



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

D.S. Vogt^{a,*}, K. Rammelkamp^a, S. Schröder^a, H.W. Hübers^{a,b}

^a Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institute of Optical Sensor Systems, Berlin, Germany

^b Humboldt-Universität zu Berlin, Department of Physics, Berlin, Germany

ARTICLE INFO

Article history:

Received 25 July 2017

Revised 18 October 2017

Accepted 4 December 2017

Available online 6 December 2017

Keywords:

Spectroscopy

Mars

Experimental techniques

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.

© 2017 Published by Elsevier Inc.

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, SuperCam will employ LIBS among other spectroscopic methods (Raman spectroscopy, visible and near infrared spectroscopy, and time-resolved

* Corresponding author.

E-mail address: david.vogt@dlr.de (D.S. Vogt).

fluorescence spectroscopy) to analyze the elemental and mineralogical composition of Martian targets.

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

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

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

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)

als 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 (MgCl₂, CaCl₂, NaCl, KCl, MgSO₄, CaSO₄), 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 (MgCl₂·6H₂O) was made for the investigation of the MgCl band. The dihydrate of calcium chloride (CaCl₂·2H₂O) 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 CaCl₂ was the heptahydrate of magnesium sulfate (MgSO₄·7H₂O). For mixtures with KCl and NaCl, the dihydrate of calcium sulfate (CaSO₄·2H₂O) 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

Download English Version:

<https://daneshyari.com/en/article/8134605>

Download Persian Version:

<https://daneshyari.com/article/8134605>

[Daneshyari.com](https://daneshyari.com)