DETECTION OF COPPER BY THE CHEMCAM INSTRUMENT ALONG THE TRAVERSE OF THE
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Introduction: The ChemCam/LIBS instrument (Laser Induced Breakdown Spectroscopy) onboard the Curiosity rover has been measuring the chemical composition of surface materials along the rover traverse. Here we provide an overview on the detection of copper by ChemCam all along the traverse. A separate work \cite{6} focuses specifically on the Kimberley region.

Copper manifests itself in ChemCam spectra by a number of lines with two being most dominant (324.84 & 327.43 nm, Fig.1), both of which are contaminated by overlapping lines from other elements (Ti, likely Fe and Na). Concerning the left Cu peak (Fig.1): The top curve (blind target BT, sol 604) shows a Cu peak broadened by the adjacent Ti line. The target Hayden_Peak (sol 785, right below) contains only little Ti, so the Cu peak is less perturbed by Ti and thus narrower. Finally, the target Ibx_Pass_785 (sol 785) is similar to the blind target, but with lower abundances in both Cu and Ti. The right Cu peak is also perturbed by neighboring lines, but less severely than the left one. Many ChemCam spectra show clearly that the left Cu line is more sensitive to the presence of copper than the right one (this is already suggested by Fig.1 and is further elaborated below). The spectra in Fig.1 have been used as training sets to infer the ‘true’ line positions & widths as generated by the ChemCam instrument on Mars and to develop a fit model (see next section).

![Fig. 1 Three ChemCam spectra (offset to emphasize line-shapes) showing the spectral region of the two dominant Cu lines as contaminated by other elements. Note how line-shapes change in presence of contaminating neighboring lines (especially Ti). Throughout the text the two peaks are referred to as ‘left’ and ‘right Cu peak’.](image1)

**Fit model for Cu:** In the first place the corrected & calibrated ChemCam spectra (of CCS type) are normalized such that their area equals one (unity) in the spectral range 242-335 nm (covered by one of ChemCam’s three detectors) \cite{1,2}. This provides a 1\textsuperscript{st} order correction for variable ChemCam-to-target distances (1.6 to 7 m). A detailed model for distance correction has been provided by \cite{3}. Next, each ‘contaminated Cu peak’ (the left and the right one, see above) has been fitted as a system of three overlapping lines of lorentzian shape. Actually four (or even more) spectral peaks overlap to form these ‘broadened Cu peaks’, but the Ti doublets (both on the left & the right side of the spectrum, see Fig. 1) cannot be resolved, so it is tempting to explore the easiest possible approach that consists in deconvolution of three partially overlapping lorentzian lines that ‘are sitting’ on top of a linear background of type A + Bx that is locked to the two end points of each spectral fit window (left: 324.63-325.18 nm; right: 326.94-327.70 nm). Each lorentzian function contains three independent parameters (referred to as ‘height’, ‘center’ (or central wavelength), and HWHM, Half Width at Half Maximum). So in total, 9 parameters are determined for deconvolution of the left side (and similarly for the right side, Fig.1) by applying a Levenberg–Marquardt algorithm as implemented by C. Markwardt, NASA-GSFC, Greenbelt \cite{4}. Fig. 2 shows fitting of Hayden_Peak (see Fig.1) as an example. Finally peak areas are determined by integration over either one of the spectral fit windows (see above).

![Fig.2 Fitting of Hayden_Peak (point #1, sol 785). The inset magnifies the fit results on the right side of the spectrum. Single (deconvolved) lorentzians are drawn by, respectively, blue, green, and red lines. Their sum is shown by a thick yellow line.](image2)

As well-known, fit results are highly sensitive to both initial conditions and parameter constraints that are specified in Table 1. All 9 parameters are assumed to be independent. In particular the Ti doublets are fitted as one broad lorentzian line (see above) without knowledge of the target’s abundance in titanium. This leads the way to future improvement of the fit model.

**Results of Cu fitting along Curiosity’s traverse:** In general a ChemCam target consists of several ChemCam points and (in most cases) 30 laser shots are...
fired at a given point. Fitting as presented in this abstract has been performed on 13700 ChemCam spectra (sols 0-1555), all of them referring to a given ChemCam point (averaged over 30 laser shots). Based on status parameters (generated by the fitting program) and manual random checks the fitting was successful in 9401 and 8302 (left and right side, separately) and in 6000 (both sides at the same time) out of 13700 cases. Such (low) score is expected, since the initial parameter settings (Table 1) did already dictate a specific behavior of ChemCam spectra within the respective fit window. Hence, the score can be easily improved by discarding spectra (e.g. Cal target or out-of-focus spectra) that are not appropriate for this kind of data processing. Finally, the fitting may be successful from the fit engine’s point of view, but may not make sense from a geochemical point of view, e.g. because the two deconvolved Cu peak areas (for a given ChemCam target & ChemCam point) are inconsistent to each other or because the inferred areas of the Ti doublets are inconsistent with the actual abundance in Ti. As mentioned above, all ChemCam spectra with a strong Cu signal confirm the higher sensitivity of the left Cu line as compared to the right one (Figs. 1-2). Therefore in order to further refine the process of data selection we also impose that the peak area of the left Cu line (deconvolved, post processing) is higher than the right one. This condition is anyway fulfilled for the highly enriched targets, but helps to discard the great many targets that have a Cu abundance below ChemCam’s Limit of Detection (LOD). In those latter cases fitting of the data is anyway of no scientific interest. This should not prevent us from refining the fit model in order to detect smaller and smaller Cu abundances.

Table 1: Details of fit model. Note, the constraint on the HWHM has been chosen such that it can easily accommodate the Ti doublets.

<table>
<thead>
<tr>
<th>fit parameter</th>
<th>initial condition</th>
<th>constraints during fit iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td>height</td>
<td>y-value – background (A + Bx)</td>
<td>must be &gt; 0</td>
</tr>
<tr>
<td>center</td>
<td>see Fig. 1: Ti doublets represented by average wavelength</td>
<td>+/- 0.15 nm off initial value for all lines, but +/- 0.50 nm for Ti doublet on the right side (Fig. 1)</td>
</tr>
<tr>
<td>HWHM</td>
<td>0.05 nm</td>
<td>must be within [0.0, 0.1 nm]</td>
</tr>
</tbody>
</table>

then we are left with 1871 fits that should represent the most reliable subset of all fit results generated. Those data points are plotted in Figs. 3-4.

**Fig. 3** Relative abundance of Cu along Curiosity’s traverse. High Cu is not restricted to the Kimberley area (yellow frame). The red points denote targets that had been identified by browsing the data set manually and visually.

**Fig. 4** Areas of both Cu peaks plotted against each other. Same data set as in Fig. 3 (1871 data points). Also the red points are the same as in Fig. 3. The data points cluster around a (yellow) straight line of slope ~1.6.

Despite considerable efforts it was not possible to extract a plot from the entire ChemCam data set that would show a strong enrichment of Cu in the Kimberley area. For sure, targets with high abundance in Cu are found in the Kimberley area [5, 6], but high-Cu targets do not seem to be restricted to that area. The distribution over the entire mission appears patchy (Fig. 3). Fig. 4 focuses on the correlation between both Cu peak areas. The left-to-right peak area ratio (Figs. 1-2) was just required to be larger than one (selection criterion), but Fig. 4 demonstrates that this ratio is ~1.6. Hence the left Cu peak is about twice as sensitive as the right one. The left peak areas (plotted on the ordinate in Fig. 4) reach ~5 x 10⁻⁵ that correspond to 1500 ppm Cu according to [6].

**Conclusions:** Coordinated analysis of two Cu peaks (324.84 & 327.43 nm) in ChemCam spectra suggests a patchy occurrence of Cu along Curiosity’s traverse, with some enrichment in the Kimberley area.

**References:**