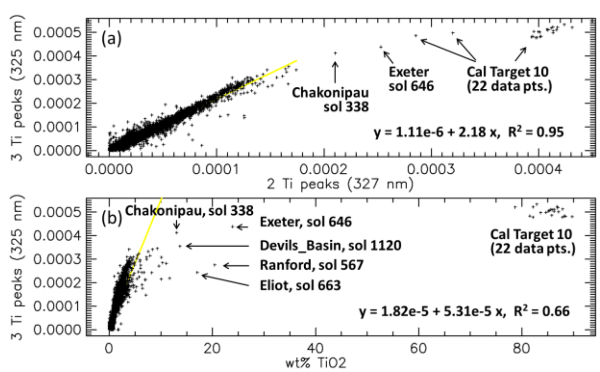

Figure 3 *Analysis of Ti-peak areas obtained from fitting of Cu/Ti bands (see Figure 2). The sum of 3 peak areas (left band) is plotted against the sum of 2 peak areas (right band, [a]) and against standard ChemCam MOC abundances [b].*

Results: The occurence of Cu along the rover traverse has been investigated in two ways: (a) by browsing through all ChemCam spectra and searching for Cuspecific spectral features (results shown in Figure 4a), and (b) by deconvolution of Cu/Ti bands and determining Cu peak areas (as described above, results shown in Figures 4b-c). The two codes work independently and complement each other. Figure 4a plots the distribution of 5846 Cu detections (in ~500000 single-shot spectra) over the entire rover traverse (especially in the Kimberley area, sols 580-630 [1-3]), except in the sol range 800-1150. Fitting of spectra requires continuous sanity and quality checks, because the fit procedure may fail (e.g. due to slow fit convergence) or may generate physically unreasonable results. 3670 (out of 14073 currently available) average spectra were found that meet these fit quality criteria (not specified here in detail) and bear credible signs of Cu. Left-Cu-peak areas (324.8 nm) of these data are plotted against sol number in Figure 4b. Finally, the left-peak areas of only 119 (out of 14073) averaged spectra are plotted in Figure 4c. The latter selection requires that Cu peaks (both the left *and* the right one!) are among the 5% strongest Cu peaks. This criterion should pick out interesting targets that deserve further detailed analysis. Figure 5 (plotting these exact 119 data points) demonstrates a fair linearity between both Cu-peak areas.

No definitive linear correlations have been observed so far between Cu peak areas and major element abundances (as taken from the *MOC data* set). In fact, such correlations *may well exist*, but the method of data analysis as applied here is too crude and inherently incapable to provide such information. However, careful selection of data (selection according to geologic context, lithology or major-element pattern) may be the key to further successful analysis. At the very least, the "anticorrelation" between Cu peak areas and CaO abundances (Figure 6) indicates that Ca-sulfate veins that are abundant in Gale crater do not coexist with elevated Cu-phases. This is consistent with the expectation that Cu is part of a reduced mineral(oid) phase.

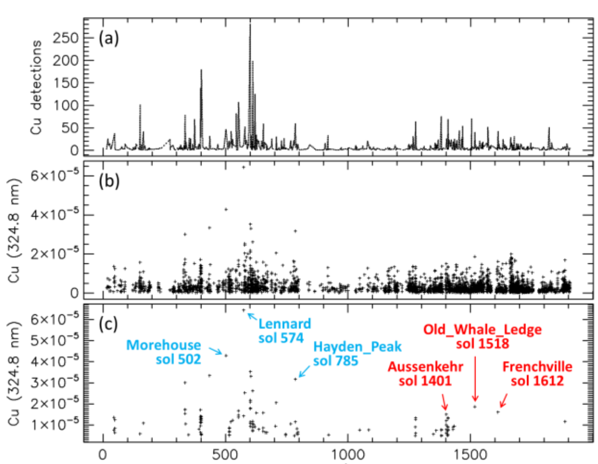

Figure 4 *Detection of Cu along the rover traverse. (a) Number of Cu detections. (b) Peak areas extracted from 3670 averaged spectra. (c) Same as (b), but making an even stronger selection (119 top-5% strongest Cu peak areas). A peak area of 6·10^{-5} may correspond to ~1000 ppm [3].*

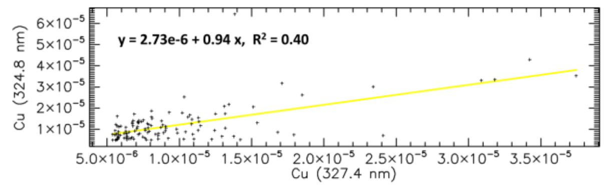

Figure 5 *Correlation between left and right Cu line for 119 ChemCam targets with strongest Cu signal (see Figure 4c). The slope is close to one in agreement with NIST's assertion that both Cu lines do have same "relative intensity".*

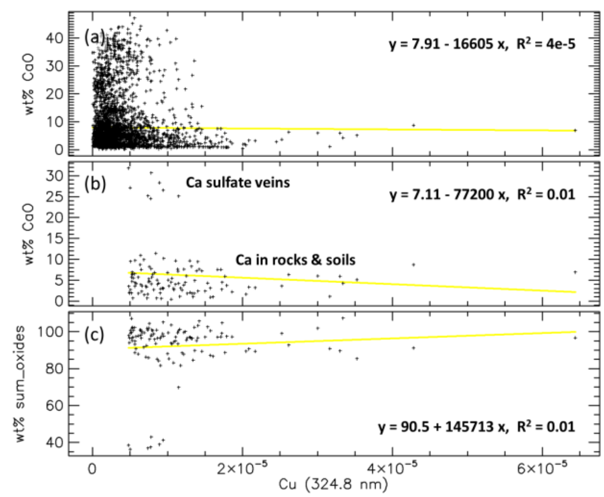

Figure 6 *(a) CaO abundance (wt%) plotted against left-Cu peak area (324.8 nm) for 3670 averaged ChemCam spectra (same selection as in Figure 4b). (b) Same as (a), but only plotting 119 data points (strongest Cu targets as in Figures 4c and 5). (c) Same as (b), but plotting the sum of (refractory) oxides on the y-axis. The rocks & soils from (b) now plot in the region near 100 %, while the veins host a "missing component" (SO_3, H_2O and maybe other volatiles).*

Conclusions: Cu has been detected by ChemCam all along the rover traverse across Gale crater, with local Cu enrichments by a factor of 10 (or larger). No correlation between Cu and major elements has been found as based on the standard *MOC data* set. Cu-enriched targets do not appear to be hosted by sulfate veins or materials rich in volatile components. Models for quantification of Cu (ppmw) are being developed.

References: [1] Payré V. et al. (2016) *LPS XLVII*, #1347. [2] Goetz W. et al. (2016) *LPS XLVII*, #2942. [3] Payré V. et al. (2017) *LPS XLVIII*, #2097. [4] Goetz W. et al. (2017) *LPS XLVIII*, #2894. [5] Clegg S. M. et al. (2017) *Spectrochim. Acta B*, *129*, 64-85.