

Molecular emission in laser-induced breakdown spectroscopy: an investigation of its suitability for chlorine quantification on Mars

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Abstract

The intensity of the molecular CaCl emission in LIBS spectra is examined in order to evaluate its suitability for the detection of chlorine in a Martian environment. Various mixtures resembling Martian targets with varying Cl content are investigated under simulated Martian conditions. The reactions leading to the formation of CaCl are modeled based on reaction kinetics and are used to fit the measured CaCl band intensities. MgCl bands are also investigated as potential alternatives to CaCl, but no MgCl bands can be identified in samples containing both Mg and Cl. The study confirms that CaCl is well suited for the indirect detection of chlorine, but finds a strong dependence on the concentrations of Ca and Cl in the sample. Spectra from samples with a high chlorine concentration can have low-intensity CaCl emission due to a deficiency of Ca. A qualitative estimate of the sample composition is possible based on the ratio of the band intensity of CaCl to the intensity of Ca emission lines. Time-resolved measurements show that the CaCl concentration in the plasma is highest after about 1 μ s.

1. Introduction

Chlorine plays an important role in the research of Martian geology. Studies of Martian meteorites (Dreibus and Wänke, 1985) and remote sensing measurements of the Martian surface (Keller et al., 2006; Taylor et al., 2010) have shown significant enrichments in chlorine, leading Dreibus and Wänke to suggest that the chlorine concentration of Mars is about three times higher than that of Earth (Dreibus and Wänke, 1987). The heterogeneous distribution of chlorine at the Martian surface has been linked to geological processes such as hydrothermal and volcanic activity (Keller et al., 2006). It has also been suggested that, instead of water, chlorine was the dominant volatile species in Martian magmas (Filiberto and Treiman, 2009). Additionally, chlorides and perchlorates are important salts in the search for liquid water on Mars. Aqueous solutions with salts have a lower freezing point and reduced equilibrium vapor pressure, which leads to an increased stability of the solution (Haberle et al., 2001; Rennó et al., 2009; Smith et al., 2009). Therefore, precipitates of salts are expected in areas where water has evaporated in the past. Both chlorides and perchlorates are among the salts that have been detected remotely and in-situ on the surface of Mars (Ehlmann and Edwards, 2014; Hecht et al., 2009; Massé et al., 2010; Osterloo et al., 2008). The detection of chlorine is important for a more complete understanding of early Mars, present Martian environments, and the history of water on Mars. This remains a major goal for current and future Mars missions.

The NASA Mars Science Laboratory (MSL) Curiosity rover has been successfully operating at Gale crater since August 2012, with the goal of searching for habitable environments (Grotzinger et al., 2012). The ChemCam instrument suite, which employs laser-induced breakdown spectroscopy (LIBS) to measure the elemental composition of a Martian target at stand-off distances between 1.3 m and 7 m from the rover (Maurice et al., 2012), has acquired more than 188,000 spectra from over 650 Martian targets during its nominal mission alone (Maurice et al., 2016), and has since surpassed 500,000 laser shots. Three spectrometers allow spectral measurements from 242 nm to 900 nm, with gaps at 335-385 nm and at 465-510 nm (Wiens et al., 2012). A camera known as the Remote Micro-Imager provides visual context for the measured spectra, and is also used to autofocus the laser on the target after the malfunction of the focusing laser on sol 801 (Peret et al., 2016). Following the ongoing success of the ChemCam instrument, an enhanced follow-up instrument called SuperCam is planned for the upcoming Mars 2020 mission (Maurice et al., 2015; Wiens et al., 2016). Like its predecessor,

61 SuperCam will employ LIBS among other spectroscopic methods (Raman spectroscopy, visible
62 and near infrared spectroscopy, and time-resolved fluorescence spectroscopy) to analyze the
63 elemental and mineralogical composition of Martian targets.

64 LIBS is a kind of atomic emission spectroscopy that uses a high-intensity laser pulse to form a
65 plasma from ablated sample material (e.g. Cremers and Radziemski, 2006). The plasma consists
66 of atoms, ions, electrons, and simple molecules. Electrons emit a continuum due to
67 bremsstrahlung and recombination events, while radiative transitions from atoms, ions, and
68 simple molecules result in characteristic emission lines and bands in the spectrum. Analysis of
69 these emissions reveals the elemental composition of the sample. LIBS is well suited for remote
70 sensing in extraterrestrial exploration, as it requires no sample preparation and can be performed
71 over distances of several meters (Knight et al., 2000). The technique can be used in a wide range
72 of environments, from vacuum to high-pressure conditions like those found on the surface of
73 Venus (Arp et al., 2004). The atmospheric pressure of around 7 hPa on Mars is near-optimal for
74 LIBS, however, as it confines the plasma plume moderately while reducing the collision
75 frequency, resulting in a high signal intensity (Knight et al., 2000).

76 The emission spectrum of an element depends on the distribution of its electronic energy
77 levels. Halogens such as chlorine have very high excited electronic energy levels, so that the
78 strongest emission lines are in the ultraviolet (UV), where common LIBS set-ups are not
79 sensitive (Cremers and Radziemski, 1983). Emission lines in the visible and near-infrared
80 spectral range, such as the neutral Cl line at 837.6 nm, are low in intensity. The detection of
81 chlorine with ChemCam has therefore been challenging (Anderson et al., 2017), and the presence
82 of chlorides in Martian targets can sometimes only be inferred from strong emissions by a likely
83 cation (e.g. Clegg et al., 2013).

84 Recently, it has been shown that LIBS sensitivity for halogens can be significantly improved
85 by using molecular emission from the simple molecules that form as the halogens recombine in
86 the plasma (Gaft et al., 2014). Emission spectra of these molecules consist of more or less
87 intense bands with characteristic shapes that can often be easily identified and are well-
88 documented (e.g. Pearse and Gaydon, 1976). The observation of molecular bands of calcium
89 monofluoride (CaF) in ChemCam spectra allowed for the detection of fluorine for the first time
90 on Mars (Forni et al., 2015). Likewise, indirect detection of chlorine via calcium monochloride
91 (CaCl) bands has improved the detection of chlorine in Martian samples (Cousin et al., 2015;

Forni et al., 2015). The most intense CaCl bands are the orange system ($B^2\Sigma - X^2\Sigma$, short “B–X band”) from 581 nm to 607 nm, and the red system ($A^2\Pi - X^2\Sigma$, short “A–X band”) from 605 nm to 636 nm (Pearse and Gaydon, 1976). Both are well within the third wavelength range of ChemCam.

A prerequisite for the analysis of CaCl bands is that both Ca and Cl are present in sufficient amounts in the plasma. The calcium that is necessary to form CaCl can be supplied by minerals such as feldspar ($KAlSi_3O_8 - NaAlSi_3O_8 - CaAl_2Si_2O_8$) or calcium sulfate ($CaSO_4$), which have been found in Martian soil and rocks (Bish et al., 2013; Ehlmann et al., 2011; Meslin et al., 2013). However, the relation between the relative concentrations of Ca and Cl and the intensity of the CaCl bands under Martian conditions is still unclear. For example, various ChemCam spectra have shown strong signals from Ca and Cl, even though no CaCl bands have been detected (Cousin et al., 2015). In order to understand these observations and to help with the interpretation of Martian LIBS data, it is important to investigate the conditions which favor the formation of CaCl.

The high intensity of the CaCl bands makes them well suited for the indirect detection of chlorine, but they are not the only molecular bands that are available. Chlorine can also recombine into other molecules, especially if alkaline earth metals are present. Magnesium is of special interest in this regard due to its occurrence on Mars, where it has been found in water-related materials such as sulfates, chlorides, and perchlorates (Ehlmann and Edwards, 2014). It is therefore important to investigate whether chlorine could be indirectly detected by MgCl emission in LIBS spectra. It might also be possible that the formation of MgCl is preferred over the formation of CaCl (Maurice et al., 2016). In this case, the intensity of CaCl bands would be reduced if Mg is present, which would significantly limit the detection of chlorine by CaCl emission in Martian spectra. It is not possible to observe the strongest MgCl band with ChemCam or SuperCam, as it is located between 375 nm and 378 nm, where these instruments have a gap in their spectral coverage.

In this study, CaCl bands in LIBS spectra measured in simulated Martian atmospheric conditions are analyzed to investigate their characteristics and dependencies with varying concentrations of Ca and Cl and to evaluate the suitability of CaCl emission for quantitative analysis of chlorine on Mars. The samples are mixtures of chloride salts, sulfate minerals and Martian regolith simulant. The chlorides and sulfates used here have already been detected on

Mars and are of high interest in the context of the search for water on Mars. The intensity of the CaCl bands in these samples is investigated in dependence of the Ca and Cl content of the samples and for different measurement times. A model is developed to simulate the reaction kinetics inside the plasma and to reveal the critical parameters affecting the intensity of the CaCl bands. Additionally, the MgCl band is investigated in order to determine its suitability for the indirect analysis of chlorine, and to find out whether the presence of Mg has an effect on the CaCl emission intensity.

2. Methods

2.1. Sample preparation

In this study, pure and mixed samples of six salts (MgCl_2 , CaCl_2 , NaCl , KCl , MgSO_4 , CaSO_4), Martian regolith simulant JSC Mars-1A (“JSC”), and a dunite reference material are investigated. The salts were selected because they are of high interest in the context of brine formation on Mars (Möhlmann and Thomsen, 2011; Schröder et al., 2013). An overview of the samples is given in Table 1.

A pure sample of the hexahydrate of magnesium chloride ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$) was made for the investigation of the MgCl band. The dihydrate of calcium chloride ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$) as well as potassium chloride (KCl) and sodium chloride (NaCl) were used for the investigation of the CaCl bands. In order to produce samples with varying concentrations of Cl and Ca, mixtures of these chlorides with sulfate minerals and with JSC were made at different weight ratios. The sulfate mineral used for mixtures with CaCl_2 was the heptahydrate of magnesium sulfate ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$). For mixtures with KCl and NaCl, the dihydrate of calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) was used, which supplies the calcium for the possible formation of CaCl inside the plasma. In mixtures with JSC, the calcium is provided by the feldspar in JSC, which contributes the equivalent of about 6.2 wt% CaO to the chemical composition of JSC (Allen et al., 1998). The concentrations of Ca and Cl are correlated in mixtures with CaCl_2 , and anti-correlated in mixtures with NaCl and KCl. Reagent-grade salts were used for the samples.

The substances were mixed and ground into powders with a typical grain size of less than 40 μm , which were then pressed into pellets of about 1 g, using a pressure of 5 tons for 10 minutes. Due to the hygroscopic nature of MgSO_4 , MgCl_2 , and CaCl_2 , samples containing

these substances were stored inside a desiccator in order to minimize the adsorption of atmospheric water.

Table 1: Overview of samples investigated in this study

Sample/mixture	Composition
CaCl ₂	100 wt%
MgCl ₂	100 wt%
Dunite (CRM 4233-88)	100 wt%
JSC	100 wt%
CaSO ₄	100 wt%
CaCl ₂ + MgSO ₄	0.2 wt% to 80 wt% CaCl ₂ (17 samples)
KCl + CaSO ₄	0.5 wt% to 80 wt% KCl (14 samples)
NaCl + CaSO ₄	1 wt% to 80 wt% NaCl (11 samples)
CaCl ₂ + JSC	1 wt% to 24 wt% CaCl ₂ (7 samples)
KCl + JSC	1.2 wt% to 17 wt% KCl (9 samples)
NaCl + JSC	5 wt% to 60 wt% NaCl (8 samples)

2.2. Experimental setup

Measurements were made with the LIBS system at Deutsches Zentrum für Luft- und Raumfahrt (DLR). The laser is a Q-switched Nd:YAG laser with a wavelength of 1064 nm and a pulse length of 8 ns. It was operated at a repetition rate of 10 Hz. The maximum laser energy of 51 mJ/pulse (measured at the sample position) was reduced to 22 mJ/pulse with gray filters in the optical path. The samples were placed inside a vacuum chamber filled with Mars-analog atmosphere consisting of 95.55 vol% CO₂, 2.7 vol% N₂, 1.6 vol% Ar, and 0.15 vol% O₂. The pressure inside the chamber was kept constant at 6.5 hPa.

The plasma emission was measured with an echelle spectrometer (LTB Aryelle Butterfly), which uses a time-gated intensified charge-coupled device (ICCD) camera (Andor iStar). The spectra cover a wavelength range from 270 nm to 850 nm, with a pixel resolution of 11 pm at 270 nm and 34 pm at 850 nm.

Each sample was measured at multiple positions in order to obtain a good representation of the sample composition. At each position, the intensity values of the plasma emissions of 30 successive laser shots were summed up to obtain a single spectrum. Measurements of mixtures

of CaCl_2 and MgSO_4 were made using three positions per sample for each setting of delay time and integration time. Because of the relatively high uncertainty values of the signals in these measurements, the decision was made to increase the number of positions from three to ten positions for the remaining samples.

2.3. Data acquisition and processing

In the early stages of the plasma evolution, radiative recombination and bremsstrahlung lead to a strong continuum emission, which can obscure the signals from molecular bands. Baseline removal algorithms can be used to remove the continuum retroactively from the recorded spectrum. However, these algorithms can remove molecular bands as well, since molecular bands cover a wide wavelength range (about 10 nm for the A-X band of CaCl) and cannot be separated from the baseline as easily as atomic or ionic emission lines. In echelle spectra, the removal of the baseline is further complicated by the fact that the apparatus function is not smooth. The total spectrum is combined from successive orders, in which the sensitivity decreases as the distance to the central wavelength (blaze angle) increases, resulting in a baseline that is not smooth at the transition between adjacent orders. As most baseline removal algorithms require a smooth baseline in order to work as intended, an additional step would be necessary in which the sensitivity of the spectrometer is normalized before removing the baseline. This is often not desirable, as each of these steps introduces new uncertainties.

A simple and common approach is to gate out the continuous emission during the experiment instead. This can be achieved with an ICCD, for example, by setting a delay time between the laser pulse and the start of the measurement. As the plasma expands and cools off, the continuum emission drops off quickly within several hundred nanoseconds, so that it will not appear in spectra with a delay time larger than that. Molecular bands produce a strong signal that can still be detected microseconds after plasma initiation, so that their signal benefits from long integration times. The delay time and the integration time are defining parameters of the LIBS measurement and have to be adjusted with regard to the measurement objective, the setup, and the samples.

Different combinations of delay time and integration time were analyzed using pure CaCl_2 samples in order to find optimal parameters for the observation of CaCl bands with our setup. Based on the comparison of the signal intensities of the A-X band of CaCl and the continuum emission (see Section 3.3), a delay time of 350 ns and an integration time of 10 μs were selected

and were used to measure spectra of all mixed samples. Additionally, the samples were measured with parameters similar to those used by ChemCam, with the delay time set to zero and an integration time of 3 ms. In order to correctly measure the intensities of emission lines and molecular bands, the continuum emission was retroactively removed from all measurements with a delay time of less than 150 ns. This was done using a custom baseline fit that multiplies a polynomial for the continuum emission with blaze functions for the orders of the echelle spectrometer.

Signals from emission lines and molecular bands were measured by taking the average intensity count in a specified wavelength range for each spectrum (Table 2). Mean value and standard deviation were then calculated from the emission intensities that were obtained at different positions on the sample.

Table 2: Spectral emissions and associated wavelength ranges used for the calculation of signal intensities in this study

Emission	Wavelength range
Ca I	422.3 – 423.0 nm
CaCl ($A^2\Pi - X^2\Sigma$)	620.4 – 621.0 nm
Continuum	637.0 – 639.0 nm

3. Experimental Results

3.1. LIBS spectra and general characteristics

In order to illustrate the measurements that were made, exemplary spectra of all mixtures are shown in Fig. 1, with labels for some of the stronger emission lines and for the A–X band. The Cl line at 837.6 nm can be clearly seen for the samples of KCl mixed with CaSO₄ and of NaCl mixed with CaSO₄ (Fig. 1a and b), which have the highest chlorine content of the shown spectra. As expected, the Cl line is less intense than the emission lines of both K and Na, which are present in equal concentrations as Cl in their respective samples. In contrast to the low intensity of the Cl line, there is a strong signal from the A–X band in many of the spectra, even when the Cl line cannot be observed.

The spectrum of CaCl_2 mixed with MgSO_4 shows a strong hydrogen emission (Fig. 1c). This indicates that, although samples containing these salts were stored in a desiccator, the hydration state was still high at the time of measurement. During the measurements, the formation of liquid water on the surface of the pellets could be observed, which further hints at strong adsorption of atmospheric water. The low total intensity of the spectrum is most likely related to the high translucence caused by the hydration and adsorption of water, as a high translucence reduces the coupling efficiency of the laser (Schröder et al., 2013). In the spectra of KCl and NaCl mixed with JSC (Fig. 1d and e), the H line is less intense, indicating that the samples were drier. Intense Ca emission lines can be observed in these samples, as JSC contains the equivalent of about 6.2 wt% CaO (Allen et al., 1998). For a mixture of 24 wt% CaCl_2 and 76 wt% JSC (Fig. 1f), Ca emissions are twice as strong as for pure JSC. This is in agreement with the chemical composition of JSC, according to which pure JSC should contain about 25,600 ppm of Ca, while a mixture with 24 wt% CaCl_2 should contain about 50,400 ppm of Ca. This concentration of Ca in JSC should be sufficient to allow for the observation of CaCl bands even in mixtures with calcium-free chlorides. Indeed, the distinct shape of the A–X band can be recognized in Fig. 1d and e, if the corresponding parts of the spectra are magnified.

In Fig. 2, spectra of mixed samples of CaCl_2 and JSC are shown which focus on the wavelength range of the B–X band and the A–X band of CaCl . As expected, the band intensities get stronger with increasing CaCl_2 content in the sample. Three band sequences can be observed in the A–X band, while individual heads can be observed in the B–X band. The B–X band is of much lower intensity than the A–X band. While a lower intensity is to be expected for the B–X band (Pearse and Gaydon, 1976), the intensity is further reduced because the band is at the transition of two adjacent echelle orders, where the sensitivity of the spectrometer is up to 45% lower than it is at the center of an order. As the A–X band shows an improved signal-to-noise ratio in comparison to the B–X band, the decision was made to focus on the A–X band for this study. The location of the A–X band at the center of an echelle order allows for detection with high sensitivity and an easy separation from the continuum emission.

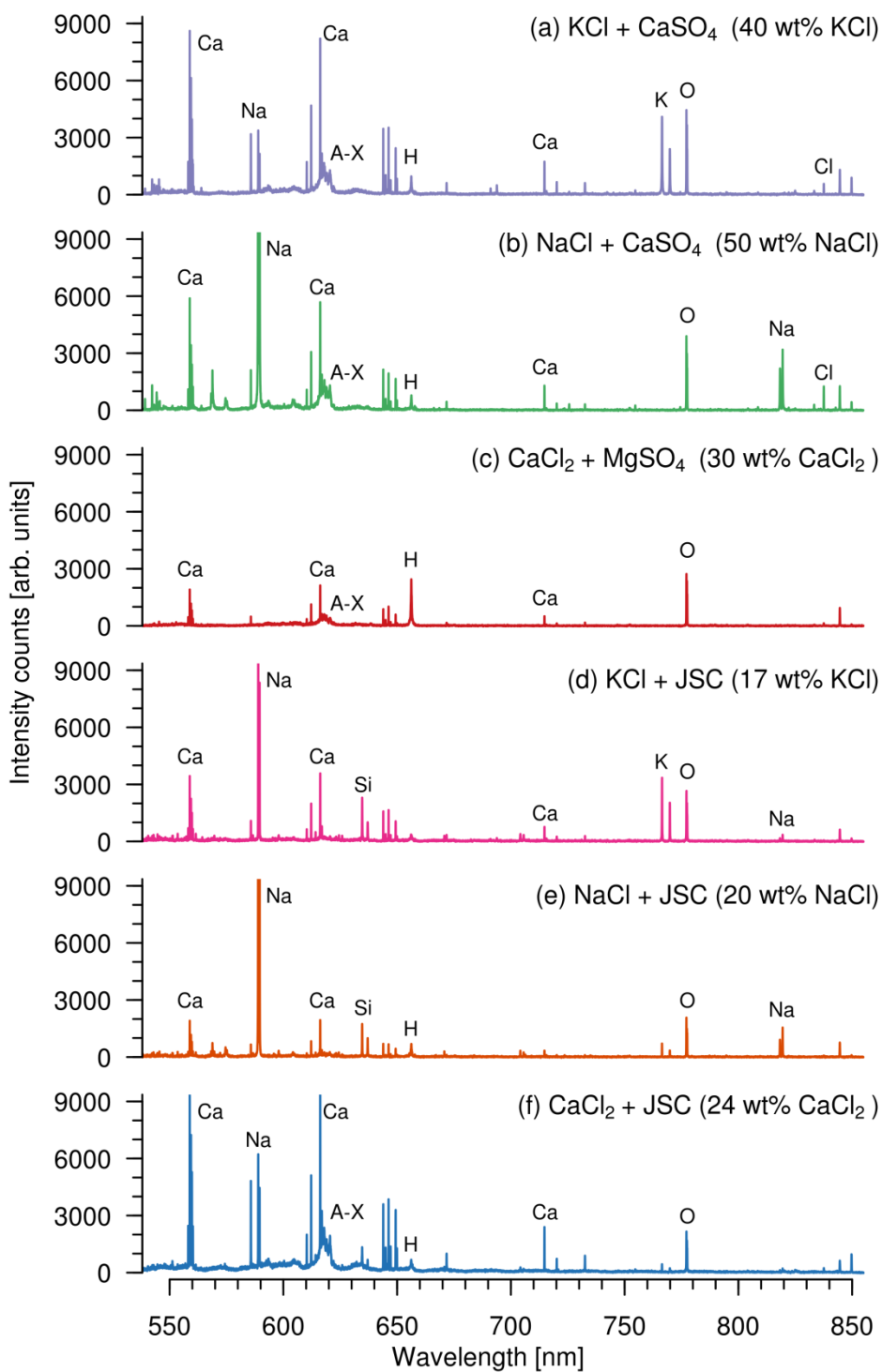


Figure 1: Spectra representing all mixed samples, with labels for important emission lines and for the A–X band of CaCl. Despite careful sample preparation, weak Na lines can be observed in (a). This hints at a (very low) contamination, most likely with NaCl.

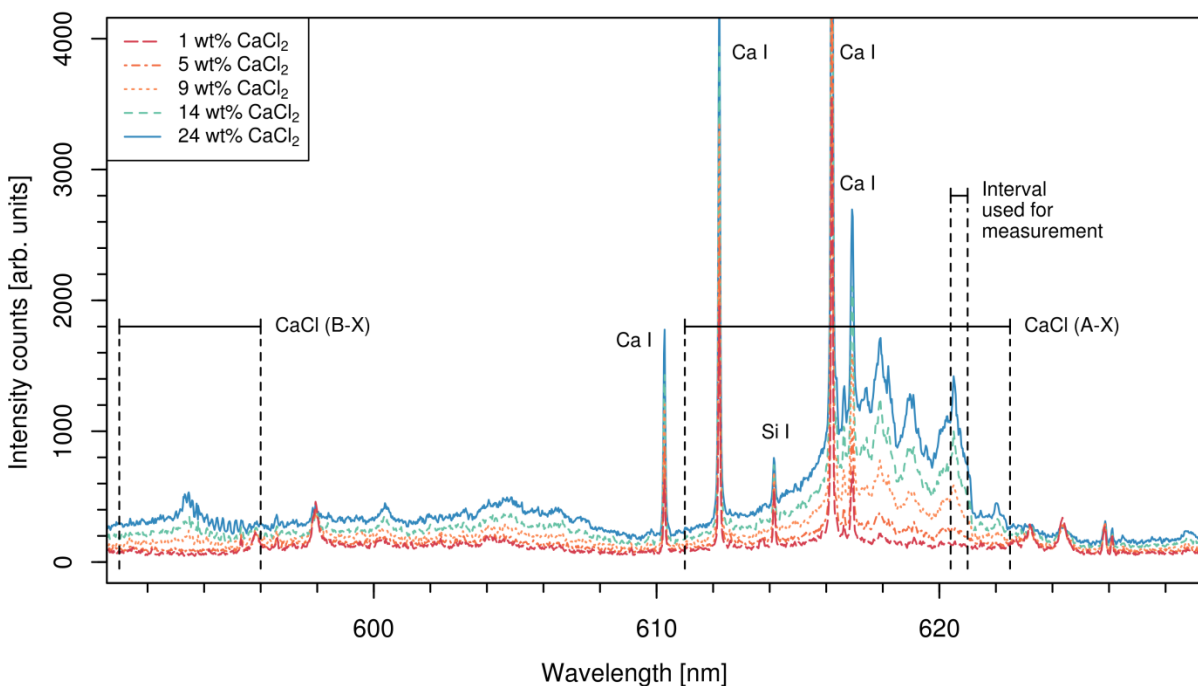


Figure 2: Spectra of JSC mixed with different amounts of CaCl_2 . The A–X band (from about 611 nm to 622.5 nm) can be seen easily, while the B–X band (from about 591 nm to 596 nm) is less intense due to the echelle spectrometer’s reduced sensitivity in this spectral range.

3.2. Comparison of MgCl and CaCl bands

Fig. 3 shows spectra of pure MgCl_2 and of the dunite reference sample, which contains the equivalent of 41.86 wt% MgO , but does not contain chlorine. The strongest MgCl band is expected to exhibit strong heads at 377 nm, 377.5 nm, and 377.9 nm (Pearse and Gaydon, 1976). Another MgCl band with heads at 787.2 nm and 789.4 nm has also been reported (Querbach, 1930).

Weak band structures can be observed between 376 nm and 379 nm. However, the observed band heads do not match the reported positions of the MgCl band heads, with the exception of the head at 377 nm. In the measured spectra, there is a head at about 377.5 nm that is unaccounted for in the literature, while the other reported heads cannot be observed at all. Most importantly, the band structures between 376 nm and 379 nm can also be observed in the spectrum of the dunite sample. This strongly indicates that these signals are not caused by molecular emissions of MgCl . As they have not been observed in samples that did not contain

magnesium, it is most likely that they are based on emissions of MgO, MgOH, or more complex polyatomic molecules containing magnesium. Potential heads of MgCl emissions cannot be distinguished from these superimposed band structures.

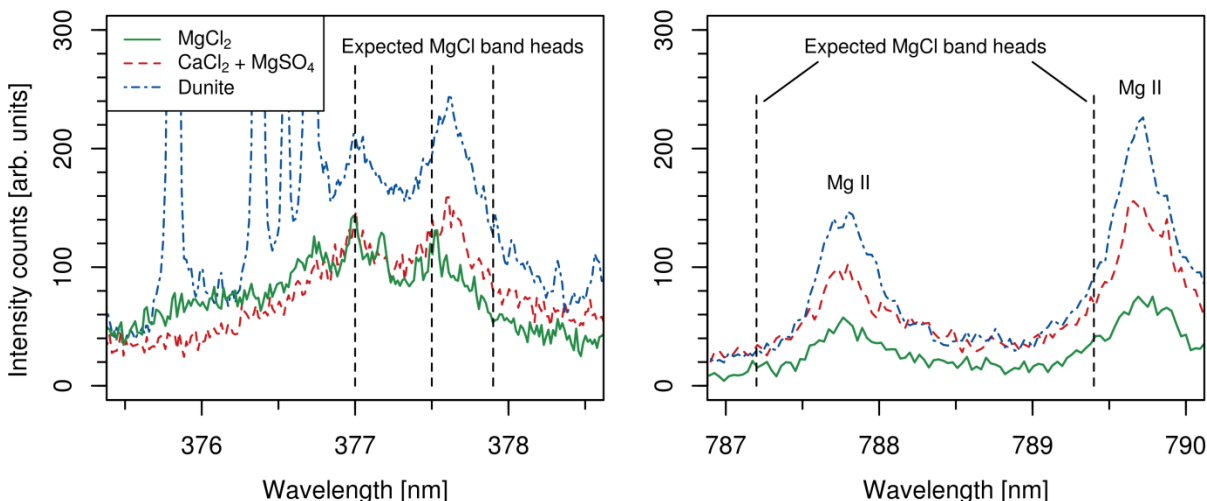


Figure 3: Spectra of pure MgCl_2 , a sample of 9 wt% CaCl_2 and 91 wt% MgSO_4 , and the dunite reference material. The observed signals around 377 nm are not the expected MgCl bands, since they are also present in the dunite sample, which contains no chlorine. It is unclear which molecules are responsible for the observed molecular bands. Between 787 nm and 790 nm, no molecular bands can be observed for any of the investigated samples.

3.3. Variation of delay time for CaCl_2

Fig. 4a shows the intensities of the A–X band and of the continuum emission at different delay times in samples of pure CaCl_2 . The integration time was kept constant at 500 ns. The continuum emission declines quickly and does not significantly contribute to the intensity of the spectrum for delay times larger than 250 ns. The CaCl band, on the other hand, reaches its highest intensity after 1 μs and decreases slowly over time, so that a clear signal can still be detected even with a delay time of 5 μs . The long delay between the formation of the plasma plume and the maximum intensity of the CaCl band can be explained by the time it takes for Ca and Cl to recombine into CaCl. The reaction kinetics model used to fit the CaCl band follows the evolution of the band intensity closely, and will be discussed in more detail in Section 4. Fig. 4b shows the temporal change in CaCl concentration as calculated from the fit model. The intensity of the continuum (Fig. 4a) was fitted by the sum of two exponential functions, in accordance with a continuum that is dominated by bremsstrahlung in the early stages and dominated by

radiative recombination in the later stages of the cooling plasma (D'Ammando et al., 2010; De Giacomo et al., 2010).

A delay time bigger than 250 ns minimizes the contribution of the continuum to the band signal intensity, while a delay time of less than 1 μ s helps to increase the intensity of the CaCl band. Based on these results, a delay time of 350 ns was set in one of the two measurement settings for the analysis of the CaCl band intensity in mixed samples. The choice of integration time depends on the intended analysis. Shorter integration times will result in more accurate snapshots of the molecular bands at a certain time after plasma initiation, while long integration times will yield stronger signals, which allow the detection of smaller quantities of chlorine. As integration times longer than 10 μ s did not significantly improve the CaCl band intensity in measurements of pure CaCl₂, the integration time for measurements with a delay time of 350 ns was set to 10 μ s.

The plasma temperature T was calculated for all delay times from individual Saha-Boltzmann plots (e.g. Aragón and Aguilera, 2008) of the most persistent Ca lines and Cl lines (Table 3) as seen in Fig. 5a. Fig. 5b shows the temporal evolution of the plasma temperatures. The decrease from initial temperature T_0 was modeled using Newton's law of cooling with the saturation temperature T_{Sat} and the cooling rate constant C_T :

$$T(t) = (T_0 - T_{Sat}) \exp(-C_T t) + T_{Sat} \quad (1)$$

In order to fit the temperature values from the Saha-Boltzmann plots, the integral of (1) over the gate time was used. The resulting fit parameters for Ca lines and Cl lines are shown in Table 4.

The saturation temperatures are reached after about 4 μ s and differ by almost 8000 K. The temperature calculated from Cl lines is higher than the temperature calculated from Ca lines. This might be an indication of a spatial separation of the species inside the plasma. Differences in the density distributions and expansion of the elements in LIBS plasma plumes have been reported in various publications (e.g. Aguilera et al., 2003; De Giacomo et al., 2008; Lee et al., 1992). Since the temperature is higher in the center of the plasma plume (Aguilera et al., 2003), the differences in the measured temperatures could be explained by different density

distributions for Cl and Ca, where Cl atoms and ions are generally closer to the center of the plasma. In this case, reactions will only take place in an overlapping region.

A very similar difference between temperatures calculated from Ca lines and from Cl lines can be observed for the mixed samples (Fig. 5c). The magnitude of the temperature stays approximately the same for all samples, although the temperatures seem to be slightly higher in JSC mixtures. It is worth noting, however, that the requirements for local thermodynamic equilibrium are not met in these measurements. Due to the long integration time, a small variation of electron number density and temperature cannot be assumed, even if the McWhirter criterion holds (Cristoforetti et al., 2010). Therefore, a high uncertainty is associated with these values and only qualitative observations can be made.

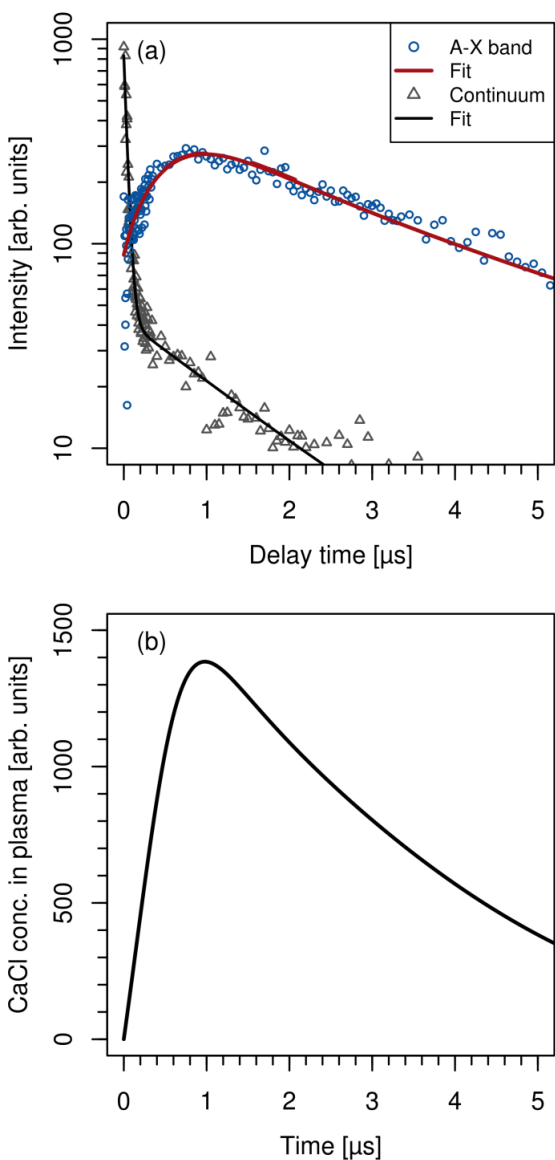


Figure 4: (a) A–X band of CaCl and continuum emission for different delay times, with constant integration times of 500 ns. The temporal evolution of the CaCl band was fitted using the reaction kinetics model (see Section 4), while the continuum was fitted by the sum of two exponential functions, indicating two separate time regimes for the continuum. (b) Calculated temporal evolution of the CaCl concentration in the plasma of CaCl₂ based on the fit seen in (a). The highest CaCl concentration is reached after about 1 μs, then it drops slowly.

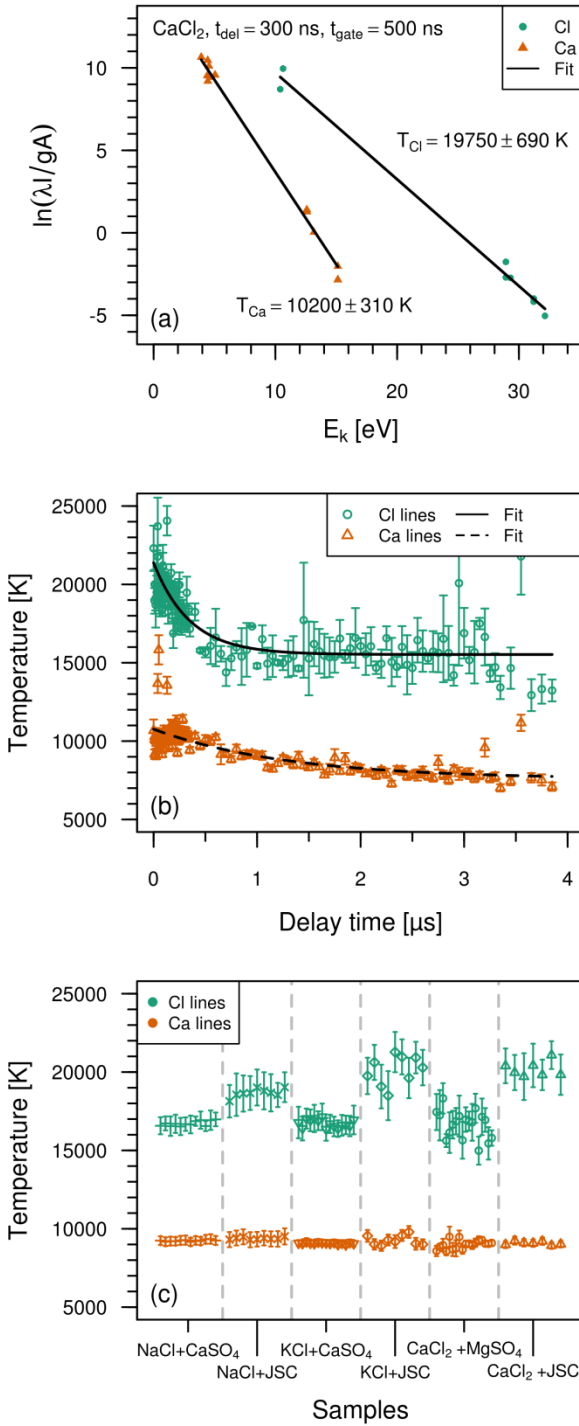


Figure 5: (a) Saha-Boltzmann plots of Ca and Cl from a measurement of pure CaCl_2 with a gate delay of 300 ns and an integration time of 500 ns. The temperature can be calculated from the slope of the fit. (b) Temperature values for pure CaCl_2 at varying gate delay times, with the integration time set to 500 ns. (c) Temperature values for all mixed samples, measured with a gate delay of 350 ns and an integration time of 10 μs . The temperatures calculated from Cl lines are significantly higher than the temperatures calculated from Ca lines.

Table 3: Emission lines used for the temperature calculation using Saha-Boltzmann plots (data from the NIST Atomic Spectra Database).

Emission	Wavelength (nm)	gA ($10^8/s$)	E_k (eV)	Emission	Wavelength (nm)	gA ($10^8/s$)	E_k (eV)
Ca I	445.48	6.1	4.68	Cl I	754.71	0.48	10.63
Ca I	585.75	3.3	5.05	Cl I	837.59	2.2	10.40
Ca I	616.22	1.43	3.91	Cl II	386.08	24	19.17
Ca I	643.91	4.8	4.45	Cl II	479.46	7.28	15.96
Ca I	644.98	0.45	4.44	Cl II	489.68	7.9	18.25
Ca I	646.26	3.3	4.44	Cl II	490.48	5.7	18.24
Ca I	649.38	2.2	4.43	Cl II	521.79	3.9	16.34
Ca I	671.77	0.36	4.55	Cl II	542.32	1.3	15.96
Ca II	315.89	12	7.05				
Ca II	370.60	1.8	6.47				
Ca II	373.69	3.4	6.47				
Ca II	820.17	2	9.02				
Ca II	824.88	3.7	9.02				

Table 4: Parameters of the temperature fit

Parameter	Ca lines	Cl lines
T_0	$(11.9 \pm 0.5) \times 10^3$ K	$(32 \pm 4) \times 10^3$ K
T_{sat}	$(7.6 \pm 0.4) \times 10^3$ K	$(15.5 \pm 0.3) \times 10^3$ K
C_T	$(0.8 \pm 0.3) \times 10^6$ s ⁻¹	$(2.8 \pm 0.5) \times 10^6$ s ⁻¹

332

333 3.4. Variation of Cl and Ca concentration

334 The primary goal of the investigation of mixed samples was to find the ratio of Ca to Cl that
 335 leads to the strongest CaCl band signal, and to find out whether the CaCl band signal scales
 336 linearly with Cl concentration. The concentrations of Ca and Cl are correlated in mixtures of
 337 CaCl₂ with MgSO₄ or JSC, and anti-correlated in mixtures of NaCl or KCl with CaSO₄ or JSC.

338 Fig. 6 shows the intensity of the A–X band for all samples, measured with a delay time of
 339 350 ns and an integration time of 10 μ s, and without a delay with an integration time of 3 ms. As
 340 expected, the highest band intensities are reached for compositions that are high in both Ca and
 341 Cl content. In samples where Ca and Cl are anti-correlated (Fig. 6a-d), this is the case for a Cl

concentration of between 1×10^5 ppm and 2×10^5 ppm, which corresponds to about 0.7×10^5 ppm to 0.5×10^5 ppm of Ca. The exact concentrations of the maximum intensity depend not only on the sample composition, but also on the choice of the measurement time. After quickly reaching the maximum at comparatively low Cl concentrations, the band intensity slowly declines as the concentration of Cl increases and that of Ca decreases in the sample. This asymmetry suggests that a high Ca content is more important for the formation of CaCl than a high Cl content.

The overall highest band intensities are reached in samples with a high content of CaCl₂, which provides both reactants (Fig. 6e, f). However, for low chlorine concentrations below 60,000 ppm, mixtures of NaCl and KCl with CaSO₄ reach higher intensities than mixtures with CaCl₂ due to the high amount of Ca supplied by the CaSO₄, which leads to an increased reaction rate. For NaCl or KCl mixed with JSC (Fig. 6b, d), the A–X band intensities are relatively low, so that they can only be used to detect Cl at high concentrations, where they might be surpassed in intensity by the atomic Cl lines.

The low CaCl band intensity in samples of NaCl or KCl mixed with JSC can be explained by the relatively low amount of Ca in JSC (about 25,000 ppm). However, the spectra still show strong Ca lines even in samples with a low JSC content. In these samples, Cl lines can also be observed, which surpass the intensity of the CaCl band. This can result in spectra that have strong atomic lines from Ca and Cl, but only have weak CaCl bands. If the plasma intensity is weak, and the spectrometer has a low resolution, then the CaCl band might not be observed at all. This has to be considered for ChemCam and SuperCam, as it means that it is possible to observe atomic lines from both Ca and Cl in Martian targets, without necessarily also detecting a CaCl band signal.

Due to the dependency of the CaCl signal on the concentrations of both Ca and Cl in the sample, it is not possible to calculate the Cl concentration directly from the intensity of the CaCl band. However, the composition of an unknown target can still be qualitatively estimated by comparing the intensity of the CaCl band to that of the emissions of Ca, Na, K, and other potential cations of chloride salts. This is illustrated in Fig. 7, which shows the intensity of atomic emission lines of Ca, Cl, K, and Na over the CaCl band intensity for all mixed samples. If the Ca line, the Cl line and the CaCl band are very intense, then the target likely contains high amounts of CaCl₂, since high band intensities can only be reached if there is an abundance of both Ca and Cl. If there is a strong signal from the Ca line, but a weak signal from the CaCl band,

then the chlorine is most likely supplied by a calcium-free salt in low concentration. In this case, emissions from the corresponding cation can be observed. Therefore, the CaCl band can be used in conjunction with other signals in the spectrum to make a qualitative assessment of the target. In simple cases, where the chloride-bearing salts can be clearly identified, a quantification of the Cl concentration is not necessary anymore, as it is sufficient to quantify the concentration of the cation. For more complex cases, a multivariate approach is required. Multivariate data analysis takes all the interdependencies into account which determine the signal intensities of CaCl, Ca, Cl, and the potential cations of the chloride salts. As a result, the quantification of chlorine via molecular emission is an ideal case for a multivariate approach and should be possible even for complex compositions.

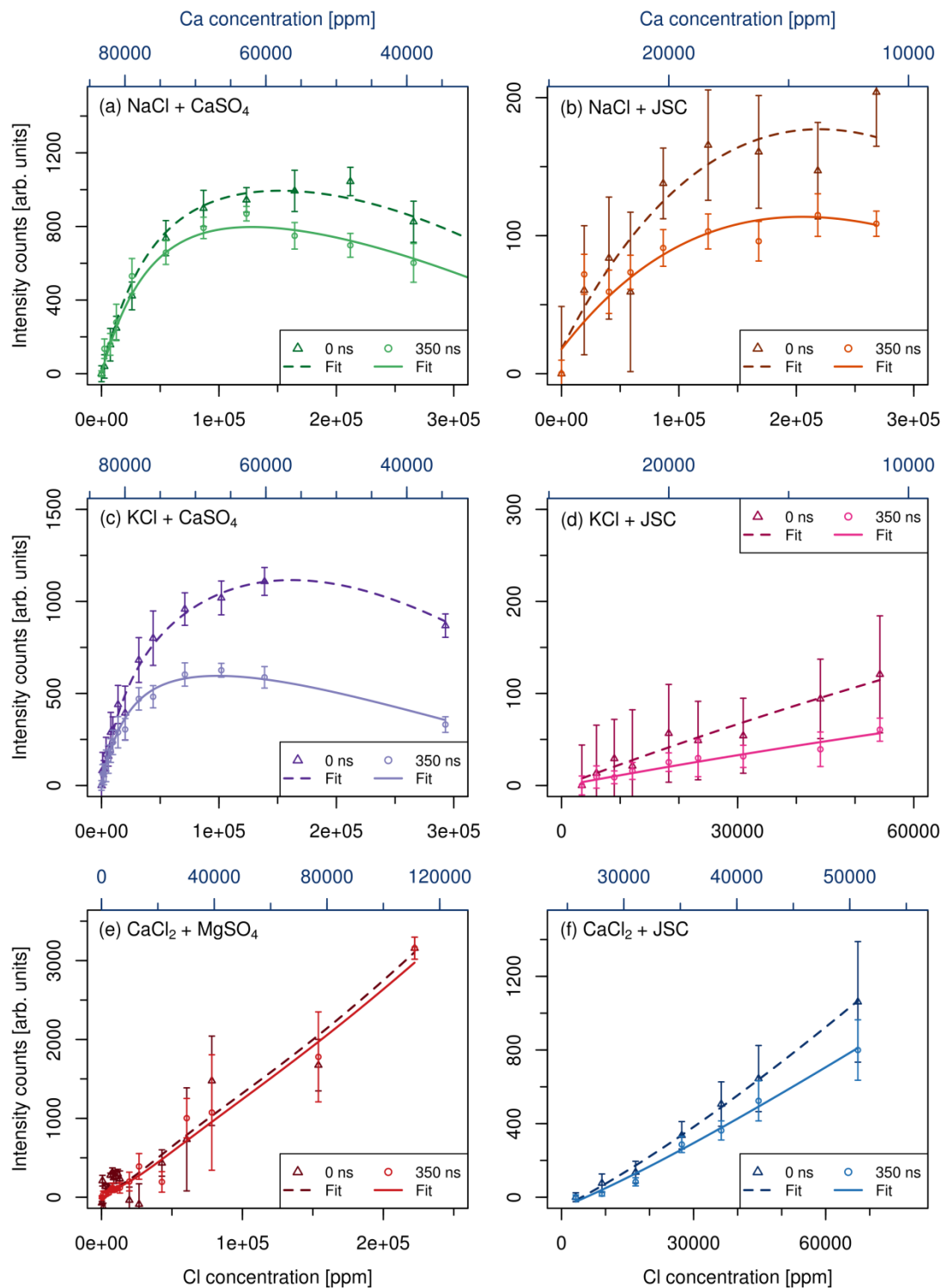


Figure 6: Intensity of the CaCl A-X band in dependence of the Ca and Cl concentrations for all mixed samples. Circles represent measurements with 350 ns delay time and 10 μ s integration time, triangles represent measurements with 0 ns delay time and 3 ms integration time. The same reaction kinetics model as in Fig. 4 is used to fit the CaCl

band intensities of all mixtures for both time gate settings. The same values are used for the majority of the fit parameters (see Section 4).

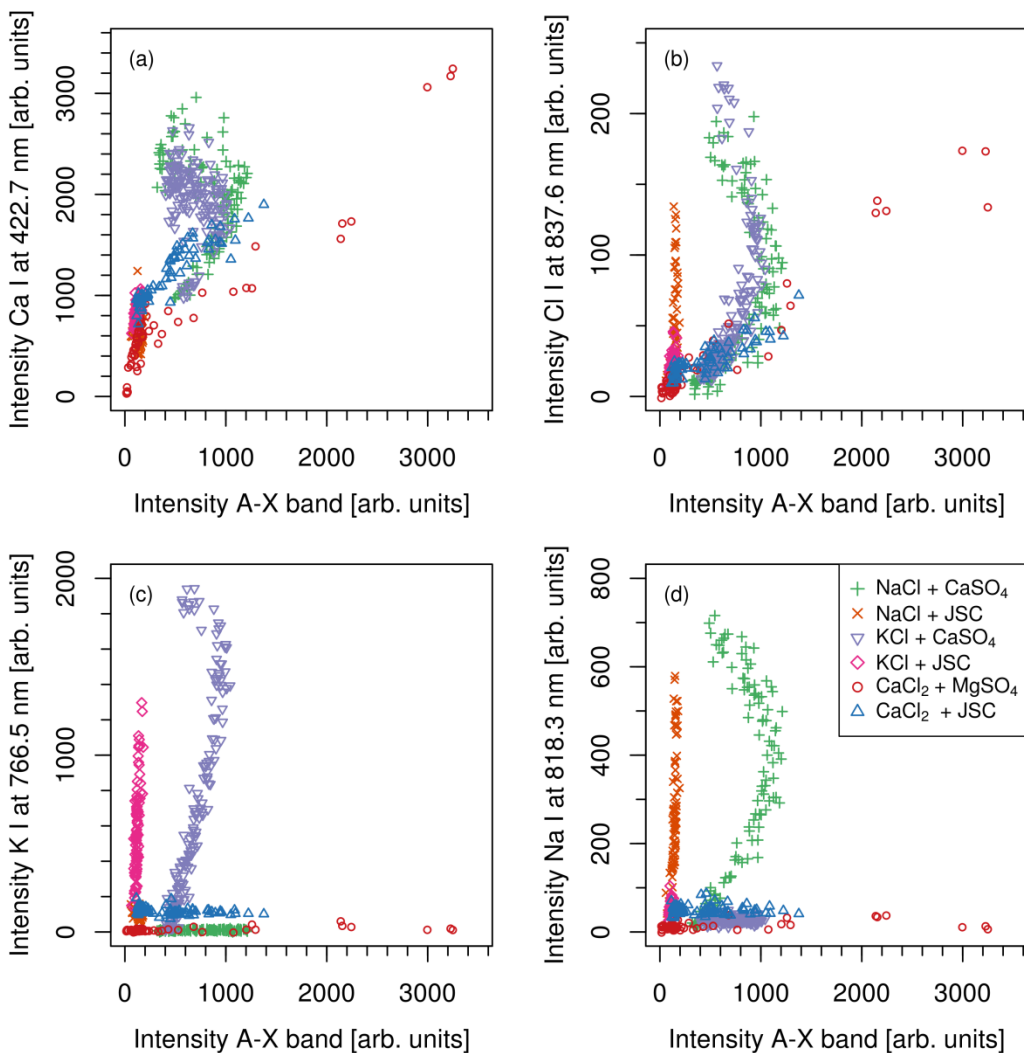


Figure 7: Intensities of Ca I, Cl I, K I, and Na I emission lines over the intensity of the CaCl A–X band for all mixed samples. It is possible to separate between samples and to estimate the composition based on the strength of the emission lines in relation to the strength of the CaCl band. (Legend in (d) applies to all plots.)

4. Modeling of Reaction Kinetics

The CaCl molecules responsible for the molecular emissions in the spectra are formed inside the plasma by recombination of atoms and ions of Ca and Cl. The concentration of CaCl

molecules therefore depends on the concentrations of Ca and Cl in the plasma, which change over time due to plasma expansion, cooling, and recombination of atoms and ions into molecules like CaCl and CaO. In order to better understand these time-dependent processes inside the plasma, a numerical model based on second-order reactions in a transient system was developed. This was used to fit the measurement data. The second-order reaction rates are given by (e.g. Laidler, 1977):

$$r_{CaCl}(t) = A_{CaCl} \exp(-E_{CaCl}/(k_B T(t))) [Ca](t) [Cl](t) \quad (2a)$$

$$r_{CaCl_2}(t) = A_{CaCl_2} \exp(-E_{CaCl_2}/(k_B T(t))) [CaCl](t) [Cl](t) \quad (2b)$$

Here, r_{CaCl} is the reaction rate of CaCl given the concentrations $[Ca]$ and $[Cl]$ and the temperature T , with the pre-exponential factor A_{CaCl} and the activation energy E_{CaCl} for the reaction. Equally, r_{CaCl_2} is the reaction rate of CaCl₂ given the concentrations $[CaCl]$ and $[Cl]$ and the temperature T with parameters A_{CaCl_2} and E_{CaCl_2} . k_B is the Boltzmann constant. Since the density distribution in a LIBS plasma is different for each species (Aguilera et al., 2003; De Giacomo et al., 2008; Lee et al., 1992), reactions between Ca and Cl can only take place in a region where their density distributions overlap. T is the temperature of this overlap region. The volume V of the overlap region is assumed to change linearly with time at a rate C_V starting with an initial volume V_0 :

$$V(t) = V_0 + C_V t \quad (3)$$

In order to model the decrease in concentration due to expansion of the plasma, concentration-dependent expansion rates with expansion parameters B_{Ca} , B_{Cl} , and B_{CaCl} were added for each species. Then the changes in concentration of Ca, Cl, and CaCl can be modeled as follows:

$$d[Ca]/dt = -C_V/V(t)[Ca](t) - r_{CaCl}(t) - B_{Ca}[Ca](t) \quad (4a)$$

$$d[Cl]/dt = -C_V/V(t)[Cl](t) - r_{CaCl}(t) - r_{CaCl_2}(t) - B_{Cl}[Cl](t) \quad (4b)$$

$$d[CaCl]/dt = -C_V/V(t)[CaCl](t) + r_{CaCl}(t) - r_{CaCl_2}(t) - B_{CaCl}[CaCl](t) \quad (4c)$$

Initially, there is no CaCl present in the plasma plume, i.e. $[CaCl](0) = 0$. For Ca and Cl, it is assumed that the initial stoichiometry of the plasma is equal to that of the sample under investigation, i.e. $[Ca](0) = n_{Ca}\rho_V$ and $[Cl](0) = n_{Cl}\rho_V$. n_{Ca} and n_{Cl} are the mole fractions of Ca and Cl in the sample, while ρ_V is the number density of atoms and ions in the overlap region V_0 . By iterating over small time steps of $\Delta t = 1$ ns, the species concentrations at time t are calculated. The CaCl band intensity I_{CaCl} is then proportional to the integral of the CaCl concentration over the time gate:

$$I_{CaCl}(n_{Ca}, n_{Cl}) = C_S \int_{t_{del}}^{t_{del}+t_{gate}} [CaCl](t) dt \quad (5)$$

Here, t_{del} is the delay time and t_{gate} is the integration time of the measurement. C_S is a parameter that relates the integral of the CaCl concentration to the band intensity.

The values for t_{del} and t_{gate} are determined by the measurement settings, n_{Ca} and n_{Cl} are given by the stoichiometry of the samples. The temperature $T(t)$ is calculated at each time using Eq. (1) with the mean values of the parameters that have been found for Ca lines and Cl lines (Table 4), since the overlap region is assumed to have a local temperature that is in between the temperatures measured for each species. The remaining parameters in the equations above can be divided into parameters which have the same value for all samples, and parameters which can have different values for each sample. The reaction parameters A_{CaCl} , E_{CaCl} , A_{CaCl_2} , and E_{CaCl_2} only depend on the reacting species, so their values are assumed to be the same for all samples. The expansion parameters B_{Ca} , B_{Cl} , and B_{CaCl} mainly depend on the atmospheric pressure, and should be the same for all samples as well.

The initial volume V_0 of the reaction region, its rate of change C_V , the number density ρ_V of atoms and ions in V_0 , and C_S might be different for the samples, as variations in composition, grain size, transparency, and hygroscopicity of the samples affect the amount of ablated material,

and likely the spatial distribution of elements inside the plasma plume as well. However, they are assumed to reach similar values for samples that were mixed from the same two substances. Therefore, the same value is used for all samples in this case.

All measurements from mixed samples and from pure CaCl_2 were fitted with the model described above. The best-fit parameter values obtained for the reaction parameters and the expansion parameters are shown in Table 5. The fit describes the measurements very well, as it accurately follows both the temporal evolution of the band intensity in pure CaCl_2 (Fig. 4a) as well as the changes in concentration for all mixed samples (Fig. 6). Differences of the intensity curves for both measurement time settings are also accurately described by the model. The adjusted coefficient of determination, R_{adj}^2 , ranges from $R_{adj}^2 = 0.86$ for the mixture of NaCl and JSC to $R_{adj}^2 = 0.99$ for the mixture of NaCl and CaSO_4 , and reaches $R_{adj}^2 = 0.96$ for the complete fit of all samples. This demonstrates the strong correlation between observed and fitted values for all mixtures.

The results from the fit with a reaction kinetics model indicate that the band intensity is linked not only to the initial concentrations of Ca and Cl in the plasma, but also to the changes of these values as the plasma expands and cools, and as the two species react with each other and with other species in the plasma. The resulting behavior over time and for varying compositions is complex. While calibration curves are assumed to be linear for atomic and ionic emissions without self-absorption, this assumption cannot be made for molecular bands. Even in mixtures of CaCl_2 and MgSO_4 or CaCl_2 and JSC, where Ca and Cl are correlated, the fit curve is not completely linear ($R_{adj}^2 = 0.971$ for the correlation between a linear function and the fit curve for mixtures of CaCl_2 and JSC).

Table 5: Fit parameters of the reaction kinetics model

Parameter	Description	Value
E_{CaCl}	CaCl activation energy	$-(11 \pm 1) \text{ eV}$
E_{CaCl_2}	CaCl_2 activation energy	$-(11 \pm 1) \text{ eV}$
A_{CaCl}	Pre-exponential factor for CaCl reaction	$(2.8 \pm 0.1) \times 10^{-8} \text{ m}^3\text{s}^{-1}$
A_{CaCl_2}	Pre-exponential factor for CaCl_2 reaction	$(1.6 \pm 0.1) \times 10^{-6} \text{ m}^3\text{s}^{-1}$
B_{Cl}	Cl expansion constant	$(0.37 \pm 0.01) \text{ s}^{-1}$
B_{Ca}	Ca expansion constant	$(2.57 \pm 0.01) \text{ s}^{-1}$

B_{CaCl}	CaCl expansion constant	$(0.14 \pm 0.01) \text{ s}^{-1}$
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5. Discussion

The analysis of the MgCl band in MgCl₂ and in mixtures of CaCl₂ and MgSO₄ indicates that the detection of MgCl emissions in LIBS spectra measured at Martian conditions is not possible with the current configuration. The molecular band that was suspected to be an MgCl band was also visible in chlorine-free dunite, suggesting that at least a large part of the signal is caused by unknown molecular emissions. As the signal could not be detected in samples that did not contain Mg, it is likely the molecular band of MgO, MgOH, or another polyatomic molecule that contains Mg. It is unclear if the lack of a clear MgCl signal in MgCl₂ is the result of an emission rate that is significantly lower than that of similar diatomic molecules, or if MgCl does not form in LIBS plasma under Martian conditions at all. Further investigation of the formation of MgCl in LIBS plasma will be necessary in order to understand why no MgCl bands could be observed.

The reactions involved in the formation and the decrease of CaCl over time have been modeled based on reaction kinetics. According to this model, the concentration of CaCl in the plasma plume of pure CaCl₂ in Martian conditions increases until about one microsecond after breakdown. At this point, the concentration reaches a maximum and then slowly decreases due to reactions and recombination processes in the cooling and expanding plasma. As the band intensity is proportional to the integral of this concentration over the measurement time, it is possible to set a delay time of 250 ns to 500 ns without losing a significant amount of intensity. This is fortunate, as the continuum emission decreases quickly over time and is not observed after about 250 ns anymore. Since it will be possible with SuperCam to set delay times for the detector that covers the wavelength of the CaCl bands, a delay time between 250 ns and 500 ns is recommended for measurements of these bands in order to exclude the continuum emission from the measurement without reducing the band intensity. This approach is generally preferable compared to post-processing the data with baseline removal algorithms, as it guarantees that no significant information is lost. Molecular bands, which cover a wide range of wavelengths, cannot always be separated from the baseline easily.

The measurements of the A–X band intensities in mixed samples confirm that the concentration of CaCl in the plasma strongly depends on the concentrations of both elements

(Fig. 6). Therefore, a one-dimensional, linear relationship between the chlorine concentration and the CaCl band intensity cannot be assumed. Even in mixtures where the Ca concentration increases proportionally to the Cl concentration, neither the observed nor the calculated band intensities depend linearly on the Cl due to the influence of the Ca concentration. In mixtures where they are anti-correlated, the band intensity instead quickly reaches a maximum and then slowly decreases. The curves are asymmetric, with the maximum at relatively small Cl concentrations and high Ca concentrations. The exact location of the maximum not only depends on the specific concentrations of Ca and Cl in the sample, but also on the delay time of the measurement.

Since it was possible to fit all samples with the same model, with the majority of the parameters values set equal for all samples, it seems that the overall composition of the investigated samples does not significantly impact the formation of CaCl, as long as Ca and Cl are present in sufficient concentrations. However, it was necessary to set volume parameters for each mixture separately. This suggests that the spatial distribution as well as movement and collisions of the species inside the plasma plume are affected by the sample composition.

In samples that contained both Mg and Ca as reaction partners for Cl, no decrease of the CaCl band intensity could be observed, which suggests that MgCl formation does not have a large impact on the Cl concentration in the plasma. It is possible that recombination of Ca with other elements in the plasma has a larger impact on the CaCl formation than recombination of Cl with other elements in the plasma. For an investigation of this effect, CaCl bands and CaF bands can be measured in spectra of mixed samples containing Ca, Cl, and F at varying concentrations. Since CaF emits very strongly even at low concentrations, formation of CaF might be preferred over the formation of CaCl. In this case, a strong dependence of the CaCl band intensity on F concentration is expected. Experiments with samples containing all three species at varying concentrations will be performed in a future study in order to test this hypothesis.

The activation energies for CaCl and for CaCl₂ listed in Table 5 are negative, suggesting that the reaction rate increases as the plasma cools, as is the case for exothermic reactions. However, they might indirectly describe influences that were not explicitly covered by the model. Examples include the spatial distribution of the elements inside the plasma over time or spatial temperature differences. Especially the observed difference of the temperature values measured using Ca lines and Cl lines indicates that these species are spatially separated from one another,

so that CaCl formation might only occur in an intermediate reaction region. In this case, special conditions may apply which have to be considered before calculating activation energies. Spatially resolved measurements of the LIBS plasma could help to better understand these influences and to adjust the model accordingly.

The results of this study explain why emission lines from both Ca and Cl might be visible in a spectrum even if no CaCl bands are observed. Since Ca II emission lines can be very strong even at low concentrations, a sample with a low amount of Ca and a high amount of Cl may show these emission lines, but the amount of Ca may not be sufficient to produce CaCl emission that can be detected. With regard to ChemCam, this may be the case for sediments of calcium-free chlorides in Martian soil with a low concentration of Ca, equivalent to the mixtures of NaCl and KCl with JSC Mars-1A. Likewise, high intensities of the CaCl bands do not necessarily indicate high concentrations of chlorine, as the band intensities will also be high if there is a high amount of Ca, but only a moderate amount of Cl. Estimations of the sample composition can be made by comparing the intensity of the CaCl band to that of the Ca emissions and those of other potential cations, which can usually be detected easily. As the concentrations of Ca and Cl are limited by the stoichiometry of the molecules in the composition, the strongest signals are only produced by a small number of possible compositions, which allow for high concentrations of both species. Meanwhile, spectra of calcium-free salts such as NaCl or KCl will also feature strong emissions of the cation.

The physical model for the calculation of the CaCl band intensity that has been presented in this study is at the moment not suited for the quantification of chlorine in Martian data, as it depends on unknown plasma parameters such as the volume of the overlap region of Ca and Cl in the plasma. In order to improve the model, the density distributions of Ca and Cl in a transient plasma plume need to be investigated for samples of different mixtures and for samples with varying homogeneity. This will be investigated in future studies with a spatially and temporally resolved LIBS setup. However, it is uncertain whether this physical model will allow for a more accurate quantification of Cl than an empirical approach based on multivariate data analysis. With multivariate data analysis of the complete spectrum, the interdependencies between multiple signals in the spectra can be taken into account, which should result in an accurate identification of the sample composition. In this context, the signals of both CaCl bands provide important information that makes the quantification of Cl possible even when no Cl signals can

be detected. At the moment, this kind of multivariate approach is probably the most reliable way to get accurate estimates of the Cl concentration and is highly recommended over a direct quantification of Cl using the CaCl band intensity.

6. Conclusion

Molecular emissions of MgCl and CaCl in LIBS spectra were investigated under Martian conditions in order to examine their potential for the quantification of Cl. It was shown that MgCl emissions are not suited for the quantification of chlorine under Martian conditions, as they could not be observed even in spectra of pure MgCl₂. It is therefore unclear whether any MgCl has formed in the LIBS plasma at all. In contrast, the formation of CaCl was observed for all investigated samples containing sufficient amounts of Ca and Cl. The intensity of the CaCl bands is highly dependent on the concentrations of both Ca and Cl in the sample, however, and will decrease in intensity if either of the elements is too low in concentration. The dependence is asymmetric, favoring high concentrations of Ca over high concentrations of Cl due to a higher expansion rate of Ca. The highest concentration of CaCl in the plasma is reached after about 1 μ s, which allows setting short delay times that filter out the continuum emission with only a minimal loss of CaCl band intensity. Using a reaction kinetics model, it was possible to fit multiple samples of varying composition with the same reaction and expansion parameters, resulting in a description of CaCl formation over time in dependence of the concentrations of Ca and Cl. Based on these results, a spatial separation of Ca and Cl inside the plasma seems likely and will be investigated in a future study. An investigation of the influence of other potential reaction partners of Ca on the intensity of CaCl bands would be very interesting as well, but went beyond the scope of this study. Especially fluorine is of high interest in the context of Martian exploration, as CaF emissions in LIBS spectra are very intense and have already been observed with ChemCam. The investigation of CaCl and CaF formation in samples containing varying amounts of Ca, Cl, and F will be addressed in a future study.

The results of this study provide insight that is important for the evaluation and interpretation of signals from molecular bands in LIBS spectra measured by ChemCam or SuperCam. Since halogens like Cl and F are difficult to detect with LIBS, they can often only be detected because of molecular bands of CaCl and CaF in spectra of Martian targets. However, as this study shows, a strong CaCl signal is not directly correlated with a high amount of Cl, and the absence of CaCl

bands does not necessarily indicate a lack of Cl. The study underlines the necessity of moving beyond the univariate approach for elements which can only be observed by molecular emission. Due to the strong interdependencies of the elemental emission lines and the molecular bands, multivariate analysis of the spectra is crucial for the quantification of these elements and for an accurate identification of the mineralogical composition of the corresponding target. Due to the importance of halogenic signals in the research of our solar system, it is important to understand the processes behind halogenic molecular emission in LIBS spectra as LIBS becomes an increasingly prevalent technique for in situ planetary exploration.

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