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Raman spectroscopy of shocked gypsum from a meteorite impact crater

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Proof For Review

18

19 **Abstract.** Impact craters and associated hydrothermal systems are regarded as
20 sites within which life could originate on Earth, and on Mars. The Haughton
21 impact crater, one of the most well preserved craters on Earth, is abundant in Ca-
22 sulphates. Selenite, a transparent form of gypsum, has been colonised by viable
23 cyanobacteria. Basement rocks which have been shocked are more abundant in
24 endolithic organisms, when compared with un-shocked basement. We infer that
25 selenitic and shocked gypsum are more suitable for microbial colonisation and
26 have enhanced habitability. This is analogous to many Martian craters, such as
27 Gale Crater which has sulphate deposits in a central layered mound, thought to be
28 formed by post-impact hydrothermal springs.

29 In preparation for the 2020 ExoMars mission, experiments were conducted to
30 determine whether Raman spectroscopy can distinguish between gypsum with
31 different degrees of habitability. Ca-sulphates were analysed using Raman
32 spectroscopy and results show no significant statistical difference between
33 gypsum that has experienced shock by meteorite impact and gypsum which has
34 been dissolved and re-precipitated as an evaporitic crust. Raman spectroscopy is
35 able to distinguish between selenite and unaltered gypsum. This shows that
36 Raman spectroscopy can identify more habitable forms of gypsum, and
37 demonstrates the current capabilities of Raman spectroscopy for the interpretation
38 of gypsum habitability.

39

40 Key words: Raman spectroscopy, habitability, shocked gypsum, impact crater

41 **1 Introduction**

42 1.1 Impact generated sulphate deposits and significance for life

43 Hydrothermal deposits within craters on Mars represent one of the most
44 important targets in the search for life on Mars (Cabrol et al. 1999; Newsom et al.
45 2001). Hydrothermal systems are realistic sites to sustain life due to the presence
46 of liquid H₂O, heat and dissolved nutrients and alkaline vents within these
47 systems are considered to be locations where life could originate (Farmer & Des
48 Marais 1999; Osinski et al. 2005; Newsom et al. 2001; Lane & Martin 2012).
49 Over 60 impact craters with associated hydrothermal activity have been
50 discovered on Earth, and given the long bombardment history of Mars, impact
51 craters could be a common site to search for life (Chapman & Jones 1977;
52 Naumov 2002). Gale Crater has sulphates present within a layered sedimentary
53 mound in the centre of the crater, named Mount Sharp, thought to be formed by
54 hydrothermal springs, as there is a lack of features associated with lacustrine
55 environments such as terraces, deltas and fans. (Rossi et al. 2008; Thomson et al.
56 2011; Schwenger et al. 2012). Semi-hydrated Ca-sulphate, bassanite has been
57 identified in Mawrth Vallis, one of the proposed landing sites for the ExoMars
58 2020 mission (Wray et al. 2010).

59
60 The Eocene Houghton impact crater, located on Devon Island in the Canadian
61 High Arctic Archipelago, provides a useful analogue site to study post impact
62 sulphate deposits (Sherlock et al. 2005). It is exceptionally well preserved, which
63 is why it has been extensively studied, and has examples of sulphate deposits
64 containing microbial life (Osinski & Spray 2001; Parnell et al. 2004). The current
65 structure is composed of a central uplift overlaid with melt breccia which is the

66 most common impactite (Lindgren et al. 2009). There is a gneissic crystalline
67 basement which is shocked and is inhabited by endolithic photosynthetic
68 microorganisms. These organisms are more abundant in the shocked material due
69 to an increased pore space as a result of impact fracturing, and increased
70 translucence due to vaporization of opaque mineral phases (Cockell et al. 2002).
71 The target rock included gypsum bearing carbonate rocks, Ordovician in age
72 (Robertson & Sweeney 1983). Impact remobilised sulphate occurs as selenite, a
73 transparent form of gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$), which cross-cuts the melt breccia
74 as veins. Viable, extant cyanobacterial colonies are present within the selenite and
75 are black in colour due to the UV protective pigments scytonemin and
76 gloeocapsin (Cockell et al. 2002; Cockell et al. 2003b). Mobilisation still occurs
77 at present in the form of evaporitic crusts on bedrock surfaces and soil (Parnell et
78 al. 2004).

79 Given that sulphates formed by hydrothermal activity are habitable substrates,
80 and that shocking increases the space for an organism to exploit; shocked
81 sulphates are important targets with which to find evidence of microbial life. If
82 instrumentation could distinguish between shocked and un-shocked phases, and
83 between various sulphate phases, this would be beneficial when identifying the
84 most likely sulphates to contain life signatures.

85 1.2 Raman for Mars

86 Raman spectroscopy uses a monochromatic laser light source to irradiate a
87 sample. Majority of the light which interacts with the sample is scattered
88 elastically, with no change in wavelength. However a small proportion of the
89 light is scattered inelastically – either an increase or decrease in wavelength,
90 known as Raman scattering. Raman spectroscopy produces a vibrational

91 'fingerprint' which is dependent on the vibrational state of molecules in a given
92 compound (Ellery & Wynn-Williams 2003).

93 The popularity of Raman spectroscopy has dramatically increased in the last 30
94 years due to its increasing range of applications (Pérez & Martinez-Frias 2006). It
95 is a useful astrobiological tool as it is a non-destructive technique, which is able
96 to be miniaturised. It is sensitive to carbonaceous materials, which is one of the
97 main targets of the ESA ExoMars mission but it is also sensitive to various
98 microbial pigments, such as chlorophylls, carotenoids and scytonemin which
99 increase its appeal (Jehlička et al. 2014; Ellery & Wynn-Williams 2003). It has a
100 wavelength range covering most vibrational modes including carbonates, silicates
101 and sulphates (i.e. most rock-forming minerals), therefore it can also be used for
102 petrographic analysis (Haskin et al. 1997; Wang et al. 1998).

103 1.3 Raman spectroscopy of gypsum & impact shocked gypsum

104 The Raman spectrum of gypsum characteristically shows a narrow intense band
105 around 1008 reciprocal centimetres (cm^{-1}) which is the ν_1 sulphate symmetric
106 stretching mode, herein referred to as ν_1 sulphate band. The stretching modes of
107 water occur around 3450 cm^{-1} (Krishnamurthy & Soots 1971; Berenblut et al.
108 1970), shown in figure 1.

109 **Fig. 1** Extended spectra $100\text{-}4000 \text{ cm}^{-1}$ showing ν_1 sulphate symmetric stretching
110 mode (1007.89 cm^{-1}) and stretching mode of H_2O ($\sim 3450 \text{ cm}^{-1}$).

111 The astrobiological community is interested in the effect of shocking on sulphates
112 as they occur on Mars. Micro-scale deformation experiments of gypsum by
113 Hogan et al. (2012), show that the ν_1 sulphate band is least intense at the centre
114 of deformation, where most load was experienced, and most intense at the outer

115 margins of the deformation structure where least load was experienced. This is
116 evidence that shocking reduces the ν_1 sulphate stretching band intensity.
117 Instantaneous compressional deformation occurs in both meteorite (macro) shock
118 events and micro-indentation experiments.

119 The effects of shock on gypsum have been discussed by Ramkissoo et al.
120 (2014), using impact shock experiments with a two stage light gas gun and
121 projectile, fired at plaster of Paris (gypsum). Their experiments show that
122 devolatilisation occurs as a result of the impact, based on the disappearance of
123 water molecule bands around 3450 cm^{-1} , and the shift of bands 427 and 487 cm^{-1} ,
124 is indicative of anhydrite. Characterising the dehydration of gypsum to anhydrite
125 using Raman spectroscopy has been well studied and shows the sulphate
126 stretching band exhibiting an increase in band position with increasing
127 dehydration (Prasad et al. 2001; Liu et al. 2009).

128 Bucio et al. (2015) used experimentally impact-shocked gypsum to characterise
129 post-impact phases using Raman spectroscopy and X-Ray diffraction. This study
130 compared Raman spectra obtained from naturally shocked samples with Raman
131 spectra obtained from experimentally impact-shocked gypsum, published by
132 previous authors, to assess if the spectral changes associated with shock are
133 comparable, and ultimately if shocked gypsum can be differentiated from other
134 phases of gypsum. The spectral changes were analysed by comparing ν_1 sulphate
135 band positions against band widths, referred to as the full width at half maximum
136 (FWHM).

137 **2 Methods**

138 **2.1 Samples**

139 **Fig 2.** Sample photographs. (a) Selenite, Haughton crater (S2), showing black
140 pigmentation of bacterial colonies. (b) Melt breccia, Haughton crater (SH1),
141 showing fragment of shocked gypsum. (c) Evaporitic gypsum crust, Haughton
142 crater (C1).

143 Gypsum samples were separated into 4 groups:

- 144 1. Unaltered gypsum – Samples which have not experienced shock or
145 dissolution and subsequent re-precipitation. The crystal habits range from
146 grainy to massive or fibrous.
- 147 2. Selenite - a transparent form of gypsum, which has a distinct platy crystal
148 habit. Selenite at the Haughton structure formed by the dissolution of gypsum
149 in the target rock, and circulated the structure before re-precipitating as
150 selenite.
- 151 3. Crusts – sulphate rich waters at the Haughton flows over the surface
152 topography and slowly evaporates, leaving a mineral ‘crust’ on outcropped
153 rock and soil.
- 154 4. Shocked gypsum – samples include a primary shocked gypsum nodule, and
155 shocked gypsum fragments within melt breccia (see figure 2).

156 The majority of the samples originate from the Haughton impact crater, Devon
157 Island, Canada; see table 1 for more information on sample locations and ages.
158 Minimal sample preparation was employed, simulating capabilities during a
159 remote mission on Mars. If necessary, samples were cut to expose the sulphate,
160 however where possible rough untreated surfaces were analysed. This study
161 would be equally appropriate for the NASA 2020, SHERLOC instrument, which
162 will have spatial mapping capabilities (Beegle et al. 2015).

163 **Table 1.** Table of sample locations and ages.

164 2.2 Raman spectroscopy configuration

165 Raman spectra were obtained using a Renishaw InVia H36031 confocal Raman
166 microscope operating at a wavelength of 514.5 nm green monochromatic laser
167 light, which is similar to the ExoMars flight instrument wavelength of 532 nm
168 (Rull et al. 2011). The laser power was 0.3 mW, avoiding laser induced heating of
169 samples. A 50 x objective lens was used giving a laser “footprint” of 1-3 μm in
170 diameter, with an extended spectral range of 100 cm^{-1} to 2000 cm^{-1} . 10 seconds
171 exposure time and 1 accumulation were used for each spectrum, giving a good
172 signal-to-noise ratio. To include the stretching modes of water molecules,
173 extended wavelength ($100\text{-}4000\text{ cm}^{-1}$) was also measured using the above
174 settings. Spectra were processed using a smooth, baseline subtraction and peak fit
175 functions using WiRE 2.0 software. Peak fitting used a mixture of Gaussian and
176 Lorentzian algorithms.

177 2.3 X-Ray Diffraction

178 Diffraction patterns were acquired on powder samples by using an X’Pert
179 diffractometer (PANalytical, NL) equipped with Cu- α radiation (1.54 \AA ; 45 kV /
180 40 mA) in θ - θ reflectance geometry; data were collected from $5 - 80^\circ 2\theta$ with a
181 step size of 0.013° and a time-per-step of 13.77 s. Crystalline phases were
182 identified by comparison to ICDD PDF # [01-074-1433] (Gypsum). Samples
183 were powdered by hand using a pestle & mortar.

184 2.4 Spectral parameter analysis

185 10 spectra were obtained from each sample and average FWHM were plotted
186 against sulphate band positions. Statistical variance tests were used to determine
187 if sample groups are statistically different from each another.

188 2.5 Statistical analysis

189 Overlapping sample fields were examined using SigmaPlot statistical software
190 package to confirm if the groups were statistically different. The sample groups
191 failed the normality test therefore a non-parametric test was used. As two
192 independent groups were compared, a Man-Whitney U test was used.

193 3 Results

194 3.1 Raman spectroscopy

195 The spectra obtained across the sample set all show a ν_1 sulphate band position of
196 around 1008 cm^{-1} which is indicative of gypsum (Krishnamurthy & Soots 1971),
197 shown in figure 3. The shocked samples, SH2 & SH3, show a sloping baseline
198 with increased signal-to-noise ratio compared with other samples e.g. selenite.
199 Additionally the shocked samples shows a weaker Raman signal, with lower band
200 intensities. The spectra from evaporitic crusts are similar spectra to that of
201 shocked samples, with low intensity bands and a higher signal-to-noise ratio, a
202 part from the central uplift crust, which has an improved signal-to-noise ratio.
203 The selenite group, have the cleanest spectra with intense ν_1 sulphate bands and a
204 better signal-to-noise ratio relative to the shocked samples. Unaltered samples
205 show similar spectra to selenite, except from U6 and U5 which have increased
206 signal-to-noise ratios. Average ν_1 band positions for each are; unaltered (U) –
207 1009.615 , selenite (S) – 1009.261 , shocked (SH) – 1008.251 , crusts (C) –

208 1008.262 cm^{-1} . Based on these band positions all samples are classed as gypsum
209 and have not experienced dehydration.

210 **Fig 3.** Extended Raman spectra for gypsum (100-2000 cm^{-1}). X axis is Raman
211 shift in reciprocal centimetres (cm^{-1}). Y axis is Raman intensity in arbitrary units
212 (a.u.). 'SH' spectra have experienced shock from meteoric impact. 'C' spectra are
213 gypsum samples which have been dissolved then re-precipitated as evaporitic
214 crusts. 'S' spectra are selenite, a transparent form of gypsum. 'U' spectra are from
215 unaltered gypsum samples unaffected by shock or dissolution and re-
216 precipitation.

217 3.2 X-ray diffraction

218 8 gypsum samples were selected from the larger sample set for XRD analysis
219 (figure 4), which cover the 4 Ca-sulphate groups. The cell parameters for each
220 sample show that all 8 samples are in the form of gypsum. It is common for
221 impact shocked sample to experience partial or complete dehydration, however
222 basanite or anhydrite phases are not found in specimen SH3, which is consistent
223 with the Raman measurements obtained.

224 **Fig. 4** X-ray diffraction patterns.

225 4 Discussion

226 4.1 Raman spectroscopy - Extended spectra

227 Selected samples were re-analysed using an extended wavelength range (100-
228 4000 cm^{-1}), to include the stretching modes of water molecules, shown in figure
229 5. An anhydrite control is included to show a completely dehydrated phase. As
230 expected the anhydrite control shows a ν_1 sulphate band position of 1015.39 cm^{-1}

231 ¹, and does not show the stretching modes of water molecules around 3450 cm⁻¹.
232 Sample SH1 has a fragment of gypsum, and the spectrum for shows a v1 band
233 position of 1007.52 cm⁻¹ which is indicative of gypsum, although it does not
234 show the presence of water molecules at the expected wavelength. As shocking
235 promotes devolatilisation, the loss of H₂O molecules would be expected, and is
236 well documented by other authors. Additionally, a change in v1 band position
237 from 1008 cm⁻¹ to 1015 cm⁻¹, would also be expected. Sample SH2 shows a band
238 position of 1006.24 cm⁻¹, and has the stretching modes of water molecules. This
239 is indicative of gypsum, and suggests that either no dehydration has occurred, or
240 that the specimens have been rehydrated.

241 Experimental work by Ramkissoon et al. (2014) and Bucio et al. (2015), clearly
242 show that shocking by impact generates, semi-hydrated and completely hydrated
243 Ca-sulphate phases in the form of basanite and anhydrite respectively. This can
244 be seen in the v1 sulphate band position and the presence, or absence, of the
245 stretching modes of water molecules. This relationship does not appear to be
246 realised in naturally impact shocked Ca-sulphates from Haughton crater.

247 **Fig 5.** Extended Raman spectra for gypsum and anhydrite (100-4000 cm⁻¹).
248 Spectra include v1 sulphate stretching mode and H₂O molecule stretching mode
249 around 3500 cm⁻¹.

250 4.2 v1 band position against band FWHM

251 The sulphate band position was plotted against the FWHM to determine if these
252 Raman parameters could distinguish between the gypsum specimens. Figure 6(a)
253 shows the 4 types of gypsum used in this study presented as fields. Each point is
254 an average of 10 spectra. Selenite has the largest field which overlaps with

255 unaltered samples. Selenite and unaltered fields plot independently from shocked
256 or crust fields, showing that Raman spectroscopy can distinguish between certain
257 phases of gypsum. The shocked field plots on the edge of the crusts field.
258 Samples with overlapping fields, were analysed for statistical significance. No
259 significant difference was found between the shocked and crust sample band
260 positions ($p=0.966$, Mann-Whitney Sum test) and FWHM ($p=0.251$), indicating
261 that Raman spectroscopy cannot currently distinguish between impact shocked
262 gypsum and gypsum which has been dissolved and re-precipitated as a mineral
263 crust. In contrast, a significant difference is evident between selenite and
264 unaltered sample band positions ($p=0.045$) and FWHM ($p=0.020$). This shows
265 that using the sulphate v1 band position vs FWHM, differences between gypsum
266 phases are evident. Raman can therefore identify gypsum phases with enhanced
267 habitability.

268 Figure 6(b) distinguishes samples according to their classification in table 1.
269 Figure 6(c) distinguishes samples according to crystal size, which was determined
270 petrographically. However, there does not appear to be any control based on
271 crystal size.

272 **Fig 6.** Sulphate band position against sulphate band FWHM, with each point
273 representing an average of 10 spectra. x-axis, is the sulphate (v1) band position in
274 reciprocal centimetres (cm^{-1}). Y-axis, is the sulphate (v1) full width at half
275 maximum (FWHM). (a) Samples are separated into their geological groups. (b)
276 Samples are distinguished by sample classification (table 1). (c) Samples are
277 distinguished based on crystal size. Squares denote a crystal size less than 0.5 cm;
278 diamonds denote a crystal size of between 0.5 and 2 cm; circles denote a crystal
279 size greater than 2 cm.

280 **5 Conclusions**

281 A range of gypsum samples were analysed using Raman spectroscopy, to
282 determine if this technique can differentiate between Ca-sulphates which have
283 enhanced habitability, and those that do not. Results show that Raman
284 spectroscopy cannot currently determine a significant difference between gypsum
285 which has been shocked by meteoric impact (enhancing the habitability), and
286 gypsum which has been dissolved and re-precipitated as an evaporitic crust.
287 Raman spectroscopy is able to differentiate between unaltered gypsum and
288 selenite by plotting ν_1 sulphate band position against ν_1 sulphate band FWHM,
289 and as selenite has been found with viable extant microbial colonies at Houghton
290 impact crater, it is regarded as having enhanced habitability.

291 The presence of H_2O bands in spectra obtained from shocked samples highlights
292 the complexity of Raman spectra observed from naturally shocked samples
293 compared with experimental shock studies. This indicates current capabilities of
294 Raman spectroscopy, for the interpretation of gypsum habitability, prior to its use
295 on the European Space Agency's ExoMars 2020 mission.

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Sample	Description/Location	Age	Group
U1	Vale of Eden, Cumbria, UK	Permian	1
U2	Kingscourt fibrous, Co. Cavan, Ireland	Triassic	1
U3	Scapa, Orkney	Devonian	1
U4	Kingscourt with hematite, Co. Cavan, Ireland	Triassic	1
U5	Gotham Triassic, England	Triassic	1
U6	Ebro Basin, Spain	Oligocene-Miocene	1
S1	Selenite, California	Paleogene	2

S2	Selenite, Haughton, Devon Island	Eocene- Oligocene	2
S3	GSC dome (NE side), Selenite Haughton, Devon Island	Eocene- Oligocene	2
S4	Selenite, Kent	Eocene	2
C1	Central uplift crust, Haughton, Devon Island	Eocene-Holocene	3
C2	GSC dome (NE side) crust, Haughton, Devon Island	Eocene-Holocene	3
C3	Gypcrete Chile	Paleogene - Holocene	3
C4	Rhino Creek, Crust on lake sediments, Haughton, Devon Island	Eocene-Holocene	3
SH1	West Rhino creek melt breccia, Haughton, Devon Island	Eocene	4
SH2	Gemini Hills Shocked A Haughton, Devon Island	Eocene	4
SH3	Gemini Hills Shocked B Haughton, Devon Island	Eocene	4

387 **Table 1** Table of sample locations and ages.

388

1 Raman spectroscopy of shocked gypsum from a
2 meteorite impact crater

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19 **Abstract.** Impact craters and associated hydrothermal systems are regarded as
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26 colonisation and have enhanced habitability. This is analogous to many Martian
27 craters, such as Gale Crater which has sulphate deposits in a central layered
28 mound, thought to be formed by post-impact hydrothermal springs.

29 In preparation for the 2020 ExoMars mission, experiments were conducted to
30 determine whether Raman spectroscopy can distinguish between gypsum with
31 different degrees of habitability. Ca-sulphates were analysed using Raman
32 spectroscopy and results show no significant statistical difference between
33 gypsum that has experienced shock by meteorite impact and gypsum which has
34 been dissolved and re-precipitated as an evaporitic crust. Raman spectroscopy is
35 able to distinguish between selenite and unaltered gypsum. This shows that
36 Raman spectroscopy can identify more habitable forms of gypsum, and
37 demonstrates the current capabilities of Raman spectroscopy for the interpretation
38 of gypsum habitability.

39

40 Key words: Raman spectroscopy, habitability, shocked gypsum, impact crater

41 1 Introduction

42 1.1 Impact generated sulphate deposits and significance for life

43 Hydrothermal deposits within craters on Mars represent one of the most
44 important targets in the search for life on Mars (Cabrol et al. 1999; Newsom et al.
45 2001). Hydrothermal systems are realistic sites ~~for life to arise~~to sustain life due
46 to the presence of liquid H₂O, heat and dissolved nutrients and alkaline vents
47 within these systems ~~therefore~~ are considered to be locations where ~~primitive~~ life
48 could ~~evolve~~originate (Farmer & Des Marais 1999; Osinski et al. 2005; Newsom
49 et al. 2001; Lane & Martin 2012). Over 60 impact craters with associated
50 hydrothermal activity have been discovered on Earth, ~~with associated~~
51 ~~hydrothermal activity~~ and given the long bombardment history of Mars, impact
52 craters could be a common site to search for life (Chapman & Jones 1977;
53 Naumov 2002). Gale Crater has sulphates present within a layered sedimentary
54 mound in the centre of the crater, named Mount Sharp, thought to be formed by
55 hydrothermal springs, as there is a lack of features associated with lacustrine
56 environments such as terraces, deltas and fans. (Rossi et al. 2008; Thomson et al.
57 2011; Schwenzer et al. 2012). Semi-hydrated Ca-sulphate, bassanite has been
58 identified in Mawrth Vallis, one of the proposed landing sites for the ExoMars
59 2020 mission (Wray et al. 2010).

60
61 The Eocene Haughton impact crater, located on Devon Island in the Canadian
62 High Arctic Archipelago, provides a useful analogue site to study post impact
63 sulphate deposits (Sherlock et al. 2005). It is exceptionally well preserved, which
64 is why it has been extensively studied, and has examples of sulphate deposits
65 containing microbial life (Osinski & Spray 2001; Parnell et al. 2004). The current

66 structure is composed of a central uplift overlaid with melt breccia which is the
67 most common impactite (Lindgren et al. 2009). There is a gneissic crystalline
68 basement which is shocked and is inhabited by endolithic photosynthetic
69 microorganisms. These organisms are more abundant in the shocked material due
70 to an increased pore space as a result of impact fracturing, and increased
71 translucence due to vaporization of opaque mineral phases (Cockell et al. 2002).
72 The target rock included gypsum bearing carbonate rocks, Ordovician in age
73 (Robertson & Sweeney 1983). Impact remobilised sulphate occurs as selenite, a
74 transparent form of gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$), which cross-cuts the melt breccia
75 as veins. Viable, extant cyanobacterial colonies are present within the selenite and
76 are black in colour due to the UV protective pigments scytonemin and
77 gloeocapsin (Cockell et al. 2002; Cockell et al. 2003b). Mobilisation still occurs
78 at present in the form of ~~evaporitic~~evaporitic crusts on bedrock surfaces and soil
79 (Parnell et al. 2004).

80 Given that sulphates formed by hydrothermal activity are ~~regarded as realistic~~
81 ~~sites for life to evolve~~habitable substrates, and that shocking increases the space
82 for an organism to exploit; ~~this suggests that~~ shocked sulphates are important
83 targets with which to find evidence of microbial life. If instrumentation could
84 distinguish between shocked and un-shocked phases, and between various
85 sulphate phases, this would be beneficial when identifying the most likely
86 sulphates to contain life signatures.

87 1.2 Raman for Mars

88 Raman spectroscopy uses a monochromatic laser light source to irradiate a
89 sample. Majority of the light which interacts with the sample is scattered
90 elastically, with no change in wavelength. However a small proportion of the

91 light is scattered inelastically – either an increase or decrease in wavelength,
92 known as Raman scattering. Raman spectroscopy produces a vibrational
93 ‘fingerprint’ which is dependent on the vibrational state of molecules in a given
94 compound (Ellery & Wynn-Williams 2003).

95 The popularity of Raman spectroscopy has dramatically increased in the last 30
96 years due to its increasing range of applications (Pérez & Martinez-Frias 2006). It
97 is a useful astrobiological tool as it is a non-destructive technique, which is able
98 to be miniaturised. It is sensitive to carbonaceous materials, which is one of the
99 main targets of the ESA ExoMars mission but it is also sensitive to various
100 microbial pigments, such as chlorophylls, carotenoids and scytonemin which
101 increase its appeal (Jehlička et al. 2014; Ellery & Wynn-Williams 2003). It has a
102 wavelength range covering most vibrational modes including carbonates, silicates
103 and sulphates (i.e. most rock-forming minerals), therefore it can also be used for
104 petrographic analysis (Haskin et al. 1997; Wang et al. 1998).

105 1.3 Raman spectroscopy of gypsum & impact shocked gypsum

106 The Raman spectrum of gypsum characteristically shows a narrow intense band
107 around 1008 reciprocal centimetres (cm^{-1}) which is the ν_1 sulphate symmetric
108 stretching mode, herein referred to as ν_1 sulphate band. The stretching modes of
109 water occur around 3450 cm^{-1} (Krishnamurthy & Soots 1971; Berenblut et al.
110 1970), shown in figure 1.

111 **Fig. 1** Extended spectra $100\text{-}4000 \text{ cm}^{-1}$ showing ν_1 sulphate symmetric stretching
112 mode (1007.89 cm^{-1}) and stretching mode of H_2O ($\sim 3450 \text{ cm}^{-1}$).

113 The astrobiological community is interested in the effect of shocking on sulphates
114 as they occur on Mars. Micro-scale deformation experiments of gypsum by

115 Hogan et al. (2012), show that the v1 sulphate band is least intense at the centre
116 of deformation, where most load was experienced, and most intense at the outer
117 margins of the deformation structure where least load was experienced. This is
118 evidence that shocking reduces the v1 sulphate stretching band intensity. ~~This is~~
119 ~~analogous because i~~ Instantaneous compressional deformation occurs in both
120 meteorite (macro) shock events and micro-indentation experiments.

121 The effects of shock on gypsum have been discussed by Ramkissoon et al.
122 (2014), using impact shock experiments with a ~~two 2~~-stage light ~~gas~~ gun and
123 projectile, fired at plaster of Paris (gypsum). Their experiments show that
124 devolatilisation occurs as a result of the impact, based on the disappearance of
125 water molecule bands around 3450 cm^{-1} , and the shift of bands 427 and 487 cm^{-1} ,
126 is indicative of anhydrite. Characterising the dehydration of gypsum to anhydrite
127 using Raman spectroscopy has been well studied and shows the sulphate
128 stretching band exhibiting an increase in band position with increasing
129 dehydration (Prasad et al. 2001; Liu et al. 2009).

130 Bucio et al. (2015) used experimentally impact-shocked gypsum ~~to and~~
131 characterise ~~s the~~ post-impact phases using Raman spectroscopy and X-Ray
132 diffraction. This study ~~will compare~~ compared Raman spectra obtained from
133 naturally shocked samples with Raman spectra obtained from experimentally
134 impact-shocked gypsum, published by previous authors, to assess if the spectral
135 changes associated with shock are comparable, and ultimately if shocked gypsum
136 can be differentiated from other phases of gypsum. The spectral changes ~~will~~
137 ~~be were~~ analysed by comparing v1 sulphate band positions against band widths,
138 referred to as the full width at half maximum (FWHM).

139 2 Methods

140 2.1 Samples

141 **Fig 2.** Sample photographs. (a) Selenite, Haughton crater (S2), showing black
142 pigmentation of bacterial colonies. (b) Melt breccia, Haughton crater (SH1),
143 showing fragment of shocked gypsum. (c) Evaporitic gypsum crust, Haughton
144 crater (C1).

145 Gypsum samples were separated into 4 groups:

- 146 1. Unaltered gypsum – Samples which have not experienced shock or
147 dissolution and subsequent re-precipitation. The crystal habits range from
148 grainy to massive or fibrous.
- 149 2. Selenite - a transparent form of gypsum, which has a distinct platy crystal
150 habit. Selenite at the Haughton structure formed by the dissolution of gypsum
151 in the target rock, and circulated the structure before re-precipitating as
152 selenite.
- 153 3. Crusts – sulphate rich waters at the Haughton flows over the surface
154 topography and slowly evaporates, leaving a mineral ‘crust’ on outcropped
155 rock and soil.
- 156 4. Shocked gypsum – samples include a primary shocked gypsum nodule, and
157 shocked gypsum fragments within melt breccia (see figure 2).

158 The majority of the samples originate from the Haughton impact crater, Devon
159 Island, Canada; ~~as it is one of the most well preserved impact craters on Earth,~~
160 see table 1 for more information on sample locations and ages. Minimal sample
161 preparation was employed, simulating capabilities during a remote mission on

162 Mars. If necessary, samples were cut to expose the sulphate, however where
163 possible rough untreated surfaces were analysed. This study would be equally
164 appropriate for the NASA 2020, SHERLOC instrument, which will have spatial
165 mapping capabilities (Beegle et al. 2015).

166 **Table 1.** Table of sample locations and ages.

167 2.2 Raman spectroscopy configuration

168 Raman spectra were obtained using a Renishaw InVia H36031 confocal Raman
169 microscope operating at a wavelength of 514.5 nm green monochromatic laser
170 light, which is similar to the ExoMars flight instrument wavelength of 532 nm
171 (Rull et al. 2011). The laser power was 0.3 mW, avoiding laser induced heating of
172 samples. A 50 x objective lens was used giving a laser “footprint” of 1-3 μm in
173 diameter, with an extended spectral range of 100 cm^{-1} to 2000 cm^{-1} . 10 seconds
174 exposure time and 1 accumulation were used for each spectrum, giving a good
175 signal-to-noise ratio. To include the stretching modes of water molecules,
176 extended wavelength ($100\text{-}4000\text{ cm}^{-1}$) was also measured using the above
177 settings. Spectra were processed using a smooth, baseline subtraction and peak fit
178 functions using WiRE 2.0 software. Peak fitting used a mixture of Gaussian and
179 Lorentzian algorithms.

180 2.3 X-Ray Diffraction

181 Diffraction patterns were acquired on powder samples by using an X'Pert
182 diffractometer (PANalytical, NL) equipped with Cu- α radiation (1.54 \AA ; 45 kV /
183 40 mA) in θ - θ reflectance geometry; data were collected from $5 - 80^\circ 2\theta$ with a
184 step size of 0.013° and a time-per-step of 13.77 s. Crystalline phases were

185 identified by comparison to ICDD PDF # [01-074-1433] (Gypsum). Samples
186 were powdered by hand using a pestle & mortar.

187 2.4 Spectral parameter analysis

188

189 10 spectra were obtained from each sample and average FWHM were plotted
190 against sulphate band positions. ~~The band position is a parameter which is~~
191 ~~commonly used to assess dehydration, whereas the FWHM is not commonly~~
192 ~~assessed. This method was used to determine dehydration but also, even small~~
193 ~~scale differences in spectral parameters would be highlighted, indicating if~~
194 ~~sample groups were different.~~ Statistical variance tests ~~will be~~ used to
195 determine if sample groups are statistically different from each another.

196 2.5 Statistical analysis

197 Overlapping sample fields were examined using SigmaPlot statistical software
198 package to confirm if the groups were statistically different. The sample groups
199 failed the normality test therefore a non-parametric test was used. As two
200 independent groups were compared, a Man-Whitney U test was used.

201 **3 Results**

202 3.1 Raman spectroscopy

203 The spectra obtained across the sample set all show a ν_1 sulphate band position of
204 around 1008 cm^{-1} which is indicative of gypsum (Krishnamurthy & Soots 1971),
205 shown in figure 3. The shocked samples, SH2 & SH3, show a sloping baseline
206 with increased signal-to-noise ratio compared with other samples e.g. selenite.

207 | Additionally the shocked samples shows a weaker Raman signal, with lower band
208 | intensities. The spectra from evaporitic crusts ~~show~~ are similar spectra to that of
209 | shocked samples, with low intensity bands and a higher signal-to-noise ratio, a
210 | part from the central uplift crust, which has an improved signal-to-noise ratio.
211 | The selenite group, have the cleanest spectra with intense ν_1 sulphate bands and a
212 | better signal-to-noise ratio relative to the shocked samples. Unaltered samples
213 | show similar spectra to selenite, except from U6 and U5 which have increased
214 | signal-to-noise ratios. Average ν_1 band positions for each are; unaltered (U) –
215 | 1009.615, selenite (S) – 1009.261, shocked (SH) – 1008.251, crusts (C) –
216 | 1008.262 cm^{-1} . Based on these band positions all samples are classed as gypsum
217 | and have not experienced dehydration.

218 | **Fig 3.** Extended Raman spectra for gypsum (100-2000 cm^{-1}). X axis is Raman
219 | shift in reciprocal centimetres (cm^{-1}). Y axis is Raman intensity in arbitrary units
220 | (a.u.). ‘SH’ spectra have experienced shock from meteoric impact. ‘C’ spectra are
221 | gypsum samples which have been dissolved then re-precipitated as evaporitic
222 | crusts. ‘S’ spectra are selenite, a transparent form of gypsum. ‘U’ spectra are from
223 | unaltered gypsum samples unaffected by shock or dissolution and re-
224 | precipitation.

225 | 3.2 X-ray diffraction

226 | 8 gypsum samples were selected from the larger sample set for XRD analysis
227 | (figure 4), which cover the 4 Ca-sulphate groups. The cell parameters for each
228 | sample show that all 8 samples are in the form of gypsum. It is common for
229 | impact shocked sample to experience partial or complete dehydration, however

230 basanite or anhydrite phases are not found in specimen SH3, which is consistent
231 with the Raman measurements obtained.

232 **Fig. 4** X-ray diffraction patterns.

233 **4 Discussion**

234 4.1 Raman spectroscopy - Extended spectra

235 Selected samples were re-analysed using an extended wavelength range (100-
236 4000 cm^{-1}), to include the stretching modes of water molecules, shown in figure
237 5. An anhydrite control is included to show a completely dehydrated phase. As
238 expected the anhydrite control shows a ν_1 sulphate band position of 1015.39 cm^{-1} ,
239 and does not show the stretching modes of water molecules around 3450 cm^{-1} .
240 Sample SH1 has a fragment of gypsum, and the spectrum for shows a ν_1 band
241 position of 1007.52 cm^{-1} which is indicative of gypsum, although it does not
242 show the presence of water molecules at the expected wavelength. As shocking
243 promotes devolatilisation, the loss of H_2O molecules would be expected, and is
244 well documented by other authors. Additionally, a change in ν_1 band position
245 from 1008 cm^{-1} to 1015 cm^{-1} , would also be expected. Sample SH2 shows a band
246 position of 1006.24 cm^{-1} , and has the stretching modes of water molecules. This
247 is indicative of gypsum, and suggests that either no dehydration has occurred, or
248 that the specimens have been rehydrated.

249 Experimental work by Ramkissoon et al. (2014) and Bucio et al. (2015), clearly
250 show that shocking by impact generates, semi-hydrated and completely hydrated
251 Ca-sulphate phases in the form of basanite and anhydrite respectively. This can
252 be seen in the ν_1 sulphate band position and the presence, or absence, of the

253 stretching modes of water molecules. This relationship does not appear to be
254 realised in naturally impact shocked Ca-sulphates from Haughton crater.

255 **Fig 5.** Extended Raman spectra for gypsum and anhydrite ($100\text{-}4000\text{ cm}^{-1}$).
256 Spectra include ν_1 sulphate stretching mode and H_2O molecule stretching mode
257 around 3500 cm^{-1} .

258 4.2 ν_1 band position against band FWHM

259 The sulphate band position was plotted against the FWHM to determine if these
260 Raman parameters could distinguish between the gypsum specimens. Figure 6(a)
261 shows the 4 types of gypsum used in this study presented as fields. Each point is
262 an average of 10 spectra. Selenite has the largest field which overlaps with
263 unaltered samples. Selenite and unaltered fields plot independently from shocked
264 or crust fields, showing that Raman spectroscopy can distinguish between certain
265 phases of gypsum. The shocked field plots on the edge of the crusts field.
266 Samples with overlapping fields, were analysed for statistical significance. No
267 significant difference was found between the shocked and crust sample band
268 positions ($p=0.966$, Mann-Whitney Sum test) and FWHM ($p=0.251$), indicating
269 that Raman spectroscopy cannot currently distinguish between impact shocked
270 gypsum and gypsum which has been dissolved and re-precipitated as a mineral
271 crust. In contrast, a significant difference is evident between selenite and
272 unaltered sample band positions ($p=0.045$) and FWHM ($p=0.020$). This shows
273 that using the sulphate ν_1 band position vs FWHM, differences between gypsum
274 phases are evident. Raman can therefore identify gypsum phases with enhanced
275 habitability.

276 Figure 6(b) distinguishes samples according to their classification in table 1.
277 Figure 6(c) distinguishes samples according to crystal size, which was determined
278 petrographically. However, there does not appear to be any control based on
279 crystal size.

280 **Fig 6.** Sulphate band position against sulphate band FWHM, with each point
281 representing an average of 10 spectra. x-axis, is the sulphate (v1) band position in
282 reciprocal centimetres (cm^{-1}). Y-axis, is the sulphate (v1) full width at half
283 maximum (FWHM). (a) Samples are separated into their geological groups. (b)
284 Samples are distinguished by sample classification (table 1). (c) Samples are
285 distinguished based on crystal size. Squares denote a crystal size less than 0.5 cm;
286 diamonds denote a crystal size of between 0.5 and 2 cm; circles denote a crystal
287 size greater than 2 cm.

288 **5 Conclusions**

289 A range of gypsum samples were analysed using Raman spectroscopy, to
290 determine if this technique can differentiate between Ca-sulphates which have
291 enhanced habitability, and those that do not. Results show that Raman
292 spectroscopy cannot currently determine a significant difference between gypsum
293 which has been shocked by meteoric impact (enhancing the habitability), and
294 gypsum which has been dissolved and re-precipitated as an evaporitic crust.
295 Raman spectroscopy is able to differentiate between unaltered gypsum and
296 selenite by plotting v1 sulphate band position against v1 sulphate band FWHM,
297 and as selenite has been found with viable extant microbial colonies at Haughton
298 impact crater, it is regarded as having enhanced habitability.

299 The presence of H₂O bands in spectra obtained from shocked samples highlights
300 the complexity of Raman spectra observed from naturally shocked samples
301 compared with experimental shock studies. This indicates current capabilities of
302 Raman spectroscopy, for the interpretation of gypsum habitability, prior to its use
303 on the European Space Agency's ExoMars 2020 mission.

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Sample	Description/Location	Age	Group
U1	Vale of Eden, Cumbria, UK	Permian	1
U2	Kingscourt fibrous, Co. Cavan, Ireland	Triassic	1
U3	Scapa, Orkney	Devonian	1
U4	Kingscourt with hematite, Co. Cavan, Ireland	Triassic	1
U5	Gotham Triassic, England	Triassic	1
U6	Ebro Basin, Spain	Oligocene-Miocene	1
S1	Selenite, California	Paleogene	2
S2	Selenite, Haughton, Devon Island	Eocene-Oligocene	2
S3	GSC dome (NE side), Selenite Haughton, Devon Island	Eocene-Oligocene	2
S4	Selenite, Kent	Eocene	2
C1	Central uplift crust, Haughton, Devon Island	Eocene-Holocene	3
C2	GSC dome (NE side) crust, Haughton, Devon Island	Eocene-Holocene	3
C3	Gypcrete Chile	Paleogene - Holocene	3
C4	Rhino Creek, Crust on lake sediments, Haughton, Devon Island	Eocene-Holocene	3
SH1	West Rhino creek melt breccia, Haughton, Devon Island	Eocene	4
SH2	Gemini Hills Shocked A Haughton, Devon Island	Eocene	4
SH3	Gemini Hills Shocked B Haughton, Devon Island	Eocene	4

415 **Table 1** Table of sample locations and ages.

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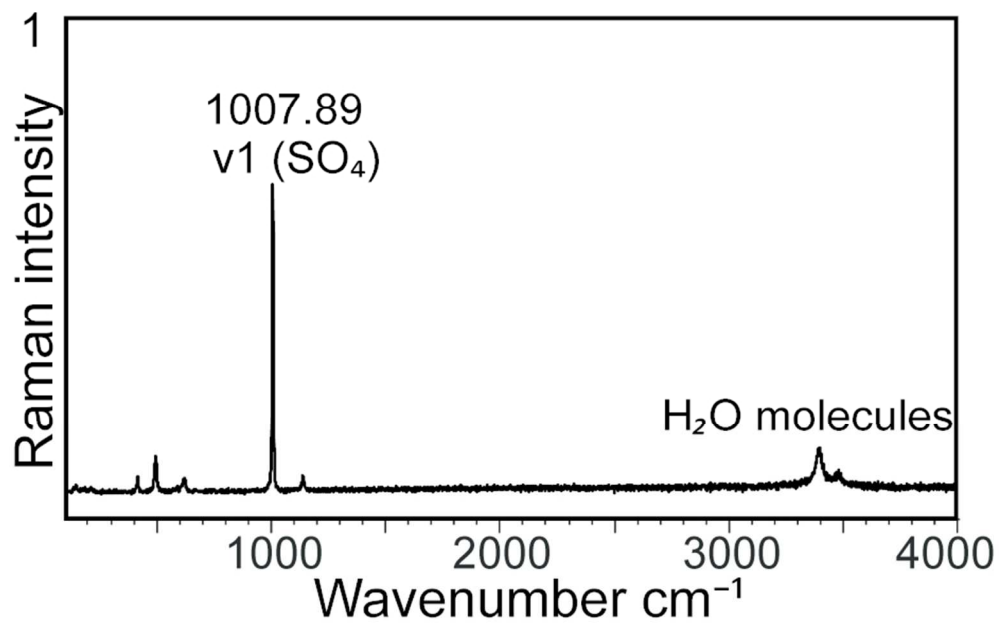


Fig. 1 Extended spectra 100-4000 cm⁻¹ showing v1 sulphate symmetric stretching mode (1007.89 cm⁻¹) and stretching mode of H₂O (~3450 cm⁻¹).

80x50mm (300 x 300 DPI)

Review

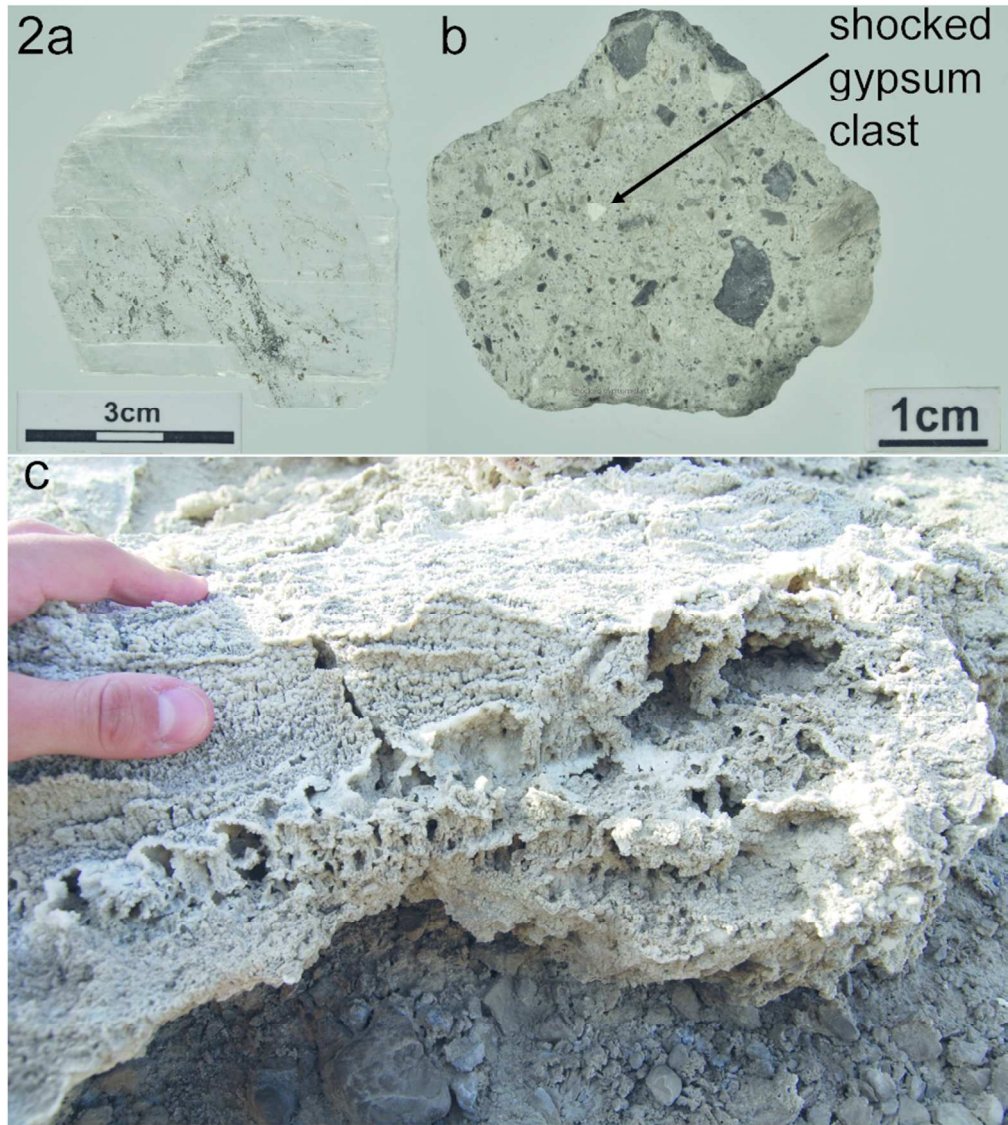


Fig 2. Sample photographs. (a) Selenite, Haughton crater (S2), showing black pigmentation of bacterial colonies. (b) Melt breccia, Haughton crater (SH1), showing fragment of shocked gypsum. (c) Evaporitic gypsum crust, Haughton crater (C1).

80x90mm (300 x 300 DPI)

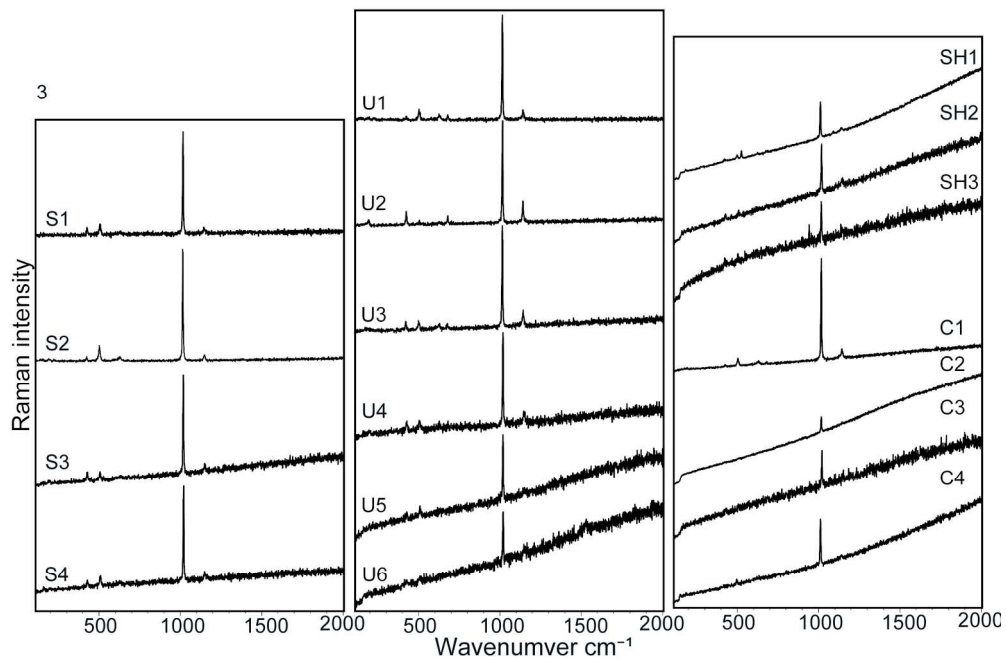


Fig 3. Extended Raman spectra for gypsum ($100\text{-}2000\text{ cm}^{-1}$). X axis is Raman shift in reciprocal centimetres (cm^{-1}). Y axis is Raman intensity in arbitrary units (a.u.). 'SH' spectra have experienced shock from meteoric impact. 'C' spectra are gypsum samples which have been dissolved then re-precipitated as evaporitic crusts. 'S' spectra are selenite, a transparent form of gypsum. 'U' spectra are from unaltered gypsum samples unaffected by shock or dissolution and re-precipitation.

175x116mm (300 x 300 DPI)

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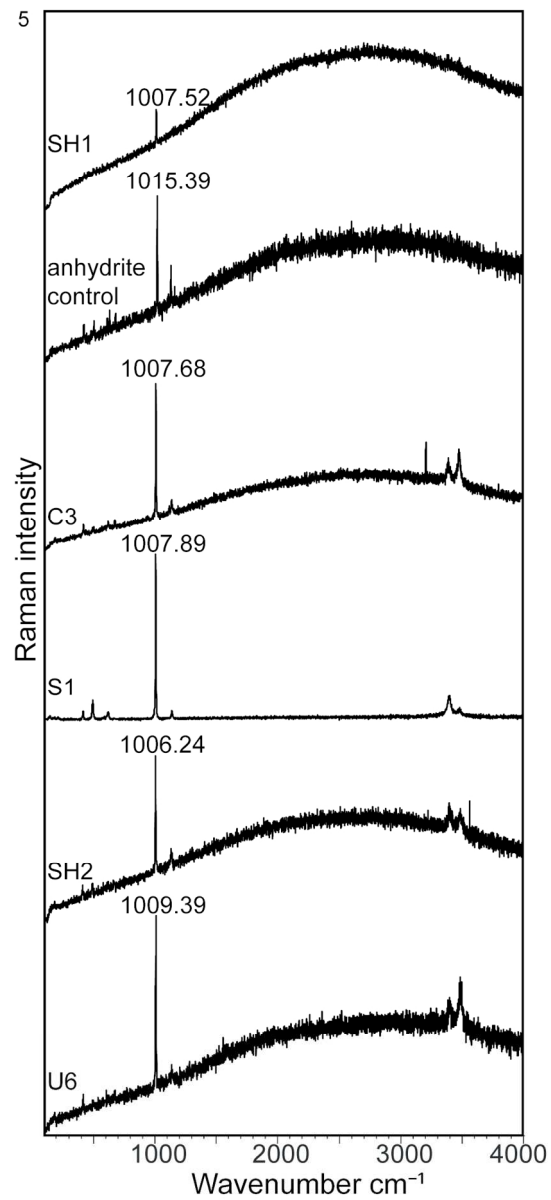


Fig 5. Extended Raman spectra for gypsum and anhydrite (100-4000 cm⁻¹). Spectra include v1 sulphate stretching mode and H₂O molecule stretching mode around 3500 cm⁻¹.

80x176mm (300 x 300 DPI)

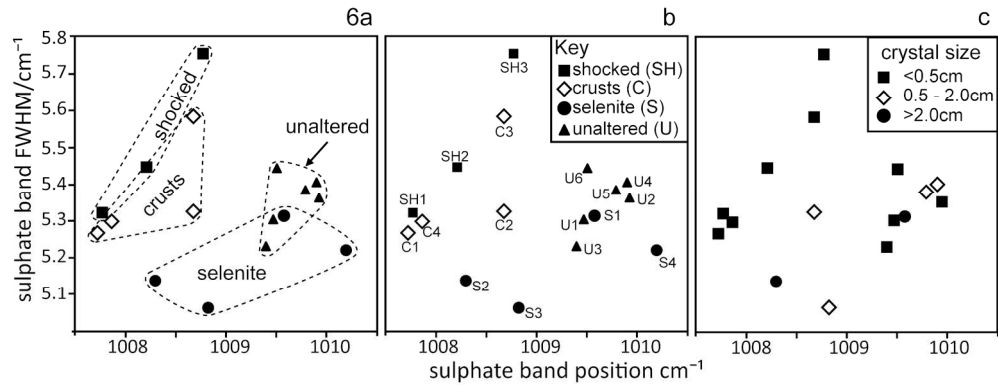


Fig 6. Sulphate band position against sulphate band FWHM. x-axis, is the sulphate (v1) band position in reciprocal centimetres (cm^{-1}). Y-axis, is the sulphate (v1) full width at half maximum (FWHM). (a) Samples are separated into their geological groups. (b) Samples are distinguished by sample classification (table 1).

(c) Samples are distinguished based on crystal size. Squares denote a crystal size less than 0.5 cm; diamonds denote a crystal size of between 0.5 and 2 cm; circles denote a crystal size greater than 2 cm.

175x67mm (300 x 300 DPI)

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