

CARBON DETECTION WITH CHEMCAM: LABORATORY STUDIES AND MARS RESULTS. P. Beck^{1,3}, O. Forni², J. Lasue², E. Lewin³, A. Cousin², S. Maurice², P.-Y. Meslin², W. Rapin², O. Gasnault², R.C. Wiens⁴, N. Mangold⁵, V. Sautter⁶, P. Coll⁷, C. Szopa⁷, T. Dequaire⁷, J.G. Blank⁸ and the MSL Science Team. ¹Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France beckp@obs.ujf-grenoble.fr. ²IRAP, 31400 Toulouse, France. ³Univ. Grenoble Alpes, IsTerre, F-38000 Grenoble, France. ⁴Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA. ⁵LPG, BP 92208, 44322 Nantes, France. ⁶IMPMC, Muséum d'Histoire Naturelle, 75005 Paris, France. ⁷LISA, Univ. Paris Diderot, France. ⁸NASA Ames Research Center/Blue Marble Space Institute of Science, Moffett Field CA 94035 USA

Introduction: While being generally rare on the Martian surface, carbonates have been detected in a variety of geological contexts. These include surface dust [1], soils [2-3] and crustal outcrops [4-6]. They have also been identified as alteration products of the Lafayette and ALH 84001 SNC meteorites [7-8].

The presence of significant amounts of carbon in Martian soils can be suspected based on calculation of exogenous influx [9]. In this case, the carbon would be present as macromolecular or polycyclic aromatic hydrocarbon, similar to chondritic insoluble organic matter (IOM).

On the basis of SAM measurements onboard MSL, carbonates have been identified at the 1 wt % level in soil and sediments from Gale crater [10-11] and potential organic carbon signatures have been reported [10]. These observations have motivated the present study to assess the detectability of carbon with MSL/ChemCam [12-13]. These follow earlier studies by Ollila et al. [14-15] to understand C detection limits and to probe the ChemCam Mars data for carbon (regardless of form). A method is presented here, based on a laboratory approach developed with IRAP's ChemCam twin instrument. In addition, potential carbon detection on the Martian surface with ChemCam are presented and discussed.

Methods: A suite of samples was prepared at IPAG and analyzed subsequently at IRAP. Samples were prepared either as pressed pellets or as raw samples embedded in epoxy. The sample suite includes carbon-free samples (basalt, obsidian, sulfates, JSC-1, monazite, serpentine, peridotite) as well as natural alpine carbonates (dolomite and calcite) and natural coals. The latter were acquired through the Penn State Coal sample bank (PSOC 1532, PSOC 1521, and DESC 09) and span a range of maturity (O/C at. ratio from 0.024 to 0.25). Extra-terrestrial organic carbon was also studied by analyzing the ALH 83100 CM chondrite that contains 1.9 wt. % carbon [16]. In three cases (calcite, CM chondrite and PSOC 1521) samples were diluted within a Reunion island basalt to test matrix effects (1-5-10-25 wt%) and assess detection limit. The mixtures were ground (<50 μm) with an automatic grinder to ensure efficient mixing.

Data analysis: A major challenge of carbon detection on the martian surface with ChemCam is the pres-

ence of a CO₂-rich atmosphere that contributes to the emitting plasma signal. In order to overcome this issue a diagram showing the joint evolution of a carbon line against an oxygen line is used (Fig. 1). The two lines selected are the 723.7 carbon line and the 777.6 oxygen line. Lines were adjusted with Voigt-function after continuum removal.

Laboratory results: The different results obtained are presented in figure 1. The carbon-free samples define a roughly linear trend in this diagram that is interpreted as a “coupling-efficiency” trend, based on contributions from atmospheric C, and oxygen from both the samples and atmosphere. The carbonate minerals define a different trend, with a lower slope in the O vs C intensity diagram, as can be expected. Surprisingly, no obvious deviation can be detected with respect to the carbon-free trend in the case of the basalt-carbonate mixtures (with up to 25 wt % carbonate). The reason for this poor detectability of carbonate still remains to be understood. The detection limit of inorganic carbon by this method seems to be of the order of 5 wt. % C, completely consistent with earlier work (Ollila et al., 2013) using a univariate approach.

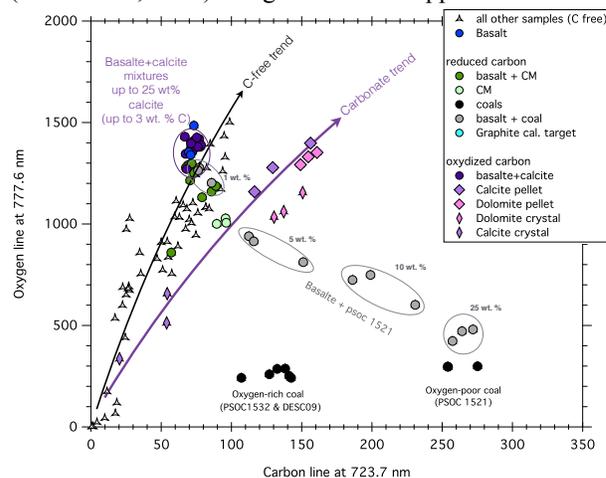


Fig. 1 : Carbon line (723.7 nm) vs Oxygen line (777.6 nm) intensity for the series of laboratory data. The graphite calibration target is outside of this range with a C line intensity of 574 counts and an O Line intensity of 437 counts.

Reduced organic C (macromolecular and graphitic) seems to have a better detectability. The carbonaceous chondrite, with only 1.9 wt. % carbon [16] is clearly

offset from the C-free trend (Fig. 1) and the basalt-coal mixtures reveal that a few wt. % of reduced carbon should be detectable with ChemCam. Finally, the coal samples define a carbon-rich trend, that extends toward the graphite calibration target (not shown in figure 1).

Results from MSL: Our initial attempt to applying this method to the MSL ChemCam dataset is presented here (Fig. 2). The whole set of Martian targets was analyzed, thus including soils, float rocks and outcrops. In addition, the procedure was also applied to the graphite calibration target analyzed on Mars. The latter define a C-rich trend that is explained by variations in coupling efficiency (Fig. 2).

The data obtained on the Martian surface define a roughly linear array that is similar to the trend of laboratory data obtained on the C-free samples. This spread is the result of varying target distances, different laser powers and focus, contrasted coupling efficiencies of the targets and possibly effects related to plasma chemistry.

Several data lie outside of the average trend. Among them, one was noticed of particular interest since 6 points out of the 20 of this target are offset toward the C-rich side of the diagram, while the other were located in the “normal” trend. This target is a blind target corresponding to a soil analysis within the Hidden Valley area (BT 711, Fig. 3). Interestingly, this target had been under high scrutiny since it corresponds to the largest hydrogen signal detected by ChemCam so far. Still, detailed investigation of this target does not show a correlation between hydrogen and carbon line intensities. This target was classified as basaltic, but the total oxides determined using ChemCam were significantly low (60-70 wt %), suggesting the possible presence of a large abundance of volatile elements (not yet quantified). It was also found to be enriched in Ba and Cl.

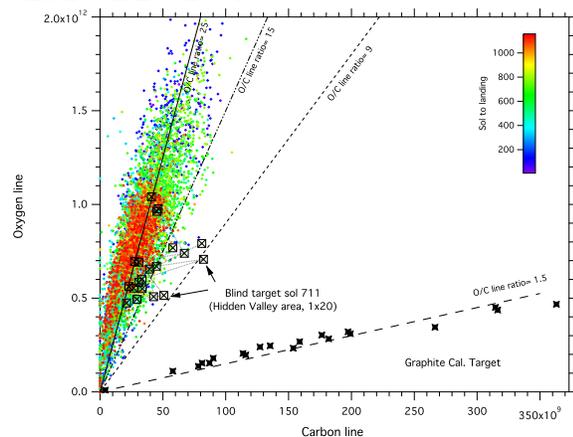


Fig. 2 : O line intensity (777.6 nm) vs C line intensity (723.7 nm). The dark squares correspond to graphite calibration target measurements. BT 711 points are connected by lines.

Conclusions: On the basis of our laboratory work, carbon seems to be detectable with ChemCam at concentrations of ~1 wt. % for organic C and ~5 wt % for inorganic C (carbonate). It is still to be understood whether the lower detectability of carbonates in the laboratory experiments (with respect to organic C) is related to a poor coupling efficiency, or to chemical matrix effects. Preliminary analysis of Martian data obtained with ChemCam suggest the presence of C. In the case of one target--a blind soil target--high carbon intensities were found, similar to those found with the testbed on pure carbonate, or basalt mixed with a few wt. % of organic carbon. More efforts are underway to confirm this detection and to provide an accurate quantification of carbon content in this target.

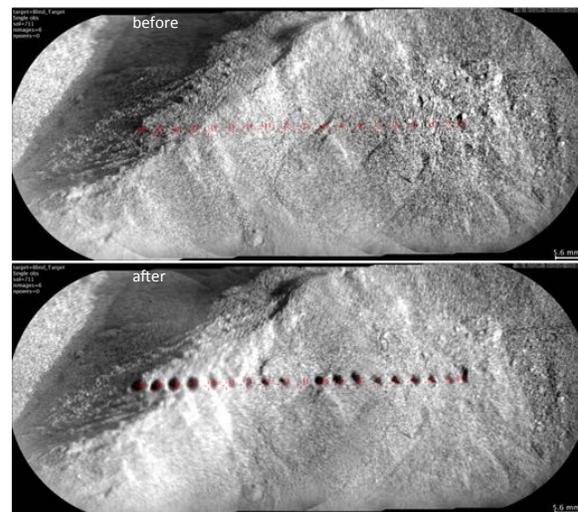


Fig. 3 : RMI image of the blind target 711, which had putative C-enrichment. This area had been disturbed by the rover wheels

References:

- [1] J.L. Bandfield et al. (2003) Science 301, 1084.
- [2] W.V. Boynton (2009) Science 325, 61.
- [3] S. P. Kounaves et al. (2010) Journal of Geophysical Research Planets.
- [4] R.V. Morris et al. (2010) 329, 301.
- [5] B.E. Ehlmann (2008) Science 322, 1828.
- [6] B. Bultel et al. (2015) 260,141.
- [7] D.W. Mittlefehldt et al. (1994) Meteoritics 29, 214.
- [8] A.H. Treiman et al. (1995) Meteoritics 30, 294.
- [9] Flynn G.J. (1993) LPZSC XXIV 493-494
- [10] L.A. Leshin et al. (2013) Science 341, DOI:10.1126/science.1238937.
- [11] D.W. Ming et al. (2014) Science 343 DOI:10.1126/science.124567.
- [12] R.C. Wiens et al. (2012) Space Sci. Rev. 170,167.
- [13] S. Maurice et al. (2012) Space Sci. Rev. 170,95.
- [14] A.M. Ollila et al (2011) LPSC XLII #1608.
- [15] A.M. Ollila et al (2013) LPSC XLIV #1719.
- [16] C.M.O'D. Alexander et al. (2012) Science 337, 721.