

**SUITABILITY OF MOLECULAR EMISSION IN LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE QUANTIFICATION OF CHLORINE UNDER MARTIAN CONDITIONS.** D. Vogt<sup>1</sup>, K. Rammelkamp<sup>1</sup>, S. Schröder<sup>1,2</sup>, H.-W. Hübers<sup>1,3</sup>; <sup>1</sup>Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, Germany; david.vogt@dlr.de; <sup>2</sup>Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France; <sup>3</sup>Humboldt-Universität zu Berlin, Berlin, Germany.

**Introduction:** The ChemCam instrument suite aboard the Mars Science Laboratory uses laser-induced breakdown spectroscopy (LIBS) at stand-off distances for the elemental analysis of Martian targets [1]. The detection of halogens like chlorine is a challenge for LIBS, as the emission lines are typically of low intensity and high concentrations are necessary [2]. For this reason, an indirect detection via molecular emissions of simple molecules that form inside the plasma has been proposed as a new way to greatly enhance the level of detection (LOD) for halogens [3]. In the case of chlorine, the molecular emissions of calcium monochloride (CaCl) were found to be useful for the identification of chlorine in ChemCam spectra [4, 5]. The strongest CaCl bands, located at 593 nm and 618 nm in the spectra, are well within ChemCam's spectral range.

Previous studies have shown that the LOD for chlorine can significantly improve when using CaCl bands instead of Cl emission lines [6]. However, the necessary circumstances under which good results can be obtained from molecular bands have not yet been studied extensively. In particular, there have been no in-depth studies of CaCl bands under Martian conditions so far.

This study investigates the relationship between the concentrations of calcium and chlorine and the intensity of CaCl emissions for mixtures that resemble Martian targets. The reactions inside the plasma are modeled in order to find the parameters which have the highest influence on the band intensity. The intensity of the CaCl bands is also compared to that of the strongest magnesium monochloride (MgCl) band, which is outside of ChemCam's spectral range.

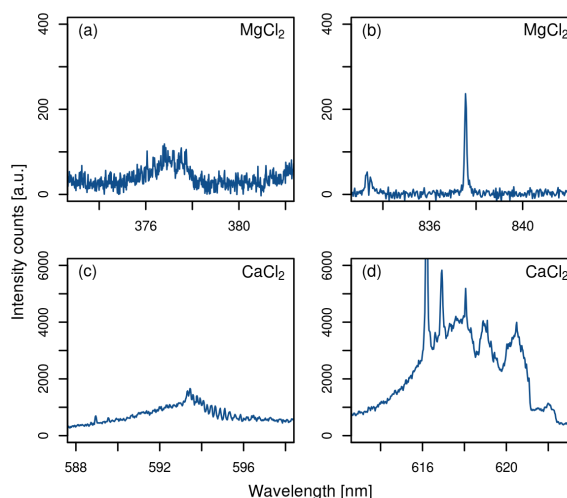
**Methods:** A sample of pure magnesium chloride (MgCl<sub>2</sub>) was used for the investigation of the MgCl band. Calcium chloride (CaCl<sub>2</sub>), potassium chloride (KCl) and sodium chloride (NaCl) were used for the investigation of the CaCl band. In order to create samples with varying amounts of chlorine and calcium, these salts were mixed with other substances at different weight ratios. CaCl<sub>2</sub> was mixed with magnesium sulfate (MgSO<sub>4</sub>) and Martian regolith simulant JSC Mars-1A (JSC) [7]. KCl and NaCl were mixed with calcium sulfate (CaSO<sub>4</sub>) and with JSC. JSC contains about 7 wt% of CaO (or 25,000 ppm of Ca), so that it should be possible to detect CaCl bands even

for mixtures with NaCl and KCl. All samples were pressed into pellets of about 1 g. In total, 81 samples were created.

Measurements were made with the LIBS system at Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, Germany, which uses a Q-switched Nd:YAG laser at 1064 nm with pulse lengths of 8-10 ns operated at a repetition rate of 10 Hz. The laser energy was set to 22 mJ/pulse. The beam was focused onto the surface of the sample, which was placed inside a simulation chamber filled with Mars-analog atmosphere at 6.5 mbar.

The plasma emissions were measured with an echelle spectrometer (LTB Aryelle Butterfly), which uses a time-gated ICCD camera (Andor iStar). The spectra cover a wavelength range from 270 nm to 850 nm with a resolution of 11 to 34 pm. Various sets of delay time and integration time were used in this study, but in the following there will be a focus on the measurements with a gate similar to that of ChemCam (no delay, 3 ms integration time).

A simple numerical reaction rate model was used to fit the measurement data. The model simulates the time-dependent concentration for Ca, Cl and CaCl inside the plasma. The expected band intensity is then calculated by integrating over the gate time of the measurement.

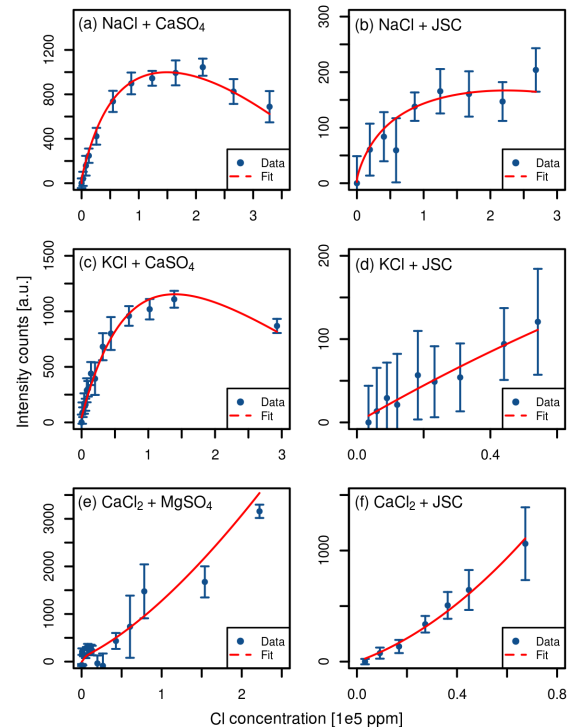


**Figure 1:** (a) MgCl band at 378 nm and (b) Cl I line at 837.6 nm in pure MgCl<sub>2</sub>. (c) CaCl band at 593 nm ("orange system") and (d) CaCl band at 618 nm ("red system") in pure CaCl<sub>2</sub>.

**Results:** *Comparison of MgCl band and CaCl bands.* The strongest MgCl band at 378 nm is barely visible even in pure MgCl<sub>2</sub> (Fig. 1a), and of lower absolute intensity than the Cl line at 837.6 nm (Fig. 1b). The MgCl band is therefore not well suited for the detection of chlorine in this data. There is also no visible deviation in the CaCl band intensity for mixtures of CaCl<sub>2</sub> and MgSO<sub>4</sub> with high Cl and Mg concentrations (Fig. 2e), which suggests that MgCl formation is negligible in comparison to CaCl formation. Both CaCl bands that can be observed by ChemCam, the orange system at 593 nm (Fig. 1c) and the red system at 618 nm (Fig. 1d), have a distinct shape and high intensity, which makes them the best choice for indirect chlorine detection. However, several calcium lines lie within the range of the CaCl band at 618 nm. It is important to carefully distinguish between these signals and that of the band itself, especially in ChemCam spectra, which are of lower resolution than the ones in this study.

*Mixed samples.* As expected, the CaCl band intensity is highest for samples in which both Ca and Cl are present in high concentrations. In the mixtures of NaCl or KCl with CaSO<sub>4</sub>, a maximum of the band intensity can be observed at about  $1.5 \times 10^5$  ppm of Cl (Fig. 2a and c), which corresponds to about  $0.6 \times 10^5$  ppm of Ca. This can be explained by the decrease in Ca concentration for increasing Cl concentrations, resulting in a band intensity which first rises and then falls. The highest band intensities are therefore only reached in samples with a high content of CaCl<sub>2</sub>, which can provide both reactants (Fig. 2e and f). However, for small chlorine concentrations below around 60,000 ppm, mixtures of NaCl and KCl with CaSO<sub>4</sub> reach higher intensities than mixtures with CaCl<sub>2</sub>, as these lack the high amount of Ca that is present in CaSO<sub>4</sub> mixtures. For NaCl and KCl in JSC, the band intensities are very low and likely not observable by ChemCam anymore (Fig. 2b and d), but they still show a clear dependency on the concentration. Even though the Ca concentration was too low to observe good CaCl signals, the spectra of these samples still showed strong Ca lines, as well as strong Cl lines for samples with higher Cl concentrations.

**Discussion:** The results confirm that CaCl bands are the best candidates for indirect detection of chlorine on Mars, as they are clearly visible under Martian conditions in multiple samples that resemble Martian targets. However, the intensity depends strongly on the composition of the sample and might be weaker than expected even in samples with high chlorine concentration. Even if peaks from both Ca and Cl can be seen in a spectrum, a clear CaCl band signal



**Figure 2:** Intensity of the CaCl band at 618 nm (“red system”) over Cl concentration for various samples.

might still not be present. The experiments also suggest that chlorine from calcium-free salts cannot be detected via CaCl in Martian regolith with lower-resolution spectrometers such as those of ChemCam, as the signal was very weak in measurements with JSC.

The upper limit for the band intensity when Ca and Cl are anti-correlated in a mixture also means that the composition of a Martian target can be estimated by looking at the strength of the CaCl bands. If the band signal is relatively strong in comparison to the intensity of the calcium lines, it is most likely that the target contains high amounts of CaCl<sub>2</sub>. If the calcium signals are strong, but the CaCl band is relatively weak, then the chlorine is most likely provided by a calcium-free salt like KCl or NaCl.

**References:** [1] Wiens, R. C. et al. (2012) *Space Sci. Rev.*, 170, 167-227. [2] Cremers, D. A. and Radziemski, L. J. (1983) *Anal. Chem.*, 55, 1252-1256. [3] Gaft et al. (2014) *Spectrochim. Acta B*, 98, 39-47. [4] Forni, O. et al. (2014) *LPS XDV*, Abstract #1328. [5] Forni, O. et al. (2015) *Geophys. Res. Lett.*, 42, 1020-1028. [6] Cousin, A. et al. (2015) *EMSLIBS 2015*, P-37. [7] Allen, C. C. et al. (1998) *LPS XXIX*, Abstract #1690.