TOWARDS LIBS CHLORINE QUANTIFICATION USING THE CACL MOLECULAR EMISSION IN MARTIAN ATMOSPHERIC CONDITIONS K. Rammelkamp[1], D. S. Vogt[1], S. Schröder[1], H.-W. Hübers[1,2],

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Introduction: The ChemCam instrument on NASA's Mars Science Laboratory (MSL) Curiosity rover has been successfully performing laser-induced breakdown spectroscopy (LIBS) at Gale crater since landing in August 2012 [1]. While alkalis, alkaline earth elements, and transition metals have strong emission lines in LIBS spectra, the detection of halogens with LIBS is challenging. This is caused by low transition probabilities or high energy excitations with emission in the UV where common spectrometers are insensitive. Chlorine is one of the halogens that is of great interest for the geological analysis of the Martian surface. Salts like chlorides and perchlorates, which have been detected remotely and in-situ on Mars, are linked to areas where liquid water has evaporated in the past, e.g. [2]. The most suitable emission line of chlorine for analysis in ChemCam data is located at 837.6 nm [3], but has low intensity and lies in the least resolved spectral range (VNIR: 473.2 - 905.6 nm, 0.65 nm FWHM spectral resolution). For this line, a detection limit in the range of 5-10 wt% chloride was found in univariate calibration [3].

Molecular emissions can improve the LIBS sensitivity for halogens, as it has been shown for fluorine [3],[4]. Molecular emission, however, only indirectly indicates the abundance of halogens, since the molecules are not necessarily present in the original sample, but form in the cooling plasma. Thus an investigation of its suitability for quantification is necessary. In the case of univariate analysis, a recent work of *Vogt et al.* [6] has shown that the CaCl emission can be misleading, since its intensity depends not only on the chlorine concentration but also on the calcium concentration. As the band intensity is described by complex reaction mechanisms with interdependencies, multivariate data analysis seems a promising tool to calibrate chlorine via the molecular emission.

Over time multivariate data analysis has become a common tool for classification and calibration of LIBS data. The ChemCam team uses a combination of independent component analysis and partial least squares regression (PLS) for the quantification of major elements [7]. A study of *Dyar et al.* [8] confirmed that an improved calibration compared to univariate calibration is possible also for minor elements by applying PLS to a large data set of geological samples measured under simulated Martian atmospheric conditions.

In this work we study potential improvements in the quantification of chlorine by using the molecular emis-

Table 1: Overview of the samples

Sample/mixture	Composition	# of samples
$CaCl_2$ + $MgSO_4$	0.2 - 80 wt% $CaCl_2$	17
KCl + $CaSO_4$	0.5 - 80 wt% KCl	14
NaCl + $CaSO_4$	1 - 80 wt% NaCl	11
$CaCl_2$ + JSC	1 - 24 wt% $CaCl_2$	7
KCl + JSC	1.2 - 17 wt% KCl	9
NaCl + JSC	5 - 60 wt% NaCl	8

sion of calcium monochloride in PLS that is applied to data with varying concentrations of calcium and chlorine. We investigate the influence of the CaCl red system from 605 to 636 nm ($A^2\Pi$-$X^2\Sigma$, "A-X band") on the outcome of the PLS model.

Samples: An overview of the used samples in this study is given in Table 1. The samples are mixtures of salts ($CaCl_2$, NaCl, KCl, $MgSO_4$, $CaSO_4$) among each other or with Martian regolith simulant JSC pressed into pellets with a diameter of 14 mm. In some mixtures the concentrations of chlorine and calcium are correlated, while they are anti-correlated in the others. A detailed description of the samples can be found in [6].

Experimental Set-Up: Data was taken with the DLR LIBS set-up with a simulation chamber, a high resolution Echelle spectrometer (Aryelle Butterfly, LTB Berlin, wavelength range: 270 - 850 nm, resolution: 11 pm at 270 nm and 34 pm at 850 nm), a time-gated intensified CCD and a Nd:YAG Laser (1064 nm, 8 ns, 10 Hz) where the energy was reduced to 22 mJ/pulse on the sample surface. The measurements were performed under simulated Martian atmospheric conditions, i.e., a pressure of about 600 Pa and the following gas composition: 95.55 CO_2, 2.7 N_2, 1.6 Ar and 0.15 O_2; all values in Vol.%.

At each position on the sample the spectra of 30 consecutive laser shots were accumulated. We took the average spectra of several sample positions for each target. Measurements were performed with the delay time set to zero and an integration time of 3 ms for better comparison to ChemCam data.

Partial Least Square Regression:
We performed Partial Least Square Regressions (PLS-R) and used the coefficient of determination (R^2) and the root mean square error (RMSE) as figure of merit. Additionally, a full cross validation evaluates the stability of the model, where the label C indicates the calibration model and CV denotes the validation model. The PLS-R was performed with selected spectral regi-
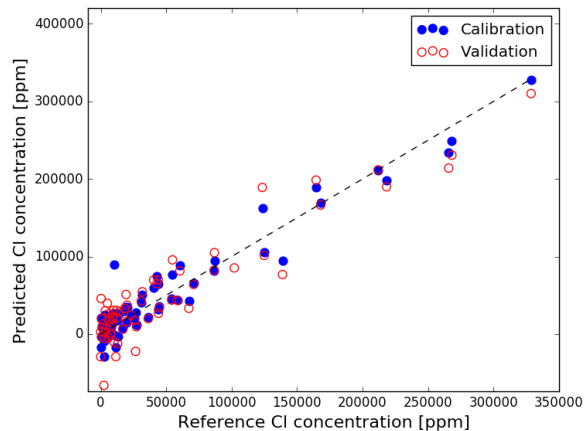
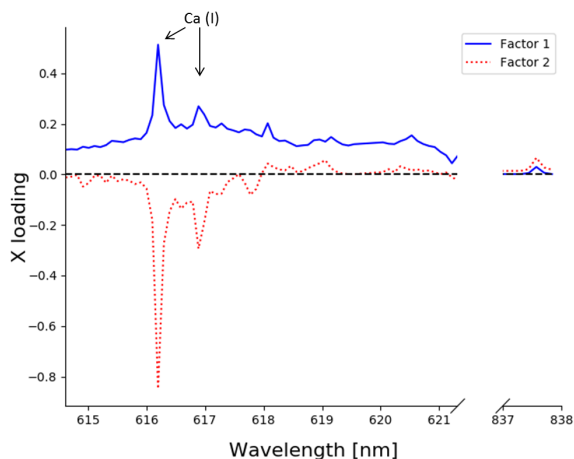Figure 1: Predicted vs. reference plot of the PLS model with all samples and the CaCl and Cl (I) region.

Figure 2: X-Loadings of first two factors, all samples, CaCl and Cl (I) region.

ons with relevance for Cl emission. We consider only a part of the CaCl A-X band that also contains neutral calcium emission (614.6 - 621.3 nm) and the neutral chlorine line (837.3 - 837.8 nm).

Various PLS regressions were investigated trying different combinations of sample classes and spectral ranges. A selection of the results is shown in Table 2. In Figure 1, a predicted vs. reference plot of the chlorine concentration is shown for the PLS with all samples and the spectral regions of Cl(I) and CaCl. For a perfect model, predicted and reference concentrations are equal (dashed line). Some of the samples have high chlorine concentrations (up to 300000 ppm), so that all chlorine peaks are clearly visible in their spectra. It can be seen that the calibration model is dominated by these samples with high chlorine concentrations. In PLS the correlation between X-variables (in this case the wavelength) and the new axes of the model (called 'factors') are known as X-loadings and represent the contribution of every wavelength channel to the model. The X-loadings

Table 2: Results of the PLS regression, RMSE values in ppm.

Samples	Range	RMSE-C	RMSE-CV	R^2-C
all	Cl (I)	21500	22600	0.913
all	CaCl + Cl (I)	16300	25500	0.950
$CaCl_2$ + JSC	Cl (I)	7241	14885	0.877
$CaCl_2$ + JSC	CaCl + Cl (I)	2000	3700	0.991
KCl + JSC	Cl (I)	5700	10200	0.882
KCl + JSC	CaCl + Cl (I)	5000	8800	0.912

of the first two factors are shown in Figure 2. The first factor indicates that the molecular emission is correlated with the chlorine emission, but the influence of the molecular emission decreases already in factor 2. The regression model including the CaCl molecular emission shows an improvement of R^2 while the RMSE-CV becomes larger, which indicates that not all samples are well described by the model.

We separately applied PLS regressions to the KCl + JSC and $CaCl_2$ + JSC samples that have the lowest mean chlorine concentrations of all sample sets, 22400 ppm and 29000 ppm respectively. An improvement of the PLS models is observable when the CaCl emission is included. The RMSE values are still larger than the lowest chlorine concentrations of the two sets (3500 and 3200 ppm), but smaller than the mean concentrations. The X-loadings (not shown here) demonstrate that for the samples with anti-correlated Ca and Cl concentrations (KCl + JSC) the Ca (I) emission in the band has the largest influence on the model and a negative correlation with the Cl concentration. The model of the samples with correlated Ca and Cl concentrations ($CaCl_2$ + JSC), however, is dominated by the molecular and the Ca (I) emission that have both positive correlations with the concentration of chlorine.

Discussion: Chlorine quantification with PLS regression gives promising results if the chlorine concentration is large enough (> 25000 ppm) to observe elemental chlorine emission. For samples with lower chlorine concentrations the quantification improves by including the CaCl emission, which is mainly caused by positive or negative correlation with the calcium concentration. Studies with an expanded set of samples with low chlorine concentrations are planned to further investigate the suitability of the molecular emission for quantification. Moreover, the calcium monofluoride band [5] will be investigated for the quantification of fluorine.

References: [1] Maurice (2016) et al., *Journal of Anal. Atomic Spectrometry*; [2] Ehlmann and Edwards (2014), *Annu. Rev. Earth Planet. Sci.*; [3] Anderson et al. (2017), *J. Geophys. Res. Planets* ; [4] Gaft et al. (2014), *Spectrochim. Acta B*; [5] Forni et al. (2015), *Geophys. Res. Lett.*; [6] Vogt et al. (2017), *Icarus*; [7] Clegg et al. (2017), *Spectrochim. Acta B*; [8] Dyar et al. (2016), *Spectrochim. Acta B*