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Introduction: In Gale crater, elevated amounts of copper have been analyzed in the Kimberley formation by two instruments, ChemCam and APXS. ChemCam combines a Laser Induced Breakdown Spectroscopy (LIBS) that acquires the light emission of rocks and soils located at 1.5-7m away from the rover, and a Remote Micro-Imager (RMI) providing a geological context [1,2]. LIBS is sensitive to major elements [3], and many trace elements [4]. Each ChemCam target is analyzed over 5-20 points with 30-150 shots in each observation points. This allows us to observe compositional variations with depth as LIBS ablates material. Elevated Cu signals in LIBS spectra encouraged us to quantify precisely their amounts. Here we present a copper LIBS calibration. The resulting abundances provide a geological context to understand possible origins of these striking Cu enrichments at Kimberley where potassic sandstones were encountered [5].

Preliminary copper calibration: The strongest Cu LIBS emission lines are at 324.8 nm and 327.428 nm. The first peak is located on the left side of a Ti I doublet 324.876 & 324.951 nm bump, and the latter line is next to Ti II/1 327.21 & 327.31 nm. For calibration, a laboratory database developed at LANL has been used [3]. More than 400 geological standards have been analyzed using a ChemCam copy in Martian conditions (P_{CO2}=7 mbars). 5 LIBS analyses/sample with 50 shots in each have been performed. The resulting spectra are processed following the ChemCam data pipeline and are corrected by an Earth-to-Mars correction. Cu is contained from 100 to 1230 ppm in 20 samples. Cu 327.428 nm has a lower detection limit (LOD) than Cu 324.8 nm but is contaminated by Na II 327.509 nm. As a result, the Cul 324.8 nm peak is fitted with a Lorentz function by deconvolution of Cu and Ti doublet.

To be conservative, copper line is fitted only when a clear Cu I 327.428 nm peak is observed. This implies quantification of elevated Cu amounts (~ > 100 ppm). Figure 1 shows a preliminary Cu calibration curve. The accuracy calculated with the Root Mean Square Error is 60 ppm and the LOD is 50 ppm [2]. The resulting equation is applied to ChemCam data.

Cu-rich materials at Kimberley: Figure 2a illustrates the localization of the highest Cu values within the Kimberley stratigraphy. The first rock encountered is a porphyritic K-rich trachy-andesite, Angelo, located at Point Coulomb (sol 553; Fig. 2b). From 100 to 880 ppm of Cu were observed within the dark matrix and in the elongated white crystals identified as andesine An70 by [6] (points 4-5, 8; Fig. 2b). Most Cu-rich targets are found as local grains within variable grain-size sedimentary materials located in every member of the Kimberley region [7]. These localized enrichments suggest the occurrence of Cu-rich grains disseminated within the material, and they could be detrital. Finally, three Mn-rich fracture fills located at Dillinger, Stephen, Neil, and Mondooma, contain elevated copper content (Cu=150-450 ppm) [8]. We can note that the latter two also contain high Zn concentrations [9].

![Figure 1. Calibration curve of Cu I 324.8 nm line. Each data point is the average ± relative standard deviation.](image)

![Figure 2. (a) Stratigraphic column of Kimberley area and Cu-rich points. (b) RMI image of Angelo target.](image)
Copper association in rocks: Elevated copper concentrations are found in various materials. Depth profiles of points with high Cu contents provide two main associations. The first can be illustrated by a K-Mg-rich bedrock Nullara points 1-2/4-6 in the Liga member for example. These points display between 250 and 320 ppm of Cu. Depth profiles of Cu show strong positive correlations with Ti, Si, Al, Na and K signals and negative correlation with Mg (Fig. 3). This supports Cu association with alkali aluminosilicates containing Ti. CheMin analyzed Windjana sample localized at Dillinger, where feldspars, pyroxenes, clays and Ti-Fe-oxides were found [10]. [10] suggested that these minerals may be also encountered in other Kimberley regions. As a result, we propose that Cu could be associated with feldspars containing Ti. The occurrence of Ti within these phases can occur at intermediate magmatic stages: Ti4+ can replace Si4+ and/or Al3+ within minerals if the temperature is sufficiently high to permit the resulting crystallographic configuration [11]. Another possibility is the occurrence of micas like phlogopite or biotite that contain titanium. Their presence is inferred by the large number and relatively high abundances of fluorine at Kimberley, where F is most often correlated with Al [12]. In addition, the Na and K contents of the K-sediment source might be consistent with a phlogopite component mantle [13].

Another kind of association can be illustrated by the Na-rich point of a bedrock (Wallal #3) located at Dillinger. We can note that this point presents a high Cl signal. This suggests the occurrence of NaCl. Depth profile analysis presents a positive correlation between Cu and Ti signals. Cu may be thus related to a Ti-phase like ilmenite within a NaCl-bearing material.

We note a particular point encountered at Square Top, Eastman #16 with 490 ppm of Cu. High FeO (>30wt. %) and K2O contents (> 1.1 wt. %) have been analyzed, and strong peaks are detected. This supports the occurrence of Fe-sulfates or Fe-sulfides. No correlation with Cu in depth is observed but Fe and S signals are still strong. It seems reasonable to suggest that copper may be associated with this iron-sulfur phase.

In conclusion, copper is mostly associated with Ti and aluminosilicates like feldspars. At Kimberley, these minerals would be detrital and magmatic phases [10]. The detrital Cu-grains may have the same origin.

Copper association in a trachyandesite: High copper concentrations are noticed within plagioclases, suggesting that Cu is probably associated with these minerals. It is likely copper has been included within these phases during a magmatic stage. As a result, since this trachyandesite has a porphyritic texture, copper might come from a porphyric deposit. On Earth, they are formed by a groundmass crystallization, if hydrothermal fluids gathered metals within sulfide minerals grains and disseminated grain in the magma [14]. A zoning pattern is typically found around the magma, including a potassic alteration zone forming K-bearing minerals like feldspars as observed in the Kimberley sandstones. In addition, APXS measured elevated amounts of Zn (up to 2000 ppm), Cu and Ge (up to 2000 ppm) at Kimberley, and [15] interpreted this by hydrothermal activity in the region source of potassic minerals [16]. This tends to be confirmed by a high H signal in a plagioclase in Angelo point 8. Hence, this kind of deposit could have been eroded, and alkaline igneous rocks and/or copper-rich grains within rocks, as well as K-phases could have been transported by a stream and deposited at Kimberley.

Copper association in fracture fills: Stephen, Neil and Mondooma contain elevated amounts of manganese that decrease with depth [8]. Copper is strongly correlated with Mn as seen by ChemCam and APXS [8]. The Mn phase is interpreted as manganese oxide. Therefore, copper would have been adsorbed on their surface as a Cu2+ cation circulating in an oxidizing and acidic stream (pH~5–6). Zn is also positively correlated with Cu and Mn in Mondooma and Neil, and an adsorption process can also be suggested. Interestingly, a compositional stratification is observed: below the Mn-Cu(Zn) layer, Si, Al, Ca, Fe and Mg contents increase with depth in proportions that suggest a pigeonite-rich bedrock.

Possible scenario: High Cu contents have been generally observed as localized points in bedrocks, and are mostly related to Ti and aluminosilicates phases. In fracture fills, they are ubiquitous and Cu is clearly adsorbed on MnO2. Hence, we suggest that these enrichments may be related to two distinct events. First, Cu-rich detrital grains, from the same source as detrital feldspars and micas, would have cemented at Kimberley. Then, fracturing of the bedrock would permit an oxidizing Mn-fluid to circulate and precipitate MnO2 along with minor amounts of Cu and Zn.