DETECTION OF COPPER IN GALE CRATER, MARS, BY THE CHEMCAM INSTRUMENT ONBOARD THE CURIOSITY ROVER.

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Introduction: The ChemCam instrument has been imaging all types of surface units by its own camera (RMI, Remote Micro-Imager) and measuring their chemical composition along Curiosity's traverse (>20 km) across Gale crater, Mars, utilizing Laser Induced Breakdown Spectroscopy (LIBS). This abstract is an update to previous work on detection, spatial distribution and abundance of copper [1-4]. Here we are using wavelength-calibrated in-focus LIBS spectra of 17276 ChemCam points acquired up to sol 2254 (Dec 10, 2018). Each ChemCam point has been hit by (typically) 30 laser pulses and is thus returning 30 chemical compositions from that point. As a result we can use ~518000 (17276 x 30) chemical compositions throughout the mission (below labeled as 'SHOT-RESOLVED'). For each ChemCam point, average chemical compositions can be calculated (labeled as 'SHOT-AVERAGED').

Data Analysis: Copper is detected by two UV emission lines at, respectively, 324.80 and 327.43 nm (also referred to as 'left' and 'right line') that – according to NIST [5]- have similar relative intensity. Both copper lines overlap with emission lines from other elements (specifically titanium) and thus appear as broad Cu-Ti bands in ChemCam spectra. Each band is modelled as a superposition of 4 emission lines of Lorentzian shape (left: 1x Cu, 3 x Ti, right: 1x Cu, 2x Ti, 1x unknown element) as detailed in [4]. Data analysis as presented in this abstract is primarily univariate, although multivariate techniques have been (and will be) applied as well, specifically in search of correlation of copper with other elements. Figure 1 shows two fit examples: Ben_Arkle (sol 2143) and Noss (sol 2242). Fig. 2 plots the number of Cu-detections versus sol number, where a "Cu detection" may be achieved when either the left Cu line exists (blue) or both Cu lines exist (ocher). The sum of Cu detections under various conditions is specified in Fig. 2. Clearly, reliable detection of Cu requires that *both conditions are fulfilled*, i.e. existence of 'left Cu-line' AND existence of 'right Cu-line'. This is required for any work on Cu [1] and will also apply to the remainder of this abstract. Fig. 3 plots the area of the left Cu-line as a function of sol-number. The variation seen is partly (but not entirely) due to operational effects (technical problems, solar conjunction, holiday breaks etc.).

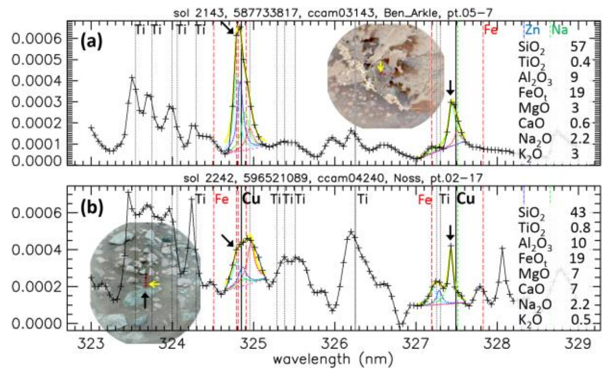

Fig. 1 Fit examples of recent targets (a) Ben_Arkle/pt.5-shot7 and (b) Noss/pt.2-shot17, felsic, high-alkali bedrock and mafic soil, respectively (point-average compositions given in wt.%). NIST-vacuum lines marked in different colors with Cu-lines emphasized by black solid lines. The black arrows mark the Cu lines in calibrated ChemCam spectra (indicating a small systematic detuning in calibration). The right Cu line in the Noss spectrum is only documented by a single observation point, but the strong Cu-specific kink of the left band lends confidence to the Cu detection. Note specifically that all Ti-lines (including those fitted) are much weaker in Ben_Arkle which contains only half the Ti contained in Noss. Insets show RMI images (colorized by co-registration with Mastcam images) with yellow arrows pointing to the location where the spectra shown were recorded. RMI insets are ~101 mm (a) and ~86 mm (b) wide.

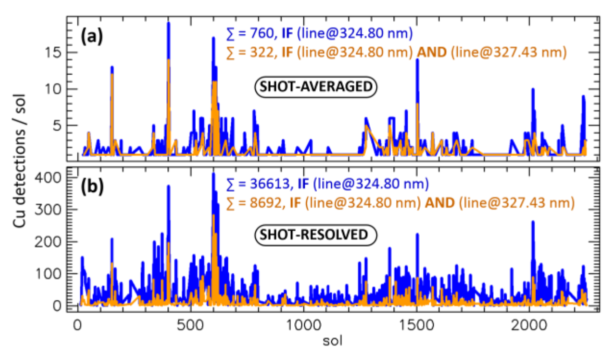

Fig. 2 Number of Cu detections (a) out of 17276 average spectra and (b) out of ~518,000 single-shot spectra [see Introduction]. Interestingly, both types of analyses, (a) for SHOT-AVERAGED & (b) for SHOT-RESOLVED analysis, lead to ~2% reliable Cu detections. Note elevated Cu around sols 150, 400, 600, 1505, 2020, and 2230 (Table 1).

sol	geologic area, waypoint	Cu-rich ChemCam targets (ChemCam ID)
~150	Yellowknife Bay	Laddie (01151), Redstone (03151), Little_Dal (04151)
~400	Darwin	Camp_Ridge_ccam (01398), Pebble (02399), Dragons_Teeth (01401), Heimdall (02401), Shackleton (04401), Ritchie_ccam (05401)
~600	Kimberley (sol 576-632)	Liga (01601), Harms (02601), Nullara (03601), Stephen (01611, 06611), Stephen_DP (03619), Neil (04619)
~1505	Murray Buttes/Ogunquit Beach	The_Tarn (02502), Cedar_Swamp (01504), Cadillac_Mountain (02504)
~2020	Lower Vera Rubin Ridge (VRR)	Kinloch_ccam (02013), Staffa_ccam (01015), Arrochar_ccam (02022)
~2230	Higher VRR	Housay (03219), Cullen (03226), Echt (03233, Fe meteorite), Little_Todday_2 (04236, Fe meteorite)

Table 1 Non-comprehensive list of "Cu Highlights" over the entire mission. Compare to Fig. 2.

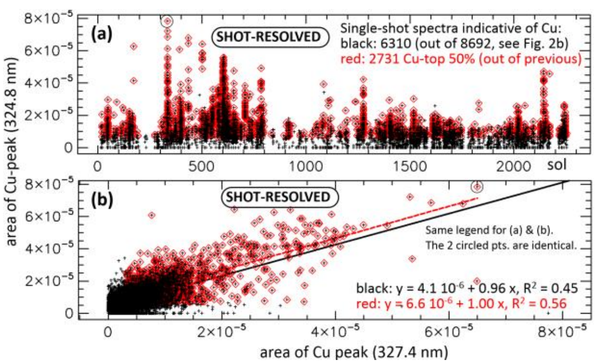

Fig.3 (a) Area of left Cu-peak versus sol number. Out of 8692 spectra with detection of Cu (Fig. 2b) 6310 spectra were chosen (down-selection according to fit quality parameters) (b) Area of left Cu-peak versus right Cu peak. The slope approaches 1.0 (in agreement with NIST [5]). This is taken as a confirmation that the complex fitting (4 Lorentzians in both Cu-Ti bands, Fig.1) is successful. A peak area (324.8 nm) of 6 10^{-5} may correspond to ~1000 ppm Cu [4].

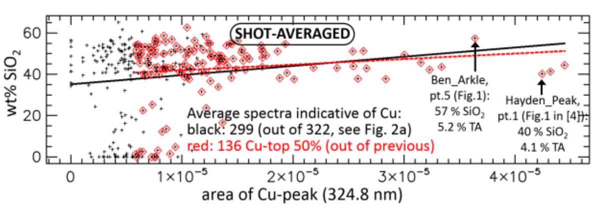

Fig. 4 Silica content versus area of left Cu peak. 299 (out of 322, Fig. 2a) spectra were chosen (down-selection according to fit quality). No dependence of Cu on silica content (the linear fits only guide the eyes, no physical significance). Two targets with, respectively, intermediate and mafic composition are highlighted (TA = Total Alkali).

Conclusions: A reliable Cu detection software is in place. Cu being a trace element (< 1000 ppm) it is of great importance to work on single-shot spectra (in addition to shot-averaged spectra). Over the course of the mission about 2% of all ChemCam spectra reveal presence of Cu. The Kimberley area (sol 576-632) is particularly rich in Cu [1], but there are other Cu-rich areas as well, namely Yellowknife Bay, Darwin, and perhaps Murray Buttes (Table 1). Not much Cu has been found in the Pahrump area (sol 760-920), which could be caused by ChemCam's reduced operational capabilities in the timeframe sol 805-980. Cu is found in all types of rocks, including igneous float rocks (e.g. Jake (01045)), sandstone bedrock (Kimberley), mudstone bedrock (Yellowknife Bay, Murray Buttes through Vera Rubin Ridge) and even –in rare cases- calcium sulfate veins (e.g. Windigo (03053), sol 2053, pt.05-26, SCLK 579743758 which figures in the group of top-5% Cu of all single-shot spectra acquired over the mission). Specifically, Cu is found in many rocks of basaltic composition (not surprisingly given their high abundance on Mars), but also in (less often encountered) rocks of mafic and felsic composition. The fact that elevated Cu is found (see Fig.4) in selected mafic rocks (e.g. Hayden_Peak, pt.01) as well as intermediate rocks (e.g. Ben_Arkle, pt.05) is taken as an indication that the overall distribution of Cu on the Martian surface is not much dependent on silica (or total-alkali) content of the rock. It cannot be ruled out that most Cu at the Martian surface is (like on Earth, see [1] & references therein) found in typical minerals of igneous rocks, - such as pyroxenes, feldspars and perhaps titanomagnetite (see e.g. ChemCam target Hayden_Peak (Fig. 1 in [4]) that contains >30% FeO_t at ChemCam pt.01). That still requires an explanation for the particularly high abundance of Cu in the Kimberley area ([1], see also Figs.2-3 in the present abstract). Some Cu enrichment may also occur in iron meteorites (see Table 1), although this requires a dedicated study that is beyond the scope of this work. Cu has been found in clay-rich areas (such as Yellowknife Bay and on more recent sols in the Murray bedrock [including VRR]). There is therefore good reason to watch out for Cu in the upcoming clay unit on the lower flank of Mt. Sharp.

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