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**Quantitative Raman calibration of sulfate-bearing polymineralic
mixtures: a S quantification in sedimentary rocks on Mars**

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Abstract

The NASA 2020 Mars mission is a Curiosity-type rover aiming to
improve the knowledge of the geologic and climatic evolution of Mars
and collect rock samples for future return to Earth. The new rover
presents a payload of seven instruments including the SuperCam
instrument which is constituted of four tools including a Raman
spectrometer. This Raman device will be non-destructive and will
analyze the surface remotely in order to determine the mineralogy of
rocks and, by extent, to detect and quantify major elements such as
sulfur. Sulfur has been detected under sulfate forms (Ca,Mg,Fe-
sulfates) in sedimentary rocks. This element is difficult to quantify

using the laser ablation tool of the ChemCam instrument onboard the Curiosity rover.

We propose a Raman calibration to constrain the sulfur abundance in multi-mineralic mixtures.. We acquired Raman signatures on binary and ternary mechanical mixtures containing Ca and Mg sulfates, mixed with natural silicate minerals: olivine, clinopyroxene, orthopyroxene and plagioclase; and supposed to be relevant of basaltic-sedimentary rocks at the surface of Mars. Specific processing of Raman spectra extracted from our mixtures using Voigt function allows us to recover the initial proportions of our preparations on Ca and Mg sulfates. From these simulations, calibration equations have been provided allowing us to determine sulfate proportions (CaSO_4 and MgSO_4) in a mixture with basaltic minerals. With the presented calibration, S can be quantified at a lower limit of 0.7 wt % in martian soil.

Keywords : Raman spectroscopy, S abundance, sulfates, sedimentary rocks, Mars.

1. Introduction

One of the main objectives of both orbital and landed Mars missions is the mineralogical characterization of the igneous and sedimentary rocks in order to constrain past geological processes such as the early volcanism and aqueous alteration. So far, many igneous rocks have been detected at the surface of Mars and basaltic rocks represent the

most abundant part (e.g., Bandfield et al. 2000; McSween et al. 2009; Taylor and McLennan 2009; Ody 2012; Baratoux et al. 2013; Sautter et al. 2016; Cousin et al. 2017). Although the Curiosity rover and the orbital spectrometer CRISM have recently discovered more felsic and alkali-rich rocks including trachyte, andesite, diorite and putative granitoïds (Wray et al. 2010; Stolper et al. 2013; Sautter et al. 2015; Mangold et al. 2016). These magmatic rocks have been altered into various minerals such as clays (various smectites, kaolinite, chlorite), sulfates (Ca-, Fe-, Mg-sulfates), which are often detected in sediment layers overlying the igneous bedrock or in crustal outcrops exhumed by impact craters (e.g., Squyres et al. 2004; Arvidson et al. 2005; Poulet et al. 2005; Gendrin et al. 2005; Elhmann et al. 2013, Carter et al. 2013).

The Curiosity rover currently analyzes rocks and soils on Mars using Laser Induced Breakdown Spectroscopy (LIBS) (Maurice et al. 2012; Wiens et al. 2012; Meslin et al. 2013; Maurice et al. 2017; Cousin et al. 2017; Mangold et al. 2017). The LIBS equipment enables the detection and quantification of all major elements (e.g., Si, Al) and the detection of volatiles and halogens (C-H-O-N-P-S-F-Cl). However, the detection of these elements is difficult with this method because of the high excitation energies, their peak positions near the instrument limit and the coupling of different major elements rays (e.g. Sallé et al. 2004, Clegg et al. 2007). This results in varying detection levels and lack of quantification for some of them. In particular, the detection limit for S is of 5 to 10 wt% S (Wiens et al. 2012). Quantitative determination of

S is of prime interest, as this element is known to be fundamental for Mars evolution (King and McLennan 2010).

In the future Mars 2020 mission, the SuperCam analytical equipment will include Raman and IR spectrometers in addition to the LIBS instrument similar to ChemCam instrument onboard Curiosity (Fouchet et al. 2016; Wiens et al. 2016, Ollila et al. 2017). Relevant interpretations of Raman spectra will require the acquisition of laboratory data under similar analytical conditions of the Raman spectrometer onboard. Although Raman spectroscopy is nominally non-quantitative with relevant calibration, it can be used for quantifying S at low concentrations (thousands of ppm) owing to the high Raman activity of S-bearing molecular groups (Morizet et al. 2017).

Previous studies have focused on the quantification of volatile species (H_2O , CO_2 and SO_4^{2-}) in silicate glasses with application to Earth volcanism (Zajacz et al. 2005; Mercier et al. 2009; Le Losq et al. 2012; Morizet et al. 2013, 2017). However, up to now, the quantification of individual mineral species in multi-minerallic mechanical mixtures have been merely addressed using Raman spectroscopy (Kontoyannis et al. 1997; Jehlicka et al. 2009; Noguchi et al. 2009; Kriskova et al. 2013). Jehlicka et al. (2009) have shown, the possibility to quantify multi-component mixtures with a portable micro-Raman spectrometer. In Kriskova et al. (2013) and Noguchi et al. (2009) only multi-minerallic mixtures with carbonates have been studied. Kontoyannis et al. (1997) have established a calibration on carbonates mixed with

gypsum using Raman spectroscopy, but not applied to mineralogical mixtures representative of Mars mineralogy.

In the present work, we propose a calibration for quantifying the sulfate content (thereby also the elemental sulfur content) in multi-minerallic mixtures. This calibration aims to be subsequently applied for quantifying S under its sulfate form on the surface of Mars with the Raman spectrometer of SuperCam. Several mixtures of sulfates (Ca-sulfate, Mg-sulfate) with silicate minerals (i.e., pyroxenes, olivine, and plagioclase) were prepared in order to reproduce sulfate-bearing Martian-like sedimentary rocks. These mixtures were analyzed by Raman spectroscopy. The equations derived from calibration curves are then used to quantify sulfates in these mixtures. Finally, we discuss the potential of this method to quantify S carried by sulfates in the Martian soil and rocks.

2. Methods

2.1. Multi-minerallic mixtures preparation:

Multi-minerallic mixtures were prepared from Ca-sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Mg-sulfate ($\text{MgSO}_4 \cdot n\text{H}_2\text{O}$) synthetic powders and silicate minerals selected from natural rocks. Pyroxenes and olivine were extracted from a xenolith collected at the maar of Borée (France) and plagioclase from a norite of Stillwater (USA). Chemical compositions of minerals selected for this study are reported in Table 1. Olivine is Mg-rich in composition (forsterite, $\text{Si}_{1.00} \text{Fe}_{0.18} \text{Mg}_{1.78}$

$\text{Na}_{0.01} \text{O}_4$). Pyroxenes have compositions close to enstatite ($\text{Si}_{1.85} \text{Al}_{0.16}$
 $\text{Fe}_{0.16} \text{Mg}_{1.62} \text{Ca}_{0.02} \text{Na}_{0.02} \text{O}_6$) and augite end-members ($\text{Si}_{1.78} \text{Al}_{0.23} \text{Fe}_{0.09}$
 $\text{Mg}_{0.95} \text{Ca}_{0.57} \text{Na}_{0.11} \text{O}_6$). The plagioclase from this study is Ca-rich and
has composition close to the anorthite end-member ($\text{Si}_{2.21} \text{Al}_{1.76} \text{Fe}_{0.01}$
 $\text{Mg}_{0.01} \text{Ca}_{0.85} \text{Na}_{0.16} \text{O}_8$). Natural silicate minerals were crushed in a
steel-mortar with pestle and crushed again in an agate mortar. Ethanol
was added during crushing to clean the samples.

Mixtures between silicate minerals and sulfates were prepared and
mixed in together. The resulting powder was not sieved because grain
size does not exceed 50 μm with this grinding procedure (see Figure
1A). Several samples at various sulfate proportions were prepared:
 $\text{WF}_{\text{gypsum}} = 0.20, 0.10, 0.05, 0.03, 0.01$ and $\text{WF}_{\text{mg-sulfate}} = 0.20, 0.10, 0.05$
and 0.03; where WF represents the Weight Fraction of sulfates. Ternary
mixtures were prepared with Ca-sulfate, clinopyroxene and olivine.
Gypsum, clinopyroxene and olivine concentrations in mixtures were
respectively: $\text{WF}_{\text{gypsum}} = 0.20, 0.10$ and 0.05, $\text{WF}_{\text{clinopyroxene}} = 0.40, 0.40$
and 0.45, $\text{WF}_{\text{olivine}} = 0.40, 0.50$ and 0.50. The investigated sulfate
concentrations are consistent with the abundances of these minerals as
locally estimated in evaporites at Meridiani Planum (McLennan et al.
2006) or in fluvio-lacustrine sedimentary rocks at Gale crater (Vaniman
et al. 2017).

We also prepared ternary mixtures in order to reproduce in a more
realistic system the suggested Martian surface mineralogy: sulfates
mixed silicate minerals resulting of basalt alteration (Carter et al. 2013;

Forni et al. 2015; Cousin et al. 2017; Mangold et al. 2017). The resulting powders were then pressed into pellets (Figure 1A). Pressures used were between 5,000 and 9,000 kg/cm² to create pellets with 7 to 10 mm in diameters, respectively.

2.2. Raman spectroscopy

The non-destructive nature of the Raman analyses will allow mineralogical characterization (e.g., Reynard et al. 2012) of the Martian rocks without any sample preparation. The Raman spectroscopy uses a laser with a specific wavelength, which will excite molecules (Brawer and White 1975; Mysen and Virgo 1980a, b; McMillan 1984; Rossano and Mysen 2009; Rull 2012). The excitation of molecules produces a Raman shift (i.e., the wavenumber differences between the signal from the laser and the response of excited molecules; Delhay and Dhamelincourt 1975; Hoehse et al. 2009; Dubessy et al. 2012). The strongest signatures received and detected by the Raman spectrometer are called ν_1 signatures and correspond to the symmetric stretching of the molecules excited by the laser (Rossano and Mysen 2009; Rull 2012).

Raman spectra for each pellet were acquired on a Jobin-Yvon Labram HR800 spectrometer equipped with a solid state laser diode operating at 532 nm. A 20X Olympus objective was used. A 785 nm solid state laser has also been used on one sample (GPG80, plagioclase-gypsum mixture with $WF_{\text{gypsum}} = 0.20$) to circumvent the fluorescence. Spectra

are acquired with a 300 grooves/mm grating with a 3 cm^{-1} spectral resolution. The output power of the laser was set to 74 mW for Ca-sulfate mixtures and 50 mW for Mg-sulfate. For binary mixtures, we did not use the confocal mode (with a hole calibrated around $50\text{ }\mu\text{m}$) and the hole was fixed at $200\text{ }\mu\text{m}$. However, ternary mixtures were analyzed in a confocal mode due to fluorescence problems (Panzcer et al. 2012) in the non-confocal configuration.

The acquisition time varied from 3 to 10 s and 3 repetitive scans were made on each point. Background subtraction for each spectrum has been applied following the procedure of Tarcea and Popp (2012): a fit of polylines (i.e., multiple lines added to create a baseline under the spectrum) was made for each spectrum to establish a baseline correction in order to measure areas and intensities for each peak. Peak intensity and area were determined on normalized spectra to the same acquisition time length (10 or 15 s). Details of the analytical conditions are reported in the Supplementary Material (Table 1).

A large mapping of 5 by 5 mm (Figure 1B) was conducted on each pellet with a spot size of about $1.6\text{ }\mu\text{m}$. Each analyses were performed every $150\text{ }\mu\text{m}$. This mapping results in 1024 spectra representing the mixture analyzed. Since grain size did not exceed $50\text{ }\mu\text{m}$, possible coupling of the same crystal analysis is expected. This phenomenon would have occurred for every crystal, since we suppose the mixture homogeneous in grain size (Figure 1A). Then, an average of these spectra, that will consider the previous artefact, is computed to obtain a

single Raman spectrum representative of the analyzed mixture (Figure 1C).

The effect of polarization was also tested on Raman spectra of pure minerals. We have observed that the spectrum intensity is modified when acquisition angle on the crystal is changed, which is consistent with the results of Bremard et al. (1986) and Rull (2012) where polarization effects have been observed and measured when changing crystal orientation. Nevertheless, we assumed that the polarization effect is averaged out by the large mapping procedure adopted and considering that crystals in the pellet have all possible crystallographic orientations from a statistical point of view.

2.2.1 Mineral Raman spectra:

The Raman spectrum of each individual mineral used in this study is reported in Figure 2. The gypsum Raman pure spectrum (Figure 2A) exhibits several peaks with low intensities in the 400-700 cm^{-1} region corresponding to the symmetric (400-500 cm^{-1}) and antisymmetric (600-700 cm^{-1}) bending vibrations of SO_4 molecules (ν_2 and ν_4). The strong peak at 1006 cm^{-1} corresponds to the symmetric stretching vibration (or ν_1) of S-O bonds in SO_4 molecular groups (Knittle et al. 2001; Buzgar et al. 2009; Bishop et al. 2014). Peaks observed in the highest frequency region ($> 1100 \text{ cm}^{-1}$) are attributed to antisymmetric stretch vibrations (ν_3) of SO_4 and have a weak Raman activity.

Similar to gypsum, the principal symmetric ν_1 vibration of Mg-sulfate is identified in Figure 2B around 1040 cm^{-1} (Buzgar et al. 2009).

Antisymmetric bending and stretching of SO_4 molecules are observed at 620 and 1110 cm^{-1} , respectively.

The Raman spectrum of olivine (Figure 2C) shows two strong peaks above 800 cm^{-1} , followed by two less intense peaks above 900 cm^{-1} , which are attributed to the symmetric stretch of the Si-O bonds of SiO_4 tetrahedrons (Chopelas 1991; Kolesov and Tanskaya 1996; Kolesov and Geiger 2004; Kuebler et al. 2006; McKeown et al 2010).

Plagioclase Raman spectrum shown in Figure 2D exhibits a strong peak around 500 cm^{-1} attributed to the ν_1 of Al_2O_3 or SiO_4 tetrahedrons in the tectosilicate structure (Sharma et al. 1983; Freeman et al. 2008). Peaks identified at higher wavenumbers correspond to the ν_3 vibrations for these tetrahedrons.

Pyroxenes spectra shown in Figures 2E and 2F are similar in the high frequency region ($> 600 \text{ cm}^{-1}$) where bending and stretching vibrations of SiO_4 tetrahedrons are observed, for signatures around 660 and 1006 cm^{-1} respectively. At low frequency, in the 200-400 cm^{-1} region, it is possible to discriminate clinopyroxene from orthopyroxene, which does not present the same peak intensities. In this region, vibrations related to Fe, Ca and Mg molecular environments are responsible for the observed peaks (Sharma et al. 1983; Huang et al. 2000; Wang et al. 2001; Prencipe et al. 2011). Specific peak assignments for each mineral in this study are described in Table 2.

2.2.2. Analytical conditions useable for the SuperCam instrument:

The new rover send for the 2020 Mars mission will use a laser-pulse Raman spectrometer with a 532 nm solid-state laser (Olila et al. 2012, Wiens et al. 2016). The rover will target rocks and soil from several meters away and with a resolution on the order of 10 cm^{-1} (Wiens et al. 2016).

Knowing those conditions, we performed several tests to analyze the pellets. A map size of 5 by 5 mm was necessary to reproduce in an adequate way the mineral mixtures. Using 2 by 2 or 3 by 3 mm map size was not sufficient to retrieve the initial mineral proportions in the mixture. Furthermore, the 5 by 5 mm size map is also consistent with the analytical conditions for the 2020 rover, which will have a large analytical area. The adopted laboratory analytical conditions (i.e., focus 20X, 300 grooves/mm grating and non-confocal mode) were optimized to obtained spectra that could be compared to the Raman spectra which will be acquired by SuperCam.

2.3. Calibration method:

The calibration method in the present study is similar to that used by Kontoyannis et al. (1997), Noguchi et al. (2009) and Kristova et al. (2013). Our method is based on the spectral deconvolution of the investigated pure minerals Raman spectrum presented in the previous section. For instance, to establish a calibration on a gypsum-olivine mixture, pure spectrum of gypsum and olivine are treated individually. The spectrum treatment consists in extracting peak information using

subsequent deconvolution. Since we are analyzing crystallized species, we expect the Raman signature to have a pure Lorentzian shape; however, a contribution of a Gaussian component in addition to the Lorentzian signal has been observed. This would likely be caused by intrinsic crystal defaults. Therefore, we used a Voigt simulation (i.e., a mix of Gaussian and Lorentzian deconvolution) which provides better simulations of our spectra. The simulation equation of a Voigt deconvolution is given below (Eq.1):

$$y = y_0 + A \frac{\frac{2 \ln 2}{\pi^2}}{\frac{3}{2}} \times \frac{W_L}{W_G^2} \times \int_{-\infty}^{\infty} \frac{e^{-t^2}}{\left(\sqrt{\ln 2} \times \frac{W_L}{W_G}\right)^2 + \left(\sqrt{4 \ln 2} \times \frac{x - x_c}{W_G} - t\right)^2} dt \quad (1)$$

Where y_0 and y are the intensity after a baseline correction of the spectrum and the intensity for the peak simulated, respectively. The parameter A represents the simulated area and W_G et W_L are respectively the Gaussian and Lorentzian widths for a given peak. The x parameter is the position in cm^{-1} ; where x is the Raman shift and x_c is the derived peak position simulated in cm^{-1} . Finally, in Eq. 1, t is the time component. Since the Raman spectra are not time-dependent, t is set to 0. We reported in the Supplementary Material (Table 1) all peaks simulated for mineral pure spectrum, with their specifics parameters (width, position, area). For clarity, simulations of silicate and sulfate minerals pure spectra are only shown in the Supplementary material (Fig.S1).

Due to the strong overlapping between the different spectral lines in the recovered average Raman spectrum for each pellet, it was not possible to perform the simulation of all the identified peaks for pure spectrum

of minerals reported in Table 2. For instance, clinopyroxene has a main peak at 1006 cm⁻¹ comparable to the one in gypsum Raman spectrum. Therefore, simulating those two peaks in the average mixed spectrum is complicated by their proximity and relevant simulation could not be achieved. Hence, for each species, we have selected peaks that are distinct in their position and indicated in Table 3.

The protocol to simulate Raman peaks is fully described in previous studies and is routinely used for the quantification of volatiles species in silicate glasses (Mysen and Virgo 1980a, b; Mercier et al. 2009; Morizet et al. 2013, 2017). First, we have fixed the peak position and widths (Gaussian and Lorentzian), leaving only the peak area optimized. Position is then optimized as we observed slight variations in the peak position in our mixture spectrum compared to the position derived from the acquired pure spectrum. These variations could be due to the dependence of the Raman signature on crystal orientation or unaccounted chemical heterogeneity. Gaussian and Lorentzian widths are also optimized to better adjust our simulations. This procedure is repeated several times until the chi-square (χ^2 parameter representing the robustness of the fit) is the lowest possible and the residual are small (see Figure 3).

With parameters extracted from simulations, we were able to calculate the mixing proportion present in the analyzed pellet. We determined a ratio R between the simulated area for the peak of the mixed spectrum and that of the pure spectrum such as:

$$R = \frac{A_{mixture}}{A_{pure}} \quad (2)$$

In Eq.2, A represents the area determined with a Voigt simulation for a same peak for the mixture ($A_{mixture}$) and the pure Raman spectrum (A_{pure}). This method differs from previous Raman calibrations studies of Kontoyannis et al. (1997) and Kriskova et al. (2013) where peak intensities were chosen instead of areas. Since we observed several variations in intensity and peak positions between pure spectrum and the average spectrum of the mixture, we consider that peak areas averaged out every possible variation between acquisitions with the 300 grooves/mm grating. The ratios are then normalized to obtain the result in weight fraction (WF). This proportion is then assimilated to a coefficient “a”:

$$a = \frac{\Sigma A_{gypsum}}{\Sigma A_{mineral}} \quad (3)$$

with A being peak areas for gypsum (A_{gypsum}) and for mineral in the mixture ($A_{mineral}$). In case of the ternary mixtures with more than 2 peaks simulated for one mineral, $A_{mineral}$ is entirely summed in the denominator. Examples of mineral pure spectrum and mixture deconvolutions are provided in the Supplementary Material (Fig.S1).

3. Results

3.1. Binary and ternary mixtures with Ca-sulfate:

A typical example of the spectral treatment is presented in Figure 3. In Figure 3A, Raman spectra collected represents olivine and gypsum

mixtures with: $WF_{\text{gypsum}} = 0.2, 0.1, 0.05$ and 0.01 . The Raman spectra
 obtained for the mixtures with other minerals (pyroxenes and
 plagioclase) are reported in the Supplementary Material (Fig.S2). In
 Figure 3A, it can be observed that the peak intensity for ν_1 gypsum at
 1006 cm^{-1} increases with increasing the proportion of gypsum in the
 mixture. For instance, in GOLI80 $WF_{\text{gypsum}} = 0.20$ (see Table 3 for
 theoretical WF of each mixture), the 1006 cm^{-1} symmetric stretch peak
 is more intense as compared to the one in GOLI90 ($WF_{\text{gypsum}} = 0.10$).
 For these two mixtures, the measured intensity in the SO_4 vibrations
 peak is twice for GOLI80 as compared to the one in GOLI90 which
 appears to be consistent with the prepared compositions (Table 3).
 Although the gypsum content in the GOLI99 mixture is extremely low
 ($WF_{\text{gypsum}} = 0.01$), the peak at 1006 cm^{-1} is still detected because of the
 strong Raman activity of symmetric stretch of the S-O bonds in SO_4
 molecular groups in gypsum (see Figure 3A).

We chose to simulate three different peaks in the $890\text{-}1100 \text{ cm}^{-1}$ region
 and located at $914, 958$ for olivine and 1006 cm^{-1} for gypsum (Figure
 3). For on olivine mixtures, relevant results were obtained when
 considering two Raman peaks identified in Table 2: 914 cm^{-1} for olivine
 and 1006 cm^{-1} for gypsum. In order to avoid contribution of the 1006
 cm^{-1} gypsum peak over the 950 cm^{-1} of olivine (see on Figure 3E-H),
 we have simulated the olivine peak at 914 cm^{-1} for our simulations. The
 robustness of our simulations is asserted by the small residual observed
 in Figure 3E-H. For a theoretical proportion mixture of 0.80 and 0.20
 weight fraction of olivine and gypsum respectively (Figure 3D), the

calculated proportions (from Eq. 2 and 3) are 0.79 (0.08, error relative to simulations) for olivine and 0.21 (0.01) for gypsum (Figure 3H). With lower Ca-sulfate proportion, we obtain consistent results in between the measured and theoretical mixtures. For initial proportions at 0.90 and 0.10, we calculate 0.91 (0.01) for olivine and 0.09 (0) for gypsum (Figure 3C and 3G). The same applies with the 0.01 and 0.05 mixtures of gypsum where 0.01 (0.01) and 0.06 (0) weight fraction of gypsum is calculated respectively, as shown in Figure 3A,B and Figure 3E,F.

On the Figure 4 is showed the calculated coefficients from simulated areas in each mixture (see Eq.3) as a function of the theoretical CaSO_4 content. The results are represented for the different mixtures with basaltic minerals: plagioclase-gypsum mixture in Figure 4A, orthopyroxene-gypsum in Figure 4B, clinopyroxene and olivine-gypsum in Figure 4C and 4D, respectively. Results from simulations are reported in Table 3. In Figure 4, we can observe that the best calibration (based on the linear regression coefficient R^2 which defines the quality of the linear regression on experimental data) is obtained for olivine-gypsum simulations comparing to the calibration with other silicate minerals. Simulations (Figures 4A to 4C) show good R^2 with 0.95, 0.94 and 0.96 for plagioclase, orthopyroxene and clinopyroxene respectively. The plagioclase-mixture with 0.20 weight fraction of gypsum (i.e., GPG80, see Table 3) has been calibrated using different peaks because of the use of the 785 nm laser for our analysis. Consequently, this point is not reported in Figure 4A.

We adopted the same procedure as for binary mixtures for ternary mixtures. The retained peak positions for our simulations are reported in Table 3. We considered the 300-390 cm^{-1} clinopyroxene peak areas, representative of Ca-O stretching vibrations, since they are isolated from the contribution of olivine and gypsum peaks in the Raman spectrum. For olivine, we consider the 947 cm^{-1} , one of SiO_4 symmetric stretching vibrations signatures, and 485 cm^{-1} for gypsum which represents the bending of SO_4 molecules. Those peaks were selected because they were the most separated from each other.

Simulations results and derived coefficients are reported in Table 3. We established a calibration expressed with the coefficient calculated (Eq.3) from areas simulated for each mineral according to the initial weight fraction of gypsum, indicated in Figure 5. In the Figure 5, we obtained a good calibration with $R^2 = 0.99$ on ternary mixtures.

3.4. Binary mixtures with Mg-sulfate

As for Ca-sulfate mixtures, we proceeded with the same method for pellets containing Mg-sulfate. We reported results from Mg-sulfate calibration on Figure 6 where the same mixtures of natural silicate minerals of olivine, pyroxenes and plagioclase are represented. In Figures 6A and 6C, pyroxenes calibration with Mg-sulfate are showed. As we can see on these results, the R^2 is fairly good (0.86 for orthopyroxene mixtures and 0.85 for clinopyroxene) and initial proportions of Mg-sulfate can be well estimated from our method.

Plagioclase mixtures with Mg-sulfate is reported on Figure 6B, where we obtained $R^2=0.43$ and show the less consistent results. Finally, olivine mixtures with initial proportions of Mg-sulfate (Figure 6D) result in a $R^2=0.69$. All results of calculated mixtures proportions are reported in Table 3.

4. Discussion

Binary and ternary mixtures with sulfates were calibrated with several proportions of sulfate tested. In this section, we discuss the limit of our calibration method and its application to the martian context.

4.1. Detection limit of sulfur:

In Figure 4 we have reported results from binary mixtures of gypsum. We reported error bars extracted from errors under peak areas simulated. As can be observed in Figures 4B and 4C, corresponding to pyroxene-bearing mixtures, samples with 0.03 and 0.01 weight fractions of gypsum present a significant vertical error. Some selected peaks for the calibration do not exhibit a high Raman activity but we had to select those peaks, , due to the necessity of choosing individual peaks for our simulations. In simulation results shown in Table 3, we can see that we have still a good agreement in between the calculated proportions and the initial proportions within the mixtures. Considering that some of molecule vibrations are less Raman active relative to Raman spectroscopy, we consider that our method of calibration is reliable until $WF_{\text{sulfate}} = 0.03$ weight fraction in a mechanical mixture.

Knowing this detection limit of our calibration, we can extrapolate this method to Martian rocks. With the proposed method and the calibration equations, S could be determined at the surface of Mars for a sedimentary rock containing sulfate until approximately $WF_S = 0.007$ weight fraction (i.e., 7 000 ppm). Below this S content, our calibration can still be applied, but the errors will be higher and results might not be reliable.

4.2. Application to the calibration curves to the determination of sulfur on the Martian surface

Results provided by the calibration are specified in Figure 7 for all mixtures created. On Figure 7, we can see the good agreement of our calibration method. This plot showed us that the calculated proportions of gypsum are close to the theoretical proportions and all data points are aligned along the 1:1 line. Ternary mixtures with gypsum are also represented and are in good accordance. Mg-sulfate mixtures in Figure 7 showed us that the calibration is also good and data points are aligned along the 1:1 line.

We have reported on Table 3, all calibrations equations calculated from our calibration method for gypsum and Mg-sulfate mixtures.

As a result, we can determine the sulfate content in a mixture with olivine, pyroxenes and plagioclase in unknown proportions according to equations extracted from our simulations shown in Figures 4, 5 and 6. Using a Raman spectrum obtained on the surface of Mars of a

mechanical solid mixture containing sulfate (Ca or Mg), and simulating specific peaks (reported in Table 3), a coefficient can be calculated (i.e., the "a" component in equations in Table 3).

The established calibration method based on Raman spectroscopy will be of use for the future 2020 Mars mission to quantify S abundance when present as sulfates. For the application of the present calibration, the peak selections from Raman spectrum must be conducted with care. We suggest using only the peaks mentioned in the present work and reported in the Supplementary Material (Table 1). However, this will be dependent on the resolution of the SuperCam Raman spectrometer and the quality of the acquired signal (Wiens et al. 2016). In the case of a low resolution, peaks with low intensities (for instance ν_3) will be difficult to constrain. However, other peaks mentioned in the Supplementary Material (Table 1), such as ν_1 or ν_2 can be well defined by the future rover and calibration can still be applicable (referred with the Table 1 in the Supplementary Material peak information). Since our analyses were performed with a high resolution Raman spectrometer, further analyses will be acquired with a pulsed-Raman with distance from the sample similar to the one presupposed for SuperCam in order to compare data and modify, if necessary, the calibration.

Furthermore, Mars mineralogy has been partly investigated using remote sensing and rover data, as well as Martian meteorites, showing that pigeonite and augite are the two most common pyroxenes found in Martian rocks (both are clinopyroxenes but with low Ca content for pigeonite) (e.g., Lodders 1998, Agee et al. 2004; Mustard et al. 2005;

Cousin et al. 2017; Morrison et al. 2017). Mg-rich olivine, orthopyroxene and plagioclase have also been detected in Martian meteorites and at the surface of the planet (Agee et al. 2004; Mustard et al. 2005; Dehouck et al. 2014; Cousin et al. 2017; Morrison et al. 2017). Nonetheless, Fe-rich olivine can be expected in small amounts which only differs in spectral signature by the relative intensity between the double peak around 800-850 cm^{-1} . Since our calibration is not based on those peaks (see Table 3), the quantification of sulfate with fayalite can still be possible. Plagioclase such as anorthite may be the most common feldspar on Mars (Bish et al. 2013, Blake et al. 2013, Vaniman et al. 2014) although andesine has been observed as the predominant plagioclase at Gale crater by the Curiosity rover instruments (Sautter et al. 2016, Morrison et al. 2017). Consequently, the proposed calibration method can be useable for a mixture of sedimentary rocks containing sulfates and silicate minerals even if the minerals present does not have the same chemical composition within a solid solution as used in our study.

5. Summary

In the present study, we have prepared pellets by mixing Ca and Mg sulfates with silicate minerals commonly found in basalt (olivine, pyroxenes and plagioclase) in order to investigate the Raman signature of multi-minerallic mechanical assemblages. The main objective was to establish a relevant calibration for the determination of S content at the

surface of Mars with analytical conditions close to the future Raman spectrometer on SuperCam equipment for the 2020 spatial mission. Calibration equations were obtained for both binary and ternary mixtures of CaSO_4 with minerals for a range of gypsum of 0.01 to 0.20 weight fraction. Equations were also estimated from Mg-sulfate mixtures with initial proportion of 0.03 to 0.20 weight fraction.

The protocol used in this study involves simulations of the resulting average Raman spectrum using a Voigt distribution on peaks attributed to each mineral. The simulation of the entire Raman spectrum is not simulated with an enough good accuracy and careful attention is necessary for peak identifications. The actual method could be applied to the quantitative characterization of the soil of Mars which is recognized to present sedimentary rocks containing sulfates and silicate minerals obtained from bedrock erosion.

Given our equations extracted from calibrations on both Mg and Ca sulfates, we would be able to calculate a coefficient from a given Raman spectrum acquired on Mars and treated according to specific peak simulations. Coupling this coefficient with the proper calibration equation (i.e., when knowing the mineralogical characterization of the mixture analyzed) we can estimate the proportion of this sulfate in weight fraction. By extent, this calibration could be used to constraint part of the S content at the surface carried by sulfate minerals phases. We have estimated the detection limit of S at 7 000 ppm which is well below the current detection limit by the LIBS technique (e.g., Wiens et al. 2012; Nachon et al. 2014, Anderson et al. 2017). Nevertheless,

further calibrations are requested involving more complex mineral mixtures, including other sulfates (Fe-sulfate) and sulfides, and mixtures with more than four compounds.

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Figure captions:

Figure 1: A: Pellet of a 90/10 mixture of olivine (weight fraction $WF_{\text{olivine}} = 0.90$) and gypsum ($WF_{\text{gypsum}} = 0.10$) named GOLI90; B: 5 mm mapping of spectrum intensities acquired by Raman spectroscopy showing the homogeneity of GOLI90; C: The average spectrum issued from the 5 mm mapping of GOLI90 with ν_1 peaks (symmetric stretching mode of SiO_4 and SO_4 molecules) of olivine and gypsum reported.

Figure 2: Multi-minerallic pure Raman spectrum with their acquisition time for A : olivine ; B: Mg-sulfate; C: gypsum; D: plagioclase; E: clinopyroxene; and F: orthopyroxene. Significant peaks for each minerals has been reported in graphs. For peak assignments see Table 2.

Figure 3: A: Global spectra for every mixtures of olivine with gypsum in different proportions: A: $WF_{\text{olivine}} = 0.99$; B: $WF_{\text{olivine}} = 0.95$; C: $WF_{\text{olivine}} = 0.90$; D: $WF_{\text{olivine}} = 0.80$; with their main peaks reported. Variations of gypsum ν_1 (symmetric stretch of SO_4) peak intensity are shown in red arrows. Zoom ($890\text{-}1100\text{ cm}^{-1}$ area) of spectra acquired by Raman spectroscopy after mapping, from different mixtures of olivine with gypsum in several proportions: E: $WF_{\text{gypsum}} = 0.01$; F: $WF_{\text{gypsum}} = 0.05$; G: $WF_{\text{gypsum}} = 0.10$; H: $WF_{\text{gypsum}} = 0.20$. Spectra are correlated with peak simulations: blue for olivine peaks and green for gypsum's. Red curves are cumulative peaks and black dotted lines are residuals from simulations. Weight fractions are calculated with peak simulations and reported in boxes in each graph and in Table 3.

Figure 4: Calibration coefficients calculated from simulated areas of gypsum and mineral mixed versus the weight fraction (WF) of gypsum theoretical. Black square are samples simulated with their relative errors. Red lines correspond to calibration lines extrapolated from calibration coefficients depending on theoretical weight fraction of gypsum. Calibration lines established on four binary mixtures of: A: plagioclase; B: orthopyroxene; C: clinopyroxene; D: olivine; with gypsum in different proportions ($WF_{\text{gypsum}} = 0.20, 0.10, 0.05, 0.03, 0.01$). Equations and linear regression coefficient (R^2) of each calibration lines are reported in boxes in each graph.

Figure 5: Calibration line for ternary mixtures of gypsum ($WF_{\text{gypsum}} = 0.2, 0.1, 0.05$) with olivine ($WF_{\text{olivine}} = 0.40, 0.50, 0.50$) and clinopyroxene ($WF_{\text{clinopyroxene}} = 0.40, 0.40, 0.45$). Black squares are simulations results with their errors (black vertical lines). Red line is the calibration line calculated from simulations results. Equation and regression linear coefficient (R^2) are specified in the graph box.

Figure 6: Calibration coefficients calculated from simulated areas of Mg-sulfate and mineral mixed versus the theoretical weight fraction (WF) of the sulfate. Black square are samples simulated with their relative errors. Red lines correspond to calibration lines extrapolated from calibration coefficients depending on theoretical weight fraction of Mg-sulfate. Calibration lines established on four binary mixtures of: A: orthopyroxene; B: plagioclase; C: clinopyroxene; D: olivine; with Mg-sulfate in different proportions ($WF_{\text{gypsum}} = 0.20, 0.10, 0.05$ and 0.03). Equations and linear regression coefficients (R^2) of each calibration lines are reported in boxes for every graph.

Figure 7: Weight fractions calculated for sulfates (Ca and Mg-sulfate) depending on its theoretical weight fraction in each mixture of olivine, clinopyroxene, orthopyroxene and plagioclase. In black, gypsum binary samples are represented. Mg-sulfate mixtures are in blue in the figure. Red diamonds: ternary mixtures of gypsum.

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890 **Tables :**

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Mineral	Origin	Chemical formula
Olivine	Forsterite from Maar de Borée (France)	$\text{Si}_{1.00} \text{Fe}_{0.18} \text{Mg}_{1.78} \text{Na}_{0.01} \text{O}_4$
Clinopyroxene	Augite from Maar de Borée (France)	$\text{Si}_{1.78} \text{Al}_{0.23} \text{Fe}_{0.09} \text{Mg}_{0.95} \text{Ca}_{0.57} \text{Na}_{0.11} \text{O}_6$
Orthopyroxene	Enstatite from Maar de Borée (France)	$\text{Si}_{1.85} \text{Al}_{0.16} \text{Fe}_{0.16} \text{Mg}_{1.62} \text{Ca}_{0.02} \text{Na}_{0.02} \text{O}_6$
Plagioclase	Anorthite from a diorite of StillWater (USA)	$\text{Si}_{2.21} \text{Al}_{1.76} \text{Fe}_{0.01} \text{Mg}_{0.01} \text{Ca}_{0.85} \text{Na}_{0.16} \text{O}_8$
Gypsum	Synthetic calcium sulfate dehydrated from MERCK (Germany)	$\text{CaSO}_4 \cdot (2\text{H}_2\text{O})$
Mg-sulfate	Synthetic magnesium sulfate hydrated from LABOSI (France)	$\text{MgSO}_4 \cdot (n\text{H}_2\text{O})$

Table 1: Origins and chemical compositions of basaltic minerals (olivine, pyroxenes and plagioclase, determined by Scanning Electron Microscopy (SEM) analysis) and sulfates used in this study.

Raman shift (cm^{-1})	Mode assignments
Orthopyroxene [1], [2], [3], [4]	
225-325	Fe-O octahedron
375-490	Mg-O octahedron
650-750	Si-O ν_3^c

800-1100	Si-O ν_1^a
Clinopyroxene [1], [2],[3], [4]	
230 and 327	M-O* stretching
255 and 360	Ca-O stretching
393	Mg-O stretch
665	Si-O-Si ν_2^b
1010	Si-O ν_1
Olivine [5], [6], [7], [8]	
820	Si-O ν_1
850	Si-O ν_1
914	Si-O ν_3
950	Si-O ν_3
Plagioclase [9] and [3]	
200-400	Lattice modes
420-503	Al-O or Si-O ν_1
900-1000	Si-O-Al ν_3
> 1000	Si-O-Si ν_3
Gypsum [10], [11], [12]	
400-500	SO ₄ ν_2
600-700	SO ₄ ν_4^d
1006	SO ₄ ν_1
>1100	SO ₄ ν_3
Mg-sulfate [11]	
400 - 600	SO ₄ ν_2
620	SO ₄ ν_4
1040	SO ₄ ν_1
1050 – 1150	SO ₄ ν_3

^a ν_1 : Symmetric stretch

^b ν_2 : symmetric bending

^c ν_3 : antisymmetric stretch

^d ν_4 : antisymmetric bending

* With M referring as different metal cations present in the chemical structure of the mineral (Buzgar et al. 2009)

Table 2: Specific peak assignments for each mineral used in this study. Principal peaks observed in spectra are described according to [1]: Huang et al. (2000), [2]: Prencipe et al. (2011), [3]: Sharma and al. (1983), [4]: Wang et al. (2001) [5]: Chopelas (1991), [6]: Kolesov and Tanskaya (1996), [7]: Kolesov and Geiger (2004), [8]: McKeown et al. (2010), [9]: Freeman et al.

(2008) [10]: Bishop et al. (2014), [11]: Buzgar et al. (2009) and [12]: Knittle et al. (2001).

Table 3: Samples created in this study for binary and ternary mixtures with sulfates (Ca and Mg) and basaltic minerals (i.e olivine, orthopyroxene, clinopyroxene and plagioclase). Peak simulated in each mixture are reported, followed by the calibration equation resulting from calibrations. Weight fractions (WF) theoretical, WF calculated and coefficients (a) are reported for each mixture. Errors relative to calculations are reported next to the WF calculated and coefficients.

Sample name	WF theoretical	WF calculated	a
Olivine – Gypsum			
Peak simulated : 914 and 1006 cm ⁻¹			

Calibration equation : $a = 81.36 \times WF_{\text{sulfate theoretical}}$			
GOLI80	0.80 - 0.20	0.79 (0.08) – 0.21 (0.01)	17.21(3.20)
GOLI90	0.90 – 0.10	0.91 (0.01) – 0.09 (0)	6.55 (0.36)
GOLI95	0.95 – 0.05	0.94 (0.01) – 0.06 (0)	4.04 (0.22)
GOLI97	0.97 – 0.03	0.97 (0.02) – 0.03 (0.04)	1.87 (0.88)
GOLI99	0.99 – 0.01	0.99 (0) – 0.01 (0)	0.76 (0.08)
Orthopyroxene - Gypsum			
Peak simulated : 230 and 491 cm^{-1}			
Calibration equation : $a = 8.23 \times WF_{\text{sulfate theoretical}}$			
GOPX80	0.80 – 0.20	0.85 (0.04) – 0.15 (0.03)	1.52 (0.01)
GOPX90	0.90 – 0.10	0.89 (0.03) – 0.11 (0.04)	0.99 (0.12)
GOPX95	0.95 – 0.05	0.94 (0.02) – 0.06 (0.05)	0.51 (0.01)
GOPX97	0.97 – 0.03	0.96 (0.01) – 0.04 (0.08)	0.34 (0.35)
GOPX99	0.99 – 0.01	0.98 (0.01) – 0.02 (0.05)	0.19 (0.23)
Clinopyroxene – Gypsum			
Peak simulated : 362 and 412 cm^{-1}			
Calibration equation : $a = 1.93 \times WF_{\text{sulfate theoretical}}$			
GCPX80	0.80 – 0.20	0.82 (0.02) – 0.18 (0.02)	0.40 (0.49)
GCPX90	0.90 – 0.10	0.92 (0.01) – 0.08 (0.03)	0.15 (0.69)
GCPX95	0.95 – 0.05	0.93 (0) – 0.07 (0.01)	0.13 (0.38)
GCPX97	0.97 – 0.03	0.96 (0.01) – 0.04 (0.06)	0.07 (0.54)
GCPX99	0.99 – 0.01	0.99 (0) – 0.01 (0)	0.02 (0.42)
Plagioclase - Gypsum			
Peak simulated : 504 and 1006 cm^{-1}			
Calibration equation : $a = 59.83 \times WF_{\text{sulfate theoretical}}$			
GPG80	0.80 – 0.20	0.83 (0.01) – 0.17 (0.01)	1.19 (0.02)
GPG90	0.90 – 0.10	0.90 (0.03) – 0.10 (0.01)	6.24 (0.89)
GPG95	0.95 – 0.05	0.95 (0.01) – 0.05 (0)	2.75 (0.10)
GPG97	0.97 – 0.03	0.98 (0.01) – 0.02 (0.01)	1.17 (0.04)
GPG99	0.99 – 0.01	0.98 (0) – 0.02 (0)	1.15 (0.01)
Olivine – Clinopyroxene - Gypsum			
Peak simulated : 947 - 310/328/359/384 - 485			
Calibration equation: $a = 1.71 \times W_{\text{sulfate theoretical}}$			
GOLCX80	0.40 – 0.40 – 0.20	0.35 (0.27) – 0.50 (0.01) – 0.15 (0.06)	0.35 (0.05)
GOLCX90	0.50 – 0.40 – 0.10	0.49 (0.16) – 0.35 (0.06) – 0.05 (0.03)	0.15 (0.03)
GOLCX95	0.50 – 0.45 – 0.05	0.39 (0.17) – 0.44 (0.07) – 0.03 (0.03)	0.07 (0.02)

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Sample name	WF theoretical	WF calculated	a
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Olivine - Mg-sulfate			
Peak simulated : 950 and 1040 cm ⁻¹			
Calibration equation: $a = 5.26 \times WF_{\text{sulfate theoretical}}$			
MgOLI80	0.80 - 0.20	0.84 (0.05) - 0.16 (0.09)	0.90 (0.19)
MgOLI90	0.90 - 0.10	0.86 (0.02) - 0.14 (0.03)	0.81 (0.03)
MgOLI95	0.95 - 0.05	0.94 (0.03) - 0.06 (0.19)	0.30 (0.59)
MgOLI97	0.97 - 0.03	0.95 (0.02) - 0.05 (0.20)	0.23 (0.63)
Orthopyroxene - Mg-sulfate			
Peak simulated: 330/370/400 - 1040 cm ⁻¹			
Calibration equation: $a = 2.19 \times WF_{\text{sulfate theoretical}}$			
MgOPX80	0.80 - 0.20	0.82 (0.02) - 0.18 (0.02)	0.43 (0.02)
MgOPX90	0.90 - 0.10	0.89 (0.01) - 0.11 (0.02)	0.25 (0)
MgOPX95	0.95 - 0.05	0.90 (0.01) - 0.10 (0.02)	0.20 (0)
MgOPX97	0.97 - 0.03	0.96 (0) - 0.04 (0.01)	0.08 (0)
Clinopyroxene - Mg-sulfate			
Peak simulated: 666/1006 and 1040 cm ⁻¹			
Calibration equation: $a = 1.05 \times WF_{\text{sulfate theoretical}}$			
MgCPX80	0.80 - 0.20	0.82 (0) - 0.18 (0.04)	0.19 (0.01)
MgCPX90	0.90 - 0.10	0.87 (0) - 0.13 (0.03)	0.14 (0.01)
MgCPX95	0.95 - 0.05	0.94 (0) - 0.06 (0.04)	0.06 (0.01)
MgCPX97	0.97 - 0.03	0.96 (0) - 0.04 (0.03)	0.03 (0.01)
Plagioclase - Mg-sulfate			
Peak simulated: 750 and 1113 cm ⁻¹			
Calibration equation: $a = 2.88 \times WF_{\text{sulfate theoretical}}$			
MgPG80	0.80 - 0.20	0.86 (0.04) - 0.14 (0.09)	0.51 (0.15)
MgPG90	0.90 - 0.10	0.91 (0.03) - 0.09 (0.12)	0.33 (0.21)
MgPG95	0.95 - 0.05	0.93 (0.01) - 0.07 (0.07)	0.23 (0.11)
MgPG97	0.97 - 0.03	0.93 (0.02) - 0.07 (0.06)	0.22 (0.10)

Table 3 (suite)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Supplementary material:

Figure caption:

Figure 1: Deconvolution of minerals pure spectrum for A: gypsum; B: clinopyroxene; C: orthopyroxene; D: plagioclase; E: olivine; and F: Mg-sulfate. With individual peaks simulated in blue, cumulative peaks simulated in red dashed lines and residuals in black dotted lines. Analytical parameters (acquisition time and confocal mode) are described for each spectrum.

Figure 2: Peak simulations for the other different mixtures: A: orthopyroxene-gypsum mixture with initial proportion of 0.8 and 0.2 respectively; B: plagioclase-gypsum mixture with theoretical proportions of 0.9 and 0.1; C: olivine-mgsulfate mixture (theoretical proportions: $WF_{\text{olivine}}=0.8$ and $WF_{\text{Mg-sulfate}}=0.2$); D: clinopyroxene-gypsum mixture of theoretical weight fraction of 0.90 and 0.10 respectively. Green peaks are attributed to sulfates vibrations (Ca or Mg) and blue ones for silicate minerals. Red dashed and black dotted lines are cumulative peaks simulated and residuals left after simulations. Weight fraction calculated by simulations for examples shown in this figure are reported in each graph. All results from simulations on the different mixtures are described in **Table 4**.