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Detection of Zn with ChemCam on Mars

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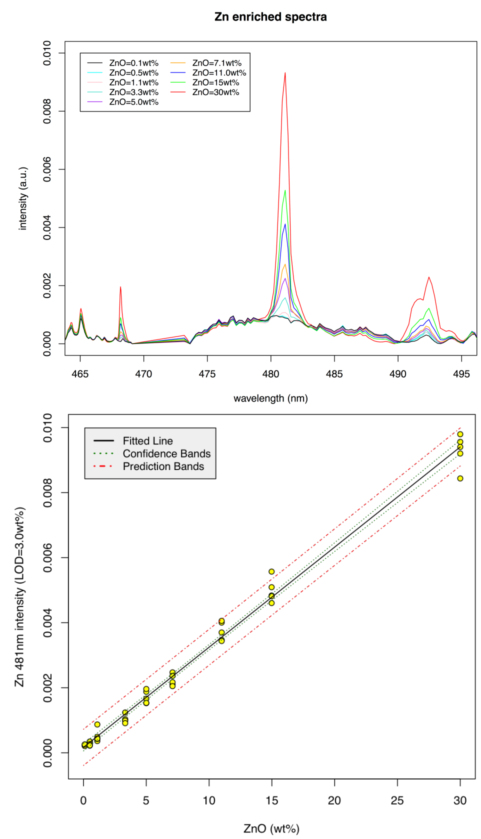
Abstract

ChemCam is a Laser-Induced Breakdown Spectroscopy (LIBS) instrument on-board the NASA Curiosity rover currently exploring Mars. ChemCam can analyze the chemical composition of geological samples without preparation and at a distance by detecting the laser induced atomic emission lines from elements present [1, 2]. ChemCam is sensitive to most chemical elements. In addition to the major elements, ChemCam can be used to detect and quantify a set of minor and trace elements such as Li, Sr, Ba, and Rb using univariate and multivariate regression techniques [3]. Mn has also been detected and quantified with ChemCam at high concentrations indicating that highly oxidizing conditions must have occurred on the surface of Mars [4]. We report here the detection of high Zn content targets with ChemCam at the Kimberley location at Gale Crater that are linked to high-Mn concentrations.

1. Zn detection and quantification

ChemCam was not initially designed to detect Zn which has a relatively high ionization energy of 9.39eV [5], higher than typical elements detected by LIBS, meaning that we expect to detect it only at the wt.% level [6]. The clear detection of Zn lines for Yarrada (sol 628) indicating strong enrichment of this element at the Kimberley outcrop triggered the need to develop a specific database to detect and quantify Zn enrichments on Mars.

The database for Zn quantification was developed at LANL by producing pressed pellets from ZnO powder intimately mixed with powdered Brammer geological standard basalt BHVO-2. Using this procedure we generated calibrated standards with 10 ZnO fractions ranging from of 0.1 wt.% to 100 wt.% in a matrix that is close to the average martian basaltic composition. After pre-processing of the spectra and normalization [7], comparison of the spectra is used to define the best Zn lines for Zn detection and quantification. Some Zn emission lines are weak, while others interfere with the emission lines of major elements and cannot be used for calibration.



Figures 1 and 2: ChemCam Zn emission line at 481.2nm shown for different ZnO contents, and the resulting linear regression model.

The best Zn emission lines for quantification purposes with ChemCam are located around 330nm, 480nm and 760nm. Figure 1 shows the effect of increasing Zn content on the emission lines located around 480nm. A Lorentzian fit of the emission lines is used to calculate their area, and generate a univariate regression model for Zn. Such a procedure has been used to generate univariate models for quantification of other elements [8]. Figure 2 presents the regression model for the Zn emission line at 481.2 nm with 95% confidence bands for the linear fit in green and 95% prediction bands in red, giving a limit of quantification (LOQ) of 3 wt.%.

The Zn emission lines of the standard containing pure ZnO behave non-linearly and were not used to generate the model, as no pure ZnO has been found on Mars. The LOQ gives the limit of quantification with ChemCam at the 95% confidence level. The limit of detection of the Zn line at 481.2 nm is lower than this limit as can be seen on Figure 1. If defined as the level at which an emission line can be detected above 3 sigma of the background noise level of the spectrum, then it is about 0.5 wt.%. The model can also be improved by using multiple line detection and multivariate regression instead of relying on a single emission line [3].

2. Zn-rich targets

We have applied the Zn detection and quantification model on all data taken by ChemCam until sol 800. First, the Zn lines intensities 3 sigma above the background noise level of the spectrum are detected. Then the univariate regression model for the emission line at 481.2 nm is applied to quantify the Zn content. The highest predicted content is obtained for target Yarrada (location 5 sol 628) with ZnO=7.0 wt.%. When considering the number of detections and the predicted ZnO content of the targets as a function of time, there is a clear enhancement in Zn content around the Kimberley outcrop (analyses done from sol 580 to sol 630).

Yarrada #5 clearly stands out as the ChemCam target with the highest content in ZnO. From the RMI context image (Figure 3), Yarrada #5 is located above the rock strata, on the flat overlying surface. Shot-to-shot analysis of the ChemCam data indicates that the first two shots are contaminated by overlaying dust cover. Below the dust, the rock is slightly hydrated, and Zn content is about constant over all the remaining 28 shots taken at that location.

3. Discussion of the results

The fact that Zn does not vary with depth suggests it is not linked to a thin weathering coating of the rock. There is no clear detection of S, indicating that Zn is unlikely to be present in the form of Zn-sulfide, sphalerite, which is its most common form on Earth. The APXS measurements at Kimberley also indicate strong enrichment in Zn on Windjana drill fines (3430-4680 ppm Zn) and Stephen (~8150 ppm Zn) on which MnO-rich coating has been detected [9].

The enrichment of Zn in Yarrada seems also linked with an increase in Mn and Na content. Overall, Kimberley is an outcrop that presents strong enrichments in alkali and especially Mn content. The strong Mn signatures detected are interpreted as oxide coatings, suggesting the presence of Mn-oxides possibly formed at a time when Mars surficial conditions involved abundant water and were more strongly oxidizing than today [10]. The Zn enrichment in Kimberley is probably also in the form of oxides and would support the conclusions derived from the presence of Mn-oxide veins in the outcrop.

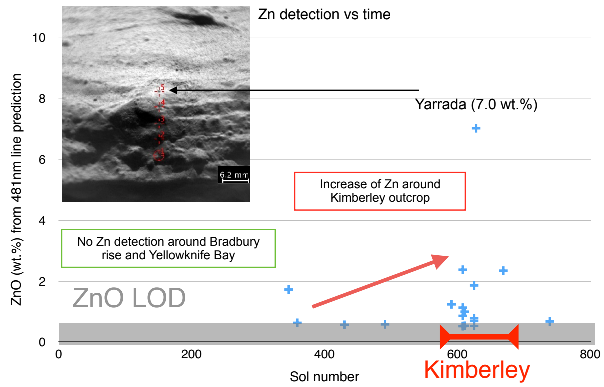


Figure 3: ChemCam Zn detection as a function of time during the first 800 sols on Mars.

6. Summary and Conclusions

High Zn content targets have been detected on Mars using the ChemCam instrument at the Kimberley outcrop. These targets are linked to a location where high Mn content was also detected. These enrichments can be interpreted as oxides deposited during previously highly oxidizing conditions on the surface of Mars. Improvements of the technique and application to the detection of Zn-enrichments in the Pahrump stratigraphy at the base of Mount Sharp will be presented.

Acknowledgements

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