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

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11
12 **Abstract**

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

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

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

37

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

40

41 **1. Introduction**

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

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

59 The Curiosity rover currently analyzes rocks and soils on Mars using
60 Laser Induced Breakdown Spectroscopy (LIBS) (Maurice et al. 2012;
61 Wiens et al. 2012; Meslin et al. 2013; Maurice et al. 2017; Cousin et al.
62 2017; Mangold et al. 2017). The LIBS equipment enables the detection
63 and quantification of all major elements (e.g., Si, Al) and the detection
64 of volatiles and halogens (C-H-O-N-P-S-F-Cl). However, the detection
65 of these elements is difficult with this method because of the high
66 excitation energies, their peak positions near the instrument limit and
67 the coupling of different major elements rays (e.g. Sallé et al. 2004,
68 Clegg et al. 2007). This results in varying detection levels and lack of
69 quantification for some of them. In particular, the detection limit for S
70 is of 5 to 10 wt% S (Wiens et al. 2012). Quantitative determination of

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

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

83 Previous studies have focused on the quantification of volatile species
84 (H_2O , CO_2 and SO_4^{2-}) in silicate glasses with application to Earth
85 volcanism (Zajacz et al. 2005; Mercier et al. 2009; Le Losq et al. 2012;
86 Morizet et al. 2013, 2017). However, up to now, the quantification of
87 individual mineral species in multi-minerallic mechanical mixtures
88 have been merely addressed using Raman spectroscopy (Kontoyannis
89 et al. 1997; Jehlicka et al. 2009; Noguchi et al. 2009; Kriskova et al.
90 2013). Jehlicka et al. (2009) have shown, the possibility to quantify
91 multi-component mixtures with a portable micro-Raman spectrometer.
92 In Kriskova et al. (2013) and Noguchi et al. (2009) only multi-
93 minerallic mixtures with carbonates have been studied. Kontoyannis et
94 al. (1997) have established a calibration on carbonates mixed with

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

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

110 **2. Methods**

111 *2.1. Multi-minerallic mixtures preparation:*

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

119 $\text{Na}_{0.01} \text{O}_4$). Pyroxenes have compositions close to enstatite ($\text{Si}_{1.85} \text{Al}_{0.16}$
120 $\text{Fe}_{0.16} \text{Mg}_{1.62} \text{Ca}_{0.02} \text{Na}_{0.02} \text{O}_6$) and augite end-members ($\text{Si}_{1.78} \text{Al}_{0.23} \text{Fe}_{0.09}$
121 $\text{Mg}_{0.95} \text{Ca}_{0.57} \text{Na}_{0.11} \text{O}_6$). The plagioclase from this study is Ca-rich and
122 has composition close to the anorthite end-member ($\text{Si}_{2.21} \text{Al}_{1.76} \text{Fe}_{0.01}$
123 $\text{Mg}_{0.01} \text{Ca}_{0.85} \text{Na}_{0.16} \text{O}_8$). Natural silicate minerals were crushed in a
124 steel-mortar with pestle and crushed again in an agate mortar. Ethanol
125 was added during crushing to clean the samples.

126 Mixtures between silicate minerals and sulfates were prepared and
127 mixed in together. The resulting powder was not sieved because grain
128 size does not exceed 50 μm with this grinding procedure (see Figure
129 1A). Several samples at various sulfate proportions were prepared:
130 $\text{WF}_{\text{gypsum}} = 0.20, 0.10, 0.05, 0.03, 0.01$ and $\text{WF}_{\text{mg-sulfate}} = 0.20, 0.10, 0.05$
131 and 0.03; where WF represents the Weight Fraction of sulfates. Ternary
132 mixtures were prepared with Ca-sulfate, clinopyroxene and olivine.
133 Gypsum, clinopyroxene and olivine concentrations in mixtures were
134 respectively: $\text{WF}_{\text{gypsum}} = 0.20, 0.10$ and 0.05, $\text{WF}_{\text{clinopyroxene}} = 0.40, 0.40$
135 and 0.45, $\text{WF}_{\text{olivine}} = 0.40, 0.50$ and 0.50. The investigated sulfate
136 concentrations are consistent with the abundances of these minerals as
137 locally estimated in evaporites at Meridiani Planum (McLennan et al.
138 2006) or in fluvio-lacustrine sedimentary rocks at Gale crater (Vaniman
139 et al. 2017).

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

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

147

148 *2.2. Raman spectroscopy*

149 The non-destructive nature of the Raman analyses will allow
150 mineralogical characterization (e.g., Reynard et al. 2012) of the Martian
151 rocks without any sample preparation. The Raman spectroscopy uses a
152 laser with a specific wavelength, which will excite molecules (Brawer
153 and White 1975; Mysen and Virgo 1980a, b; McMillan 1984; Rossano
154 and Mysen 2009; Rull 2012). The excitation of molecules produces a
155 Raman shift (i.e., the wavenumber differences between the signal from
156 the laser and the response of excited molecules; Delhaye and
157 Dhamelincourt 1975; Hoehse et al. 2009; Dubessy et al. 2012). The
158 strongest signatures received and detected by the Raman spectrometer
159 are called ν_1 signatures and correspond to the symmetric stretching of
160 the molecules excited by the laser (Rossano and Mysen 2009; Rull
161 2012).

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

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

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

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

191 single Raman spectrum representative of the analyzed mixture (Figure
192 1C).

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

202 *2.2.1 Mineral Raman spectra:*

203 The Raman spectrum of each individual mineral used in this study is
204 reported in Figure 2. The gypsum Raman pure spectrum (Figure 2A)
205 exhibits several peaks with low intensities in the 400-700 cm^{-1} region
206 corresponding to the symmetric (400-500 cm^{-1}) and antisymmetric
207 (600-700 cm^{-1}) bending vibrations of SO_4 molecules (ν_2 and ν_4). The
208 strong peak at 1006 cm^{-1} corresponds to the symmetric stretching
209 vibration (or ν_1) of S-O bonds in SO_4 molecular groups (Knittle et al.
210 2001; Buzgar et al. 2009; Bishop et al. 2014). Peaks observed in the
211 highest frequency region ($> 1100 \text{ cm}^{-1}$) are attributed to antisymmetric
212 stretch vibrations (ν_3) of SO_4 and have a weak Raman activity.

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

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

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

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

227 Pyroxenes spectra shown in Figures 2E and 2F are similar in the high
228 frequency region ($> 600 \text{ cm}^{-1}$) where bending and stretching vibrations
229 of SiO_4 tetrahedrons are observed, for signatures around 660 and 1006
230 cm^{-1} respectively. At low frequency, in the $200\text{-}400 \text{ cm}^{-1}$ region, it is
231 possible to discriminate clinopyroxene from orthopyroxene, which does
232 not present the same peak intensities. In this region, vibrations related
233 to Fe, Ca and Mg molecular environments are responsible for the
234 observed peaks (Sharma et al. 1983; Huang et al. 2000; Wang et al.
235 2001; Prencipe et al. 2011). Specific peak assignments for each mineral
236 in this study are described in Table 2.

237 *2.2.2. Analytical conditions useable for the SuperCam instrument:*

238 The new rover send for the 2020 Mars mission will use a laser-pulse
239 Raman spectrometer with a 532 nm solid-state laser (Olila et al. 2012,
240 Wiens et al. 2016). The rover will target rocks and soil from several
241 meters away and with a resolution on the order of 10 cm^{-1} (Wiens et al.
242 2016).

243 Knowing those conditions, we performed several tests to analyze the
244 pellets. A map size of 5 by 5 mm was necessary to reproduce in an
245 adequate way the mineral mixtures. Using 2 by 2 or 3 by 3 mm map
246 size was not sufficient to retrieve the initial mineral proportions in the
247 mixture. Furthermore, the 5 by 5 mm size map is also consistent with
248 the analytical conditions for the 2020 rover, which will have a large
249 analytical area. The adopted laboratory analytical conditions (i.e., focus
250 20X, 300 grooves/mm grating and non-confocal mode) were optimized
251 to obtained spectra that could be compared to the Raman spectra which
252 will be acquired by SuperCam.

253

254 *2.3. Calibration method:*

255 The calibration method in the present study is similar to that used by
256 Kontoyannis et al. (1997), Noguchi et al. (2009) and Kristova et al.
257 (2013). Our method is based on the spectral deconvolution of the
258 investigated pure minerals Raman spectrum presented in the previous
259 section. For instance, to establish a calibration on a gypsum-olivine
260 mixture, pure spectrum of gypsum and olivine are treated individually.
261 The spectrum treatment consists in extracting peak information using

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

$$270 \quad y = y_0 + A \frac{2 \ln 2}{\pi^2} \times \frac{W_L}{W_G^2} \times \int_{-\infty}^{\infty} \frac{e^{-t^2}}{\left(\sqrt{\ln 2} \times \frac{W_L}{W_G}\right)^2 + \left(\sqrt{4 \ln 2} \times \frac{x - x_c}{W_G} - t\right)^2} dt \quad (1)$$

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

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

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

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

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

310
$$R = \frac{A_{mixture}}{A_{pure}} \quad (2)$$

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

322
$$a = \frac{\Sigma A_{gypsum}}{\Sigma A_{mineral}} \quad (3)$$

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

328

329 **3. Results**

330 *3.1. Binary and ternary mixtures with Ca-sulfate:*

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

333 mixtures with: $WF_{\text{gypsum}} = 0.2, 0.1, 0.05$ and 0.01 . The Raman spectra
334 obtained for the mixtures with other minerals (pyroxenes and
335 plagioclase) are reported in the Supplementary Material (Fig.S2). In
336 Figure 3A, it can be observed that the peak intensity for ν_1 gypsum at
337 1006 cm^{-1} increases with increasing the proportion of gypsum in the
338 mixture. For instance, in GOLI80 $WF_{\text{gypsum}} = 0.20$ (see Table 3 for
339 theoretical WF of each mixture), the 1006 cm^{-1} symmetric stretch peak
340 is more intense as compared to the one in GOLI90 ($WF_{\text{gypsum}} = 0.10$).
341 For these two mixtures, the measured intensity in the SO_4 vibrations
342 peak is twice for GOLI80 as compared to the one in GOLI90 which
343 appears to be consistent with the prepared compositions (Table 3).
344 Although the gypsum content in the GOLI99 mixture is extremely low
345 ($WF_{\text{gypsum}} = 0.01$), the peak at 1006 cm^{-1} is still detected because of the
346 strong Raman activity of symmetric stretch of the S-O bonds in SO_4
347 molecular groups in gypsum (see Figure 3A).

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

358 calculated proportions (from Eq. 2 and 3) are 0.79 (0.08, error relative
359 to simulations) for olivine and 0.21 (0.01) for gypsum (Figure 3H).
360 With lower Ca-sulfate proportion, we obtain consistent results in
361 between the measured and theoretical mixtures. For initial proportions
362 at 0.90 and 0.10, we calculate 0.91 (0.01) for olivine and 0.09 (0) for
363 gypsum (Figure 3C and 3G). The same applies with the 0.01 and 0.05
364 mixtures of gypsum where 0.01 (0.01) and 0.06 (0) weight fraction of
365 gypsum is calculated respectively, as shown in Figure 3A,B and Figure
366 3E,F.

367 On the Figure 4 is showed the calculated coefficients from simulated
368 areas in each mixture (see Eq.3) as a function of the theoretical CaSO_4
369 content. The results are represented for the different mixtures with
370 basaltic minerals: plagioclase-gypsum mixture in Figure 4A,
371 orthopyroxene-gypsum in Figure 4B, clinopyroxene and olivine-
372 gypsum in Figure 4C and 4D, respectively. Results from simulations
373 are reported in Table 3. In Figure 4, we can observe that the best
374 calibration (based on the linear regression coefficient R^2 which defines
375 the quality of the linear regression on experimental data) is obtained for
376 olivine-gypsum simulations comparing to the calibration with other
377 silicate minerals. Simulations (Figures 4A to 4C) show good R^2 with
378 0.95, 0.94 and 0.96 for plagioclase, orthopyroxene and clinopyroxene
379 respectively. The plagioclase-mixture with 0.20 weight fraction of
380 gypsum (i.e., GPG80, see Table 3) has been calibrated using different
381 peaks because of the use of the 785 nm laser for our analysis.
382 Consequently, this point is not reported in Figure 4A.

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

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

397

398 *3.4. Binary mixtures with Mg-sulfate*

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

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

412

413 **4. Discussion**

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

417 *4.1. Detection limit of sulfur:*

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

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

438

439 *4.2. Application to the calibration curves to the determination of sulfur*
440 *on the Martian surface*

441 Results provided by the calibration are specified in Figure 7 for all
442 mixtures created. On Figure 7, we can see the good agreement of our
443 calibration method. This plot showed us that the calculated proportions
444 of gypsum are close to the theoretical proportions and all data points are
445 aligned along the 1:1 line. Ternary mixtures with gypsum are also
446 represented and are in good accordance. Mg-sulfate mixtures in Figure
447 7 showed us that the calibration is also good and data points are aligned
448 along the 1:1 line.

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

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

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

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

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

480 Cousin et al. 2017; Morrison et al. 2017). Mg-rich olivine,
481 orthopyroxene and plagioclase have also been detected in Martian
482 meteorites and at the surface of the planet(Agee et al. 2004; Mustard et
483 al. 2005; Dehouck et al. 2014; Cousin et al. 2017; Morrison et al. 2017).
484 Nonetheless, Fe-rich olivine can be expected in small amounts which
485 only differs in spectral signature by the relative intensity between the
486 double peak around 800-850 cm^{-1} . Since our calibration is not based on
487 those peaks (see Table 3), the quantification of sulfate with fayalite can
488 still be possible. Plagioclase such as anorthite may be the most common
489 feldspar on Mars (Bish et al. 2013, Blake et al. 2013, Vaniman et al.
490 2014) although andesine has been observed as the predominant
491 plagioclase at Gale crater by the Curiosity rover instruments (Sautter et
492 al. 2016, Morrison et al. 2017). Consequently, the proposed calibration
493 method can be useable for a mixture of sedimentary rocks containing
494 sulfates and silicate minerals even if the minerals present does not have
495 the same chemical composition within a solid solution as used in our
496 study.

497

498 **5. Summary**

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

504 surface of Mars with analytical conditions close to the future Raman
505 spectrometer on SuperCam equipment for the 2020 spatial mission.
506 Calibration equations were obtained for both binary and ternary
507 mixtures of CaSO₄ with minerals for a range of gypsum of 0.01 to 0.20
508 weight fraction. Equations were also estimated from Mg-sulfate
509 mixtures with initial proportion of 0.03 to 0.20 weight fraction.

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

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

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

532

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541

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813

814 **Figure captions:**

815 Figure 1: A: Pellet of a 90/10 mixture of olivine (weight fraction
816 $WF_{\text{olivine}} = 0.90$) and gypsum ($WF_{\text{gypsum}} = 0.10$) named GOLI90; B: 5
817 mm mapping of spectrum intensities acquired by Raman spectroscopy
818 showing the homogeneity of GOLI90; C: The average spectrum issued
819 from the 5 mm mapping of GOLI90 with ν_1 peaks (symmetric stretching
820 mode of SiO_4 and SO_4 molecules) of olivine and gypsum reported.

821 Figure 2: Multi-minerallic pure Raman spectrum with their acquisition
822 time for A : olivine ; B: Mg-sulfate; C: gypsum; D: plagioclase; E:
823 clinopyroxene; and F: orthopyroxene. Significant peaks for each
824 minerals has been reported in graphs. For peak assignments see Table
825 2.

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827 Figure 3: A: Global spectra for every mixtures of olivine with gypsum
828 in different proportions: A: $WF_{\text{olivine}} = 0.99$; B: $WF_{\text{olivine}} = 0.95$; C:
829 $WF_{\text{olivine}} = 0.90$; D: $WF_{\text{olivine}} = 0.80$; with their main peaks reported.
830 Variations of gypsum ν_1 (symmetric stretch of SO_4) peak intensity are
831 shown in red arrows. Zoom ($890\text{-}1100\text{ cm}^{-1}$ area) of spectra acquired
832 by Raman spectroscopy after mapping, from different mixtures of
833 olivine with gypsum in several proportions: E: $WF_{\text{gypsum}} = 0.01$; F:
834 $WF_{\text{gypsum}} = 0.05$; G: $WF_{\text{gypsum}} = 0.10$; H: $WF_{\text{gypsum}} = 0.20$. Spectra are
835 correlated with peak simulations: blue for olivine peaks and green for
836 gypsum's. Red curves are cumulative peaks and black dotted lines are
837 residuals from simulations. Weight fractions are calculated with peak
838 simulations and reported in boxes in each graph and in Table 3.

839
840 Figure 4: Calibration coefficients calculated from simulated areas of
841 gypsum and mineral mixed versus the weight fraction (WF) of gypsum
842 theoretical. Black square are samples simulated with their relative
843 errors. Red lines correspond to calibration lines extrapolated from
844 calibration coefficients depending on theoretical weight fraction of
845 gypsum. Calibration lines established on four binary mixtures of: A:
846 plagioclase; B: orthopyroxene; C: clinopyroxene; D: olivine; with
847 gypsum in different proportions ($WF_{\text{gypsum}} = 0.20, 0.10, 0.05, 0.03,$
848 0.01). Equations and linear regression coefficient (R^2) of each
849 calibration lines are reported in boxes in each graph.

850

851 Figure 5: Calibration line for ternary mixtures of gypsum (WF_{gypsum}
852 $=0.2, 0.1, 0.05$) with olivine ($WF_{\text{olivine}} = 0.40, 0.50, 0.50$) and
853 clinopyroxene ($WF_{\text{clinopyroxene}} = 0.40, 0.40, 0.45$). Black squares are
854 simulations results with their errors (black vertical lines). Red line is
855 the calibration line calculated from simulations results. Equation and
856 regression linear coefficient (R^2) are specified in the graph box.

857

858 Figure 6: Calibration coefficients calculated from simulated areas of
859 Mg-sulfate and mineral mixed versus the theoretical weight fraction
860 (WF) of the sulfate. Black square are samples simulated with their
861 relative errors. Red lines correspond to calibration lines extrapolated
862 from calibration coefficients depending on theoretical weight fraction
863 of Mg-sulfate. Calibration lines established on four binary mixtures of:
864 A: orthopyroxene; B: plagioclase; C: clinopyroxene; D: olivine; with
865 Mg-sulfate in different proportions ($WF_{\text{gypsum}} = 0.20, 0.10, 0.05$ and
866 0.03). Equations and linear regression coefficients (R^2) of each
867 calibration lines are reported in boxes for every graph.

868

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

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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)	$\text{MgSO}_4 \cdot (n\text{H}_2\text{O})$

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Table 1: Origins and chemical compositions of basaltic minerals (olivine,

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pyroxenes and plagioclase, determined by Scanning Electron Microscopy

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(SEM) analysis) and sulfates used in this study.

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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

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^a ν_1 : Symmetric stretch

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^b ν_2 : symmetric bending

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^c ν_3 : antisymmetric stretch

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^d ν_4 : antisymmetric bending

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* With M referring as different metal cations present in the chemical structure

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of the mineral (Buzgar et al. 2009)

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Table 2: Specific peak assignments for each mineral used in this study.

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Principal peaks observed in spectra are described according to [1]: Huang et

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al. (2000), [2]: Prencipe et al. (2011), [3]: Sharma and al. (1983), [4]: Wang

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et al. (2001) [5]: Chopelas (1991), [6]: Kolesov and Tanskaya (1996), [7]:

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Kolesov and Geiger (2004), [8]: McKeown et al. (2010), [9]: Freeman et al.

917 (2008) [10]: Bishop et al. (2014), [11]: Buzgar et al. (2009) and [12]: Knittle
918 et al. (2001).

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

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

Calibration equation : $a = 81.36 \times W_{\text{sulfate theoretical}}$			
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 : $a = 8.23 \times W_{\text{sulfate theoretical}}$			
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 : $a = 1.93 \times W_{\text{sulfate theoretical}}$			
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 : $a = 59.83 \times W_{\text{sulfate theoretical}}$			
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)

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Table 3 (suite)

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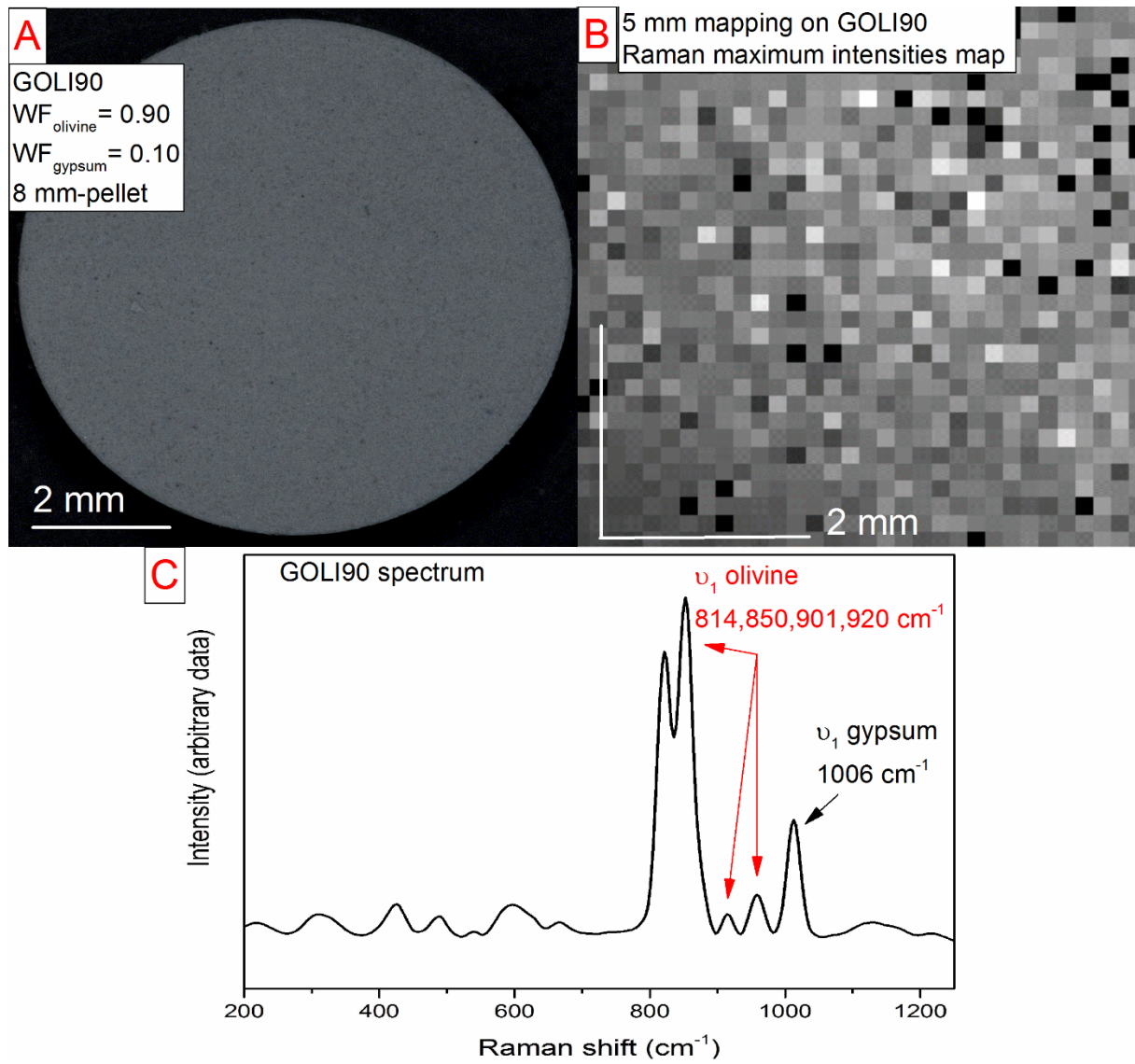


Figure 1

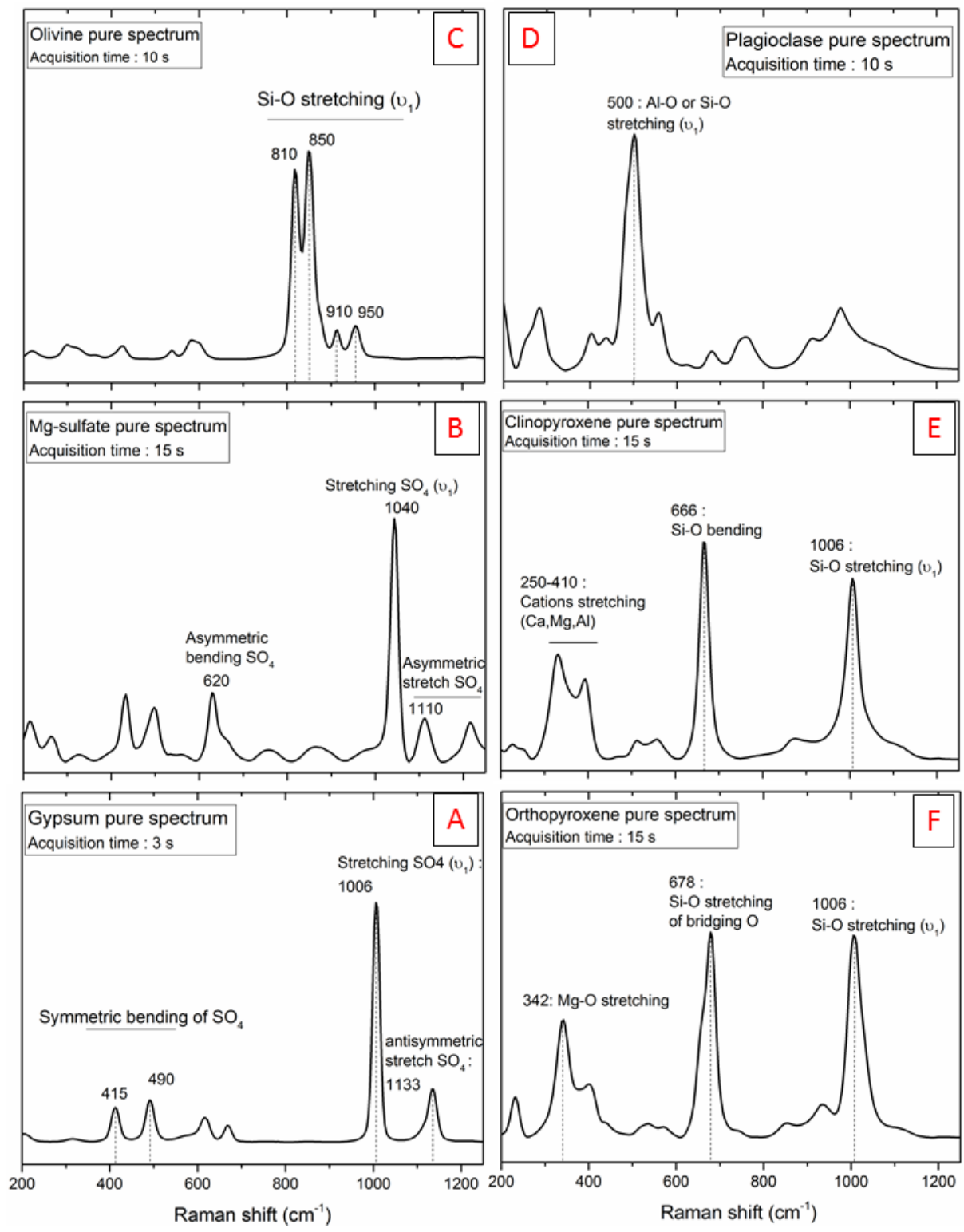


Figure 2

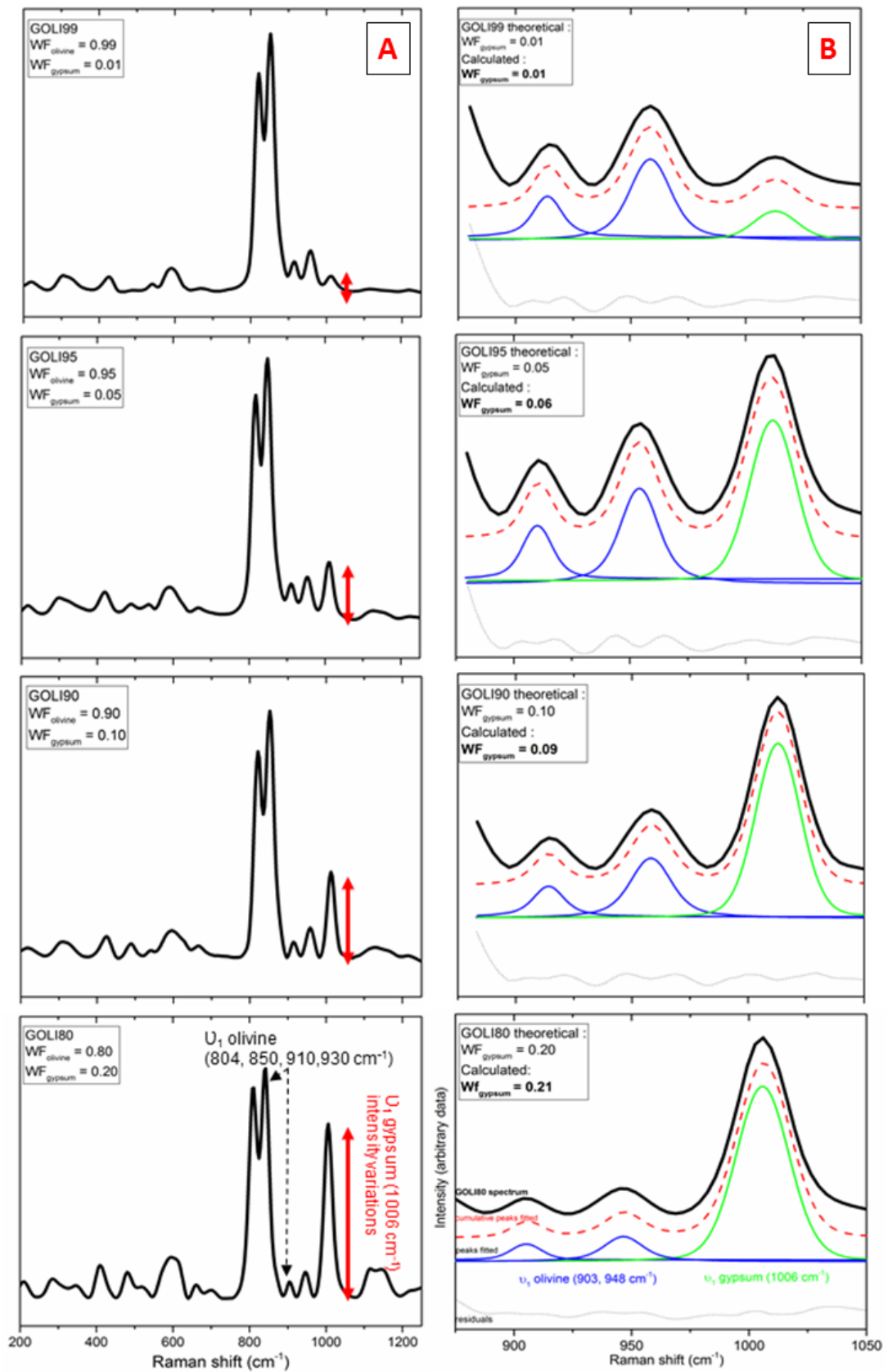


Figure 3

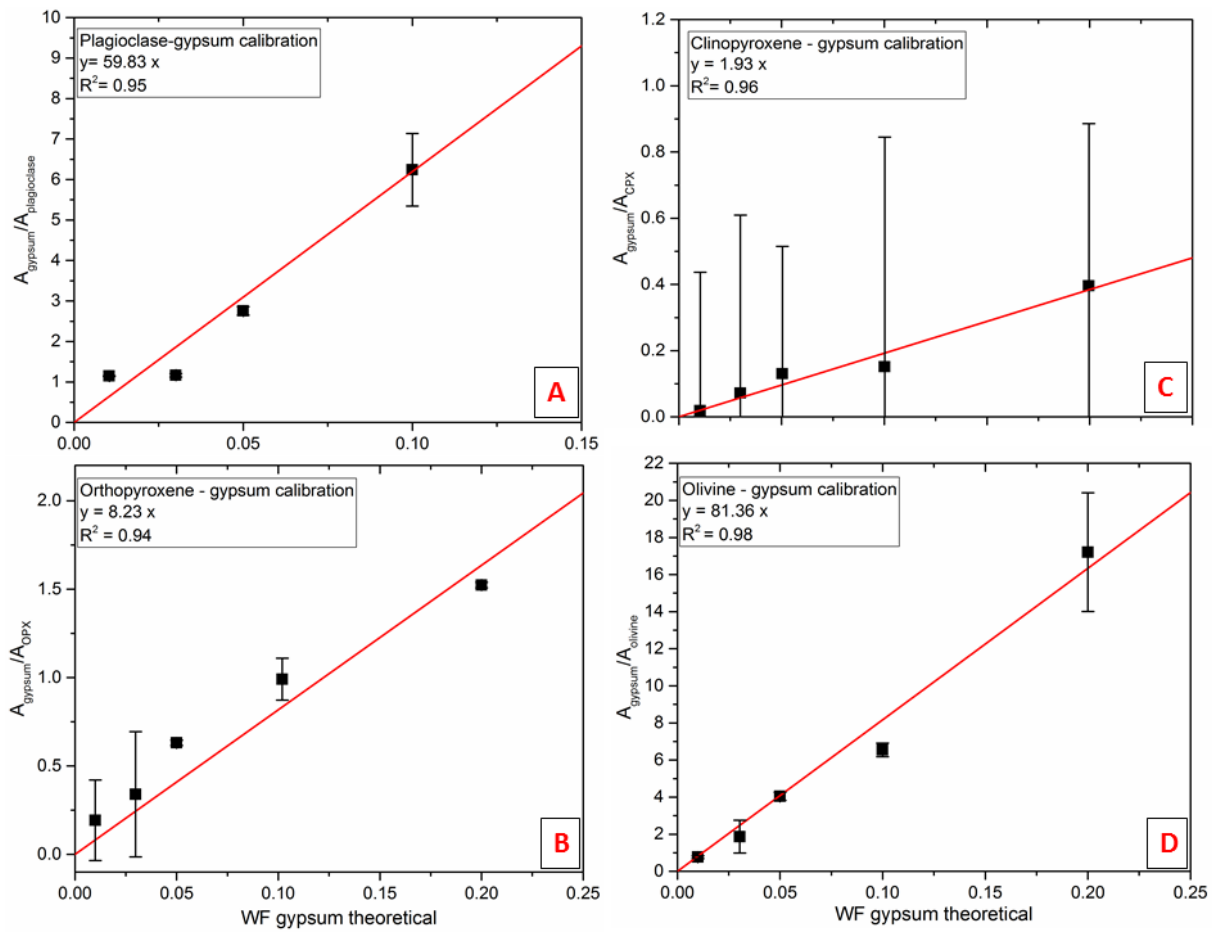


Figure 4

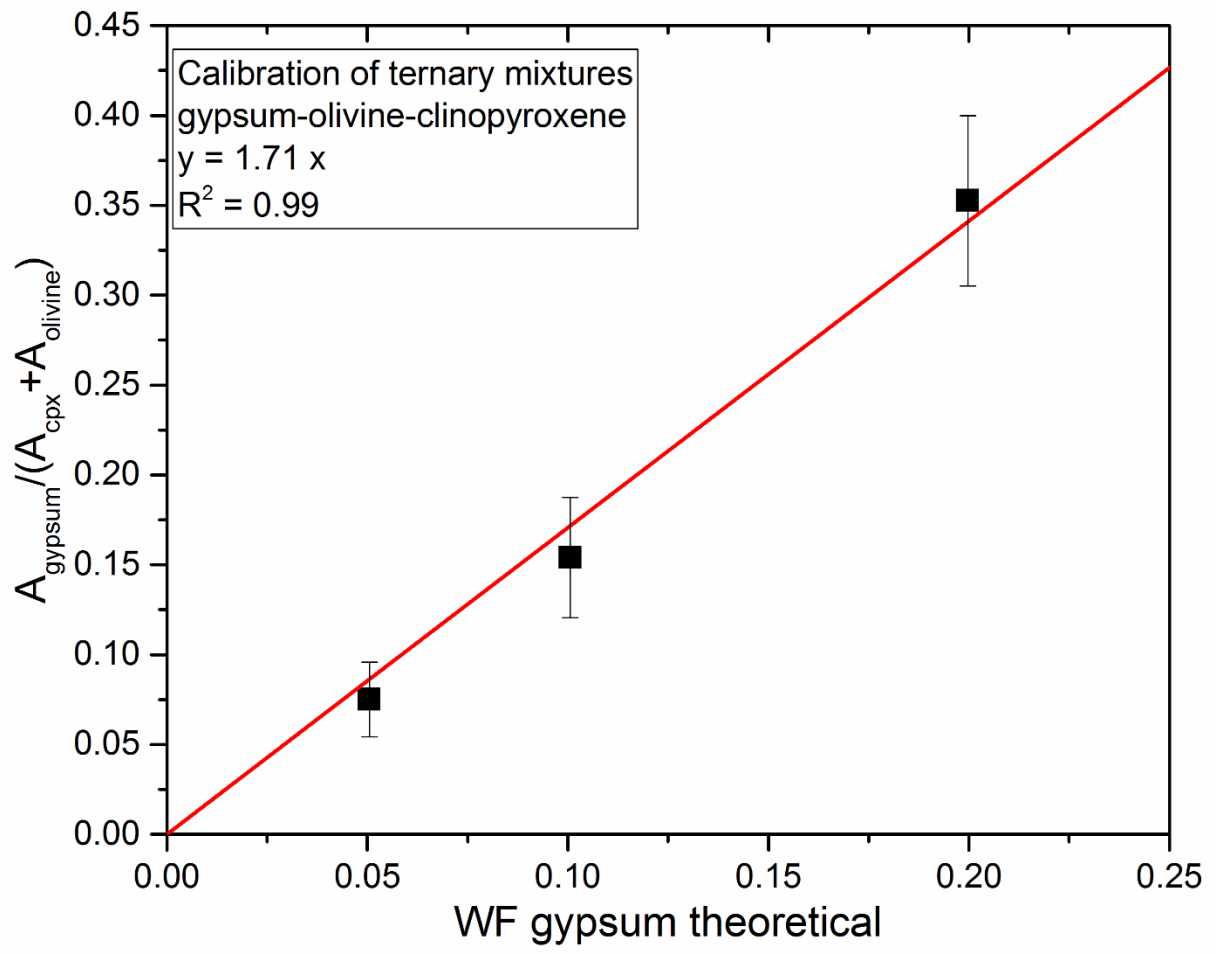


Figure 5

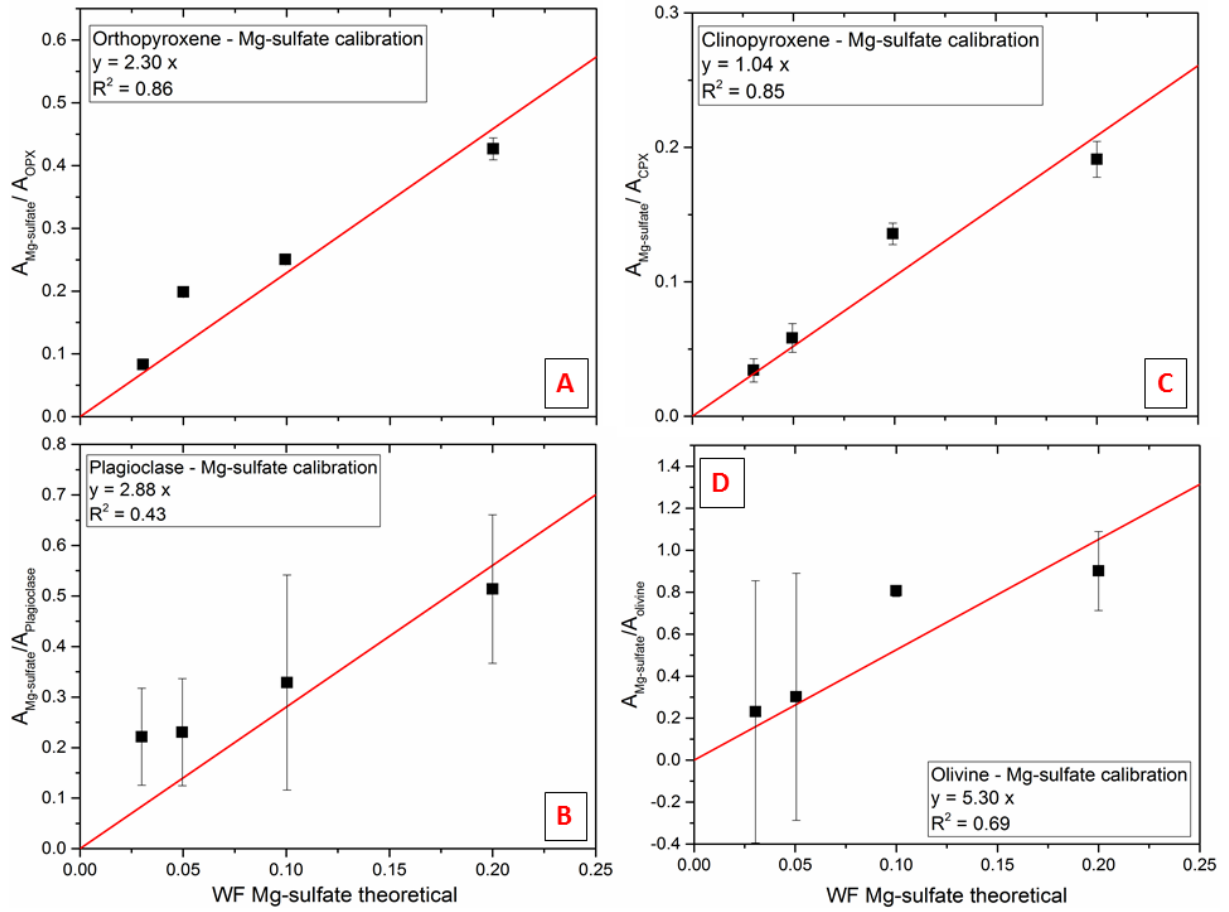


Figure 6

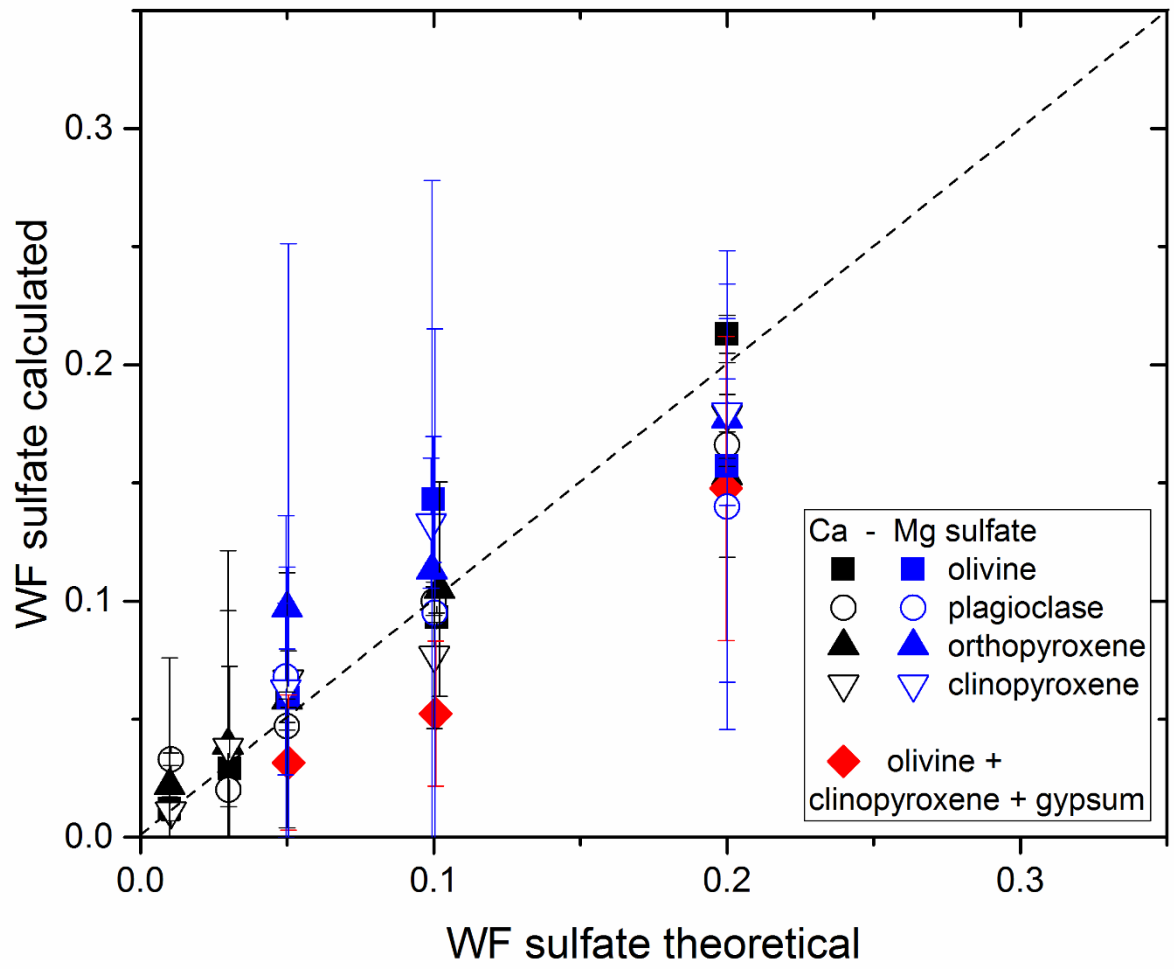


Figure 7

Supplementary material:

Figure caption:

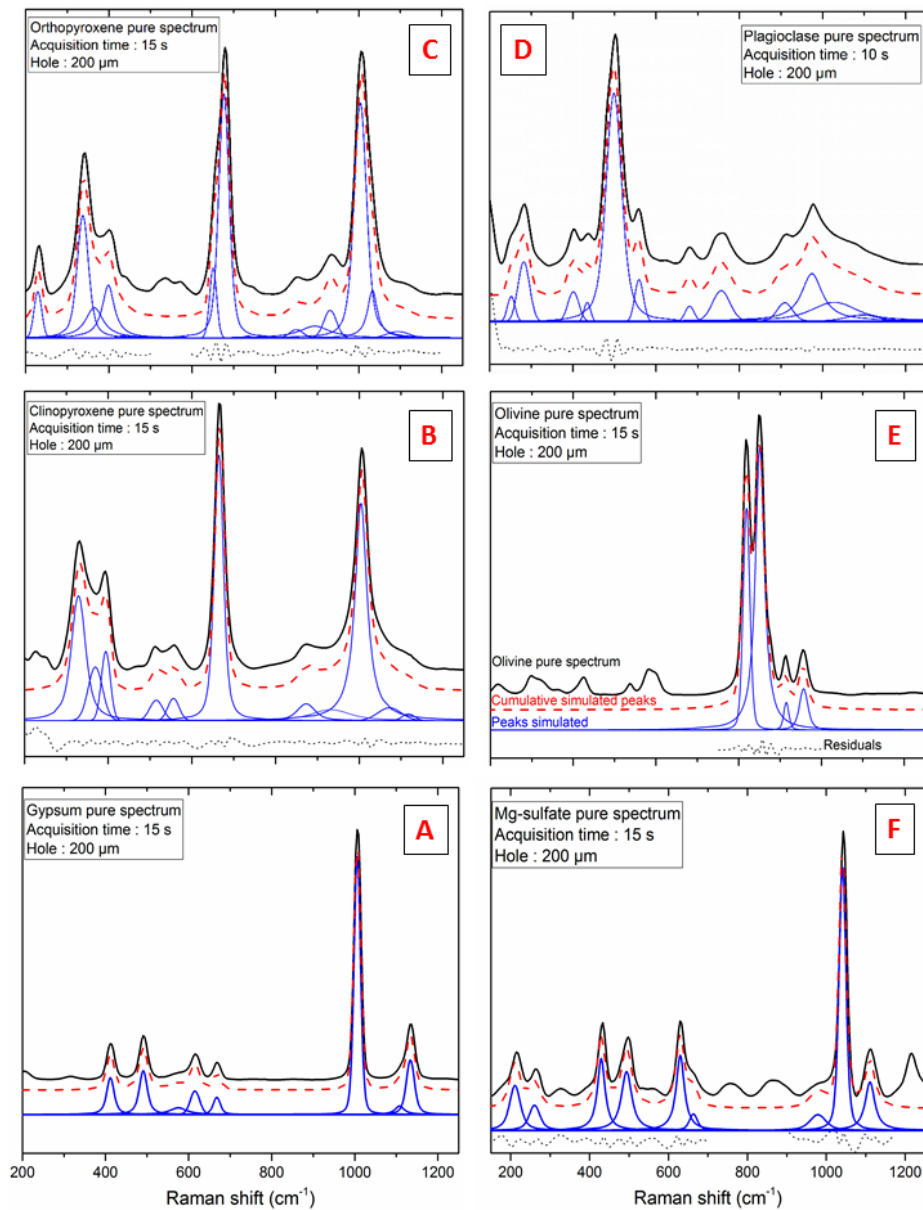


Figure 1: Deconvolution of minerals pure spectrum for A: gypsum; B: clinopyroxene; C: orthopyroxene; D: plagioclase; E: olivine; and F: Mg-sulfate. With individual peaks simulated in blue, cumulative peaks simulated in red dashed lines and residuals in black dotted lines. Analytical parameters (acquisition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

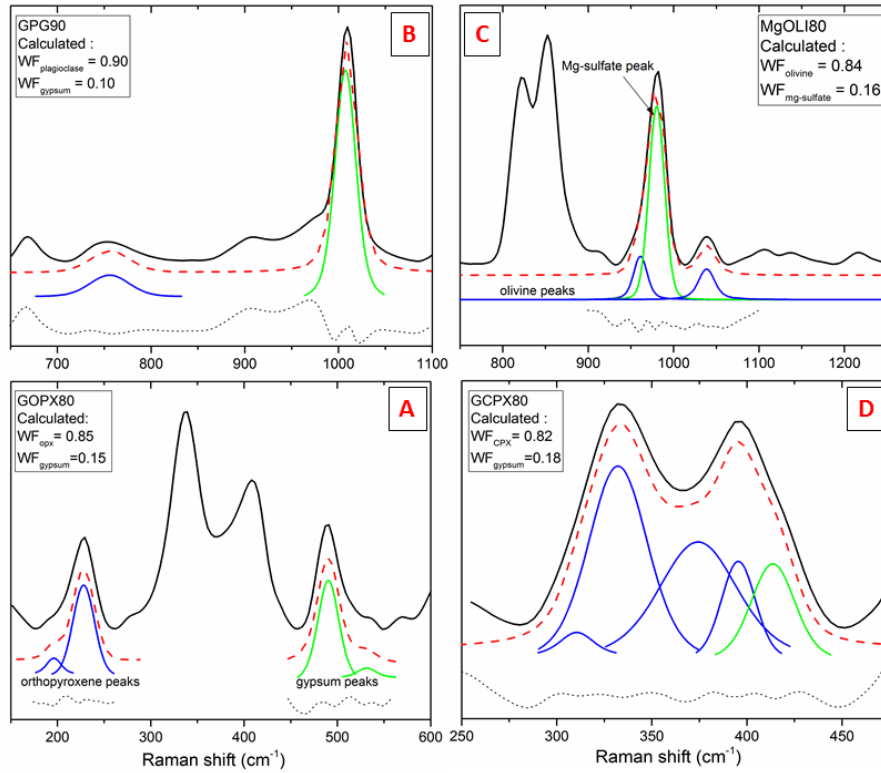


Figure 2: Peak simulations for the other different mixtures: A: orthopyroxene-gypsum mixture with initial proportion of 0.8 and 0.2 respectively; B: plagioclase-gypsum mixture with theoretical proportions of 0.9 and 0.1; C: olivine-mgsulfate mixture (theoretical proportions: $WF_{\text{olivine}}=0.8$ 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 blacks dotted lines are cumulative peaks simulated and residuals left after simulations. Weight fraction calculated by simulations for examples shows in this figure are reported in each graph. All results from simulations on the different mixtures are described in **Table 4**.