

Quantification of Chlorine via Molecular Emissions of CaCl in Laser-induced Breakdown Spectroscopy under Martian Conditions

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ABSTRACT: The ChemCam instrument suite on board the Mars Science Laboratory and its successor, SuperCam, use laser-induced breakdown spectroscopy (LIBS) at stand-off distances for the elemental analysis of Martian targets [1–3]. The detection of halogens like chlorine in Martian targets has been a challenge for ChemCam, as the emission lines are typically of low intensity, so that high concentrations are necessary. An indirect detection via molecular emissions of simple molecules that form inside the plasma has been proposed as a way to enhance the level of detection (LOD) for halogens [4]. In the case of chlorine, the molecular emissions of calcium monochloride (CaCl) have been useful for the identification of chlorine in ChemCam spectra [5]. Its strongest bands, located at 593 nm and 618 nm in the spectra, lie within ChemCam’s spectral range. The LOD for chlorine can significantly improve when using CaCl bands instead of atomic emission lines [6]. However, the dependency on compositional changes of the samples has not yet been investigated extensively. Since the formation of a diatomic molecule is a prerequisite for these molecular emissions, the concentrations of both elements inside the laser-induced plasma are likely to have a big influence on the intensity of the molecular bands. This study investigates these effects under Martian conditions. Samples were created with compositions that resemble Martian targets, and were measured in 6.5 mbar of Mars-analog atmosphere. The reactions inside the plasma are modeled in order to investigate the changes in CaCl concentration over time. The concentration of Ca is found as a strong limiting factor for the band intensity. Since time-resolved LIBS measurements on Mars will be possible for the first time with SuperCam, the optimization of the delay time for measurements of CaCl bands on Mars will also be discussed.

References: [1] Wiens, R. C. et al. (2012) Space Sci. Rev., 170, 167-227. [2] Maurice, S. et al. (2012) Space Sci. Rev., 170, 95-166. [3] Clegg, S. M. et al. (2015) LPS XDVI, Abstract #2781. [4] Gaft et al. (2014) Spectrochim. Acta B, 98, 39-47. [5] Forni, O. (2014) LPS XDV, Abstract #1328. [6] Cousin, A. et al. (2015) EMSLIBS 2015, P-37.
