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NIR reflectance spectroscopy of hydrated and anhydrous sodium carbonates at different temperatures

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Abstract

Recent space-based observations have revealed or suggested the existence of various types of carbonate salts in several Solar System bodies, such as Mars, Ceres, Enceladus, and Europa. Natrite is the main component of the crater Occator's faculae observed in detail by the Dawn spacecraft on the dwarf planet Ceres. Sodium carbonates are thought to form as precipitates in brines, originating in aqueous environments in the subsurface of Ceres and icy bodies. Here we report about near-infrared (0.8-4.2 μm) reflectance spectroscopic investigations on three compounds, namely natrite (anhydrous Na_2CO_3), monohydrated sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, thermonatrite) and decahydrate sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, natron). Spectral measurements have been carried out in the overall temperature range 93-279 K, representative of planetary surfaces. The analysis of diagnostic spectral signatures shows different temperature-dependent trends for several band parameters, as well as different behavior as a function of the the grain size for a given temperature. While spectra of natrite are characterized by several CO_3 absorptions, broad and strong absorption features due to H_2O dominate the spectra of heavily hydrated natron. The intermediate sample (monohydrated) shows multiple bands due to the overlap of CO_3 and H_2O vibrational modes. Our temperature-dependent laboratory spectra are compared with Dawn-VIR spectra of Ceres and with Galileo-NIMS spectra of Europa.

1. Introduction

Sodium carbonate minerals are rarely seen on the surfaces of Solar System bodies other than the Earth, both in the anhydrous form and in hydrated forms. Remote sensing observations returned by planetary space missions have confidently identified various types of carbonate compounds in different hydration states on Mars and on the dwarf planet Ceres, while their existence has been ascertained in Saturn's satellite Enceladus and suggested in Jupiter's satellite Europa.

Occurrence of Na-carbonates on Earth.

On Earth, anhydrous and hydrated sodium carbonates appear in different environments. Natrite (Na_2CO_3) is not widespread and typically occurs in localized volcanic areas, especially in pegmatites from alkaline massifs (Russia) (Khomyakov, 1983) or in xenoliths from intrusive alkaline complexes (Canada) (Anthony et al., 2003), and rarely it also occurs in carbonatites (Jones et al., 2013). The two most common hydrated phases, thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), are evaporite minerals typically found in saline lacustrine environments (Jones & Deocampo, 2003). In particular, these minerals are frequently associated with sodium-rich waters produced in geologic settings where calc-alkaline volcanic activity was predominant, and Na^+ ions are often the most common species

50 in solution (Jones & Deocampo, 2003). In the chemical evolution path of brine due to
51 evaporation, typically Na-carbonates are the last species to precipitate, following the
52 sequence: Ca-Mg carbonates → gypsum → Mg-sulfates → Na-sulfates → Na-carbonates.
53 Rarely thermonatrite and natron are also found as high temperature fumarole volcanic
54 products (Russo, 2006).

55 56 *Ceres.*

57 Spectroscopic observations by the Visible and InfraRed mapping spectrometer (VIR) onboard
58 the NASA Dawn mission indicate that the bright material units (*faculae*) seen in the floor of
59 the 92-km crater Occator on Ceres are mainly composed of natrite (Na_2CO_3) mixed with
60 phyllosilicates, ammonium chloride and a dark, spectrally featureless absorbing material (De
61 Sanctis, et al., 2016; Raponi et al., 2018). Many other occurrences of Na-carbonates have been
62 identified on Ceres (Carozzo et al., 2018; De Sanctis et al., 2017), mostly in anhydrous form.
63 The main evidence for natrite in the Ceres spectra of Occator's faculae comes from the shape
64 and central wavelengths of the of CO_3^{2-} absorption bands at approximately 3.3-3.5 and 3.95-
65 4.0 μm (Hunt & Salisbury, 1971) together with its contribution in increasing the reflectance
66 level with respect to the average spectrum of Ceres (De Sanctis, et al., 2016). Occator's faculae
67 spectra show strong carbonate bands, with a clear shift of the band center longward of 3.98
68 micron, which is indicative of sodium carbonate. The estimated amount of sodium carbonate
69 in Cerealia Facula, i.e. the brightest spot found in crater Occator and one of the brightest spots
70 across Ceres, is up to 70-80 vol%, making it the largest carbonate concentration found on an
71 extraterrestrial body (De Sanctis et al., 2016; Raponi et al., 2018).

72 Its co-occurrence with ammonium salts near impact craters on Ceres has been interpreted as
73 due to liquid brines upwelling from depth and crystallization on the surface (Zolotov, 2017).
74 The formation mechanisms and stability fields of natrite and other chemical species have
75 been recently investigated both in terms of laboratory experiments and modeling. Based on
76 laboratory studies of freezing liquid brines containing $\text{Na}^+ - (\text{NH}_4)^+ - \text{Cl}^- - (\text{CO}_3)^{2-}$ ions, Vu et
77 al. (2017) showed that mainly preferential precipitation of Na-carbonates occurs due to the
78 lowest aqueous solubility at cryogenic temperatures, confirming the scenario in which natrite
79 crystallized on the surface of Ceres from liquid brines ascending from below. Zolotov (2017)
80 used a chemistry model to investigate the formation of compounds starting from water
81 solutions containing H-C-N-O-Na-Cl ions. Natron and nahcolite (NaHCO_3)
82 precipitate/crystallize as starting species in liquid brines reaching the surface of Ceres, and
83 subsequent dehydration, due to instability at vacuum conditions, results in deposition of
84 Na_2CO_3 .

85 The laboratory detailed spectral analyses of natrite and natron at cryogenic temperatures will
86 be of interest for the analyses and interpretation of Dawn data, as well as for data from future
87 missions to Ceres.

88 89 *Europa.*

90 Sodium compounds have been suggested to exist on the surface of Jupiter's icy Galilean moon
91 Europa, both in the form of carbonates and sulfates, in various hydration states and mixed
92 with water ice (Carlson et al., 2009). In particular, natron is among the best candidates to
93 explain spectra of visually dark, non-icy terrains on Europa (McCord et al., 1998a) as revealed
94 by the Near Infrared Mapping Spectrometer (NIMS) onboard the NASA Galileo spacecraft
95 (Carlson et al., 1992). Spectra of non-icy terrains as measured by Galileo-NIMS display
96 broadened and distorted water ice absorption features in the 1-3 μm region, combined with
97 the lack of metal-OH signatures. This has been interpreted as evidence for a high hydration
98 state, i.e. a high number of H_2O molecules bonded in the mineral structure in different crystal
99 sites, pointing to the presence of heavily hydrated sodium carbonates (e.g., natron), likely

100 intermixed with Mg-sulfates, rather than clays and phyllosilicates (McCord et al., 1998b).
101 Although a specific salt mineral perfectly matching the spectral profiles of Europa in non-icy
102 regions has not been yet unanimously identified, natron has been used as a plausible spectral
103 endmember in mixtures to model the measured NIMS spectra, together with hydrated Mg-
104 sulfates such as bloedite, mirabilite, hexahydrate, and epsomite (McCord et al., 1999; McCord
105 et al., 2010). Previous laboratory studies (see for example Dalton et al., 2005; De Angelis et al.,
106 2017) have investigated the temperature-dependent behavior of magnesium sulfates as
107 analogues for the Europa spectra modeling. Further laboratory work on hydrated Na-
108 carbonates at cryogenic temperatures will be helpful in the comprehension of data from
109 future missions to Europa and Jovian icy moons (ESA/JUICE and NASA/Europa Clipper).

110

111 *Enceladus.*

112 Sodium salts have been reported to occur in Saturn's E-ring, which originates from the jets
113 emanating from the southern polar region of its icy moon Enceladus. In particular Na_2CO_3 ,
114 NaCl and NaHCO_3 were detected *in situ* by the Cosmic Dust Analyser onboard the Cassini
115 spacecraft (Postberg et al., 2009, 2011). The sodium salts observed by means of mass
116 spectrometry within both Saturn's E-ring and the plumes of Enceladus are believed to
117 originate from a liquid ocean located some tens of km beneath the surface (Postberg et al.,
118 2009, 2011).

119

120 *Mars.*

121 Carbonates with different compositions have been detected on Mars by means of remote
122 sensing techniques, both in the atmospheric dust and on the surface, as well as by *in situ*
123 instruments onboard landers and rovers (Niles et al., 2013). Nevertheless, the observations
124 are so far in agreement with the presence of Ca-Mg-Fe carbonates, while Na-carbonates have
125 not yet been detected. For example, carbonates in martian dust have been observed by means
126 of thermal infrared measurements obtained by the Thermal Emission Spectrometer (TES)
127 onboard Mars Global Surveyor (Bandfield et al., 2003). Several spectroscopic evidences
128 obtained from orbit attest the presence of carbonates on the surface (Ehlmann et al., 2008;
129 Ehlmann & Edwards, 2014; Wray et al., 2016), while MER rovers (Morris et al., 2010) and the
130 Phoenix lander (Boynton et al., 2009) also evidenced their occurrence in several sites.

131

132 So far sodium carbonates have been missing both in remote sensing observations and in
133 landers/rovers analyses at Mars, although their presence is predicted by models. According to
134 some authors Na-carbonates, which are highly soluble, should be present in the upper layers
135 of a model evaporitic sedimentation stratigraphy (Catling, 1999), while Fe/Mg-carbonates are
136 expected to be deeply buried. In this case Na-carbonates would be completely hidden by the
137 oxidized surface layer. Other authors (Grotzinger & Milliken, 2012) point out that the global
138 low-pH (acidic) conditions of ancient Martian aqueous environments prevented the formation
139 of Na-carbonates on a global scale. According to McLennan (2012) sedimentary secondary
140 minerals tend to be Fe- and Mg-rich and Na- and K- poor, reflecting differences in crustal
141 composition between Earth and Mars as well as differences in the aqueous environment of
142 alteration (more acidic).

143 In-situ data from forthcoming rover missions (ESA/ExoMars 2020, NASA/Mars 2020) will
144 provide additional information about mineralogy at small scales, and data interpretation will
145 be aided by detailed laboratory studies of sodium (and not only) carbonates at low
146 temperatures.

147

148

149

150 *Laboratory studies.*

151 Several laboratory studies exist up to now that investigated sodium carbonates in detail by
152 means of visible-near infrared (NIR) spectroscopy and at various P-T conditions. Bujis &
153 Schutte (1961a,b) measured mid-infrared transmission spectra of anhydrous sodium
154 carbonate and various forms of its hydrates, at room temperature. Mid-infrared (Mid-IR)
155 spectra of natrite were acquired in the 5-50- μm range at 300K and 80K by Brooker & Bates
156 (1971). Meekes et al. (1986) published reflection spectra of natrite at various temperatures in
157 the far infrared (Far-IR, 25 μm – 0.1 mm), and also Harris & Salje (1992) investigated
158 anhydrous sodium carbonate by means of transmission spectroscopy in the mid-IR (5-25- μm)
159 at various temperatures. McCord et al. (2001) measured Near-IR spectra (1-2.7 μm) of natron,
160 together with mirabilite and epsomite, under vacuum conditions at ambient and cryogenic
161 temperatures in the range 100-300K, in order to study the stability field of these minerals.
162 Crowley (1991) and Harner & Gilmore (2015) acquired spectra of natron, among many other
163 evaporitic playa minerals, in the 0.35-2.5- μm range at room temperature. Drake (1995) and
164 Harner & Gilmore (2014) published room temperature reflectance spectra of thermonatrite in
165 the 0.35-2.5- μm range.

166
167 Several studies report on the phase transitions underwent by Na_2CO_3 because of temperature
168 variations. Natrite presents four phases: α , β , γ , δ in the temperature range <170-1000K. In
169 the 170-605K temperature range, natrite is in the form γ (incommensurate, space group
170 $C2/m$) with cell parameters $a=8.920 \text{ \AA}$, $b=5.245 \text{ \AA}$ and $c=6.050 \text{ \AA}$ (Harris & Salje, 1992;
171 Arakcheeva & Chapuis, 2005). For temperatures below 130-170K, natrite undergoes a fourth
172 phase transition, to δ -phase named “lock-in”, with cell parameters $a=8.898 \text{ \AA}$, $b=5.237 \text{ \AA}$ and
173 $c=5.996 \text{ \AA}$ (Meekes et al., 1986; Arakcheeva & Chapuis, 2005). In the δ -phase below 130K the
174 sodium carbonate assumes a commensurate structure. As the temperature decreases, a
175 gradual strengthening of C–Na interactions occurs, with shortening of C–Na interatomic
176 distances. The number of C–Na bonds (Na^+ ions surrounding C atoms) increases as T
177 decreases. These changes produce modifications in the O atomic positions, and result in
178 increasing of C–O distances, and tilting and distortion of CO_3 units (Arakcheeva & Chapuis,
179 2005). Moreover, order-to-disorder changes are related to phase transitions, involving
180 changes in the structure of lattice bands (Brooker & Bates, 1971). Meekes et al. (1986) in their
181 IR and Raman study observe a change with temperature in peak intensity relative to ν_1
182 frequency mode (1080 cm^{-1}). In general they report the appearance of new sharp absorption
183 lines in mid-IR and Raman spectra acquired below 130 K, instead of broad bands occurring at
184 higher temperatures. Analogously Harris & Salje (1992) report the appearance of two weak
185 absorption bands in their IR spectra at low temperatures. They measured IR spectra in the 5-
186 25- μm range and in the 45-800K temperature range, finding that new absorption features
187 appeared in the 14 μm region (ν_4 fundamental vibration) in <130K spectra: the room-
188 temperature band corresponding to ν_4 consists of two peaks, while below 130K it is
189 composed of seven separate peaks. In our measurements we do not probe the mid-IR range,
190 so we are not directly sensitive to the fundamental carbonate vibrations, but only to their
191 overtones and combinations. Nevertheless, the temperature-dependent spectral changes that
192 we observe in the VNIR are undoubtedly related to the change in the mineral structure. Here
193 we probe the overtone at 2.12-2.16 μm ($\nu_1+2\nu_3+\nu_4$ or $3\nu_1+2\nu_4$), so we expect some changes
194 could be seen below 130K in this feature, although probably requiring very high spectral
195 resolution.

196
197 In all these works cryogenic spectra of natrite are only described in the range above 5 μm and
198 in transmission mode (Brooker & Bates, 1971; Harris & Salje, 1992). Thus cryogenic

199 reflectance spectra of natrite in the $<5 \mu\text{m}$ spectral range seem to be lacking in the literature.
200 Concerning natron, cryogenic spectra are only described at 100K (McCord et al., 2001) and in
201 the 1-2.7 μm range: so cryogenic reflectance spectra of natron are lacking in the 2.7-5 μm
202 range. Finally no cryogenic spectra of thermonatrite seem to be present in the literature.
203 Moreover literature transmission studies typically focused on samples in thin films.
204 Reflectance studies instead used single grain size ranges ($d < 125 \mu\text{m}$ (Harner & Gilmore,
205 2015) or 355-500 μm (McCord et al., 2001)) or generic powders. A systematic work is thus
206 missing dedicated to a comparative study of different grain sizes.

207

208

209 *Our work.*

210 In this laboratory work we present the results of near infrared reflectance spectroscopy
211 measurements obtained for three sodium carbonates, two hydrated and one anhydrous,
212 namely natrite (Na_2CO_3), thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).
213 Reflectance spectra were acquired for these samples, in the 0.8-4.2- μm range, in three
214 different grain sizes, and at several temperatures in the overall range 93-279 K.

215 While previous work mainly focused on a particular type of sample at a fixed temperature,
216 here we describe a systematic comparative spectral study on sodium carbonate in its
217 anhydrous form and in its two natural hydrated stable forms.

218 Our study is based on the analyses of spectral data for numerous temperatures (10-11 steps
219 for each ramp) in the above-mentioned range; other studies concerning low-temperature
220 measurements described spectra acquired at few selected temperatures.

221 Here we also present a systematic study dealing with different grain sizes and comparing
222 their spectral effects.

223

224 In Section 2 we describe the experimental setup that we used at the Institut de Planétologie et
225 d'Astrophysique de Grenoble (IPAG). In Section 3 and 4 we present the spectral analysis and
226 results, followed by a discussion in terms of their relevance for Ceres and Europa.

227

228 **2. Methods.**

229

230 **2.1 Experimental setup**

231

232 Our measurements were carried out in November 2016 with the SHINE Spectro-Gonio
233 Radiometer facility (Brissaud et al, 2004) at the Institut de Planétologie et d'Astrophysique de
234 Grenoble (IPAG). The instrument is a bidirectional VIS-NIR reflectance spectrometer, which
235 we operated in the overall 0.8–4.2- μm spectral interval by means of two detectors: a silicon
236 photodiode in the 0.5–1.0 μm range and an InSb IR detector in the 1.0–4.2 μm range. The
237 anhydrous sample was acquired in the range 1-4.2 μm , in order to fully measure the
238 carbonate band at 4 μm . Conversely, the two hydrated samples were acquired in the range
239 0.8-4.0 μm . This choice was motivated by the fact that the 3-4 μm region is expected to be
240 dominated by water absorption, and by the time required to measure the full range up to 4.2
241 μm .

242 The sample is illuminated with monochromatic light. Spectralon and Infragold (Labsphere ©)
243 were used as standard reference targets, measured at room temperature and radiometrically
244 characterized in terms of BRDF (Bonnetoy 2001). All spectra were acquired with an
245 illumination angle $i = 0^\circ$ and an emission angle $e = 15^\circ$. We used the following spectral
246 sampling: (i) natrite, $\Delta\lambda = 20 \text{ nm}$ in the 0.8-4.2 μm range; (ii) thermonatrite and natron,
247 $\Delta\lambda = 20 \text{ nm}$ in the 0.4-1.2 μm range, $\Delta\lambda = 10 \text{ nm}$ in the 1.2-3 μm range, $\Delta\lambda = 20 \text{ nm}$ in the 3-4.2 μm

248 range. The average spectral resolution was: 10 nm for $\lambda=0.8-1.6 \mu\text{m}$, 19 nm for $\lambda=1.6-3.0 \mu\text{m}$,
249 and 39 nm for $\lambda=3.0-4.2 \mu\text{m}$.

250 The CarboN-IR environmental chamber coupled with the spectro-gonio-radiometer (Grisolle
251 2013; Grisolle et al., 2014; Beck et al., 2015) was used to perform measurements. The cham-
252 ber consists of a large closed isothermal copper cell (8-cm diameter) placed within a stainless
253 steel chamber. The sample is placed within the inner closed cell. A helium cryocooler is used
254 to cool down the cell and the optical access is enabled by a sapphire window viewport. This
255 setup allows the acquisition of reflectance spectra at temperatures down to 50 K. A few mbar
256 of dry air were purged into the cell with the aim of ensuring efficient thermal coupling of the
257 sample and avoiding dehydration. The temperature of the cell is monitored during the
258 measurement runs, and the associated error on the effective sample temperature is of the
259 order of 1 K.

260

261 2.2 Samples

262

263 We analyzed three sodium carbonate compounds: natrite (anhydrous, Na_2CO_3), thermonatrite
264 ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). These samples are available on the market,
265 supplied by Sigma Aldrich and characterized by a >99% purity level. All materials were
266 ground, sieved and sorted at three different grain sizes: 36-50 μm , 75-100 μm , and 125-150
267 μm . The choice of these grain size ranges is motivated by measuring fine, medium and coarse
268 particles, avoiding at the same time any overlap in particle dimensions among these three
269 classes. These grain sizes fall in the range of particle dimensions that constitute typical
270 planetary regoliths ($20 \mu\text{m} < d < 20 \text{mm}$ (Gundlach & Blum, 2013)). In particular for Ceres
271 regolith the mean expected grain size is about 100 μm . According to Hapke modeling (De
272 Sanctis et al., 2015) grain sizes in the range 2-190 μm are expected for minerals and 300 μm
273 for water ice. Concerning Europa surface particles sizes in the range between $d < 50 \mu\text{m}$ and a
274 few hundreds of micrometers are inferred from NIR observations (McCord et al., 1999).

275

276 2.3 Spectra acquisitions and data reduction

277

278 Reflectance spectra were acquired at different temperatures for each grain size (Figs. 1-3), in
279 the range 93-279 K. The first spectrum was acquired at room temperature (279 K), whereas
280 all other measurements were recorded starting from the lowest temperature ($T_0 = 93 \text{K}$) and
281 acquiring consecutive spectra at increasing temperature values, up to 279 K again.
282 Measurements have been performed at steps of 10-15 K in the low temperature range, and at
283 steps of 20-25 K in the high temperature range, for a total of 10-11 steps on average for each
284 grain size.

285 Different spectral parameters were computed starting from the measured spectra: band area,
286 band depth, band width, and band position for each of the absorptions visible in the spectra.
287 The reflectance value has also been evaluated for the three samples, at 279 and 93 K, as a
288 function of the water content (see Section 4: Discussion).

289 All of the spectral indices have been computed after removing the spectral continuum: a
290 straight line has been drawn between the edges for each band, by intersecting the visually
291 identified maxima on both sides of the band (Fig. 4), and then has been removed by dividing
292 the spectrum by this line. For each grain size and a given absorption band, shoulder positions
293 used for continuum removal were the same for all spectra (all temperatures). We applied a
294 second-order polynomial fit around the band minimum (after resampling) in order to
295 compute the band position value (minimum of the fit). Following Clark & Roush (1984), we
296 determined the band depth as: $D = (R_C - R_B) / R_C$, where R_B and R_C are the reflectance factor of
297 the band at its minimum and the level of the spectral continuum at the position of the band

298 minimum, respectively. The width has been computed by intersecting the continuum-
299 removed band with a horizontal line passing through half depth. Finally the band area has
300 been computed between the continuum maxima as the total area between the continuum line
301 and the absorption band. For those absorption bands showing multiple minima, the spectral
302 continuum is computed between the two shoulders of the band, and the position of each
303 single minimum is fitted with a second-order polynomial. The band area and band width are
304 also computed only for the entire band and not for every single relative minima, for which it is
305 not unambiguous to select the shoulders. The features near 1 μm are likely instrumental
306 artifacts and thus they have not been analyzed. All retrieved spectral parameters and input
307 shoulder positions for continuum removal are listed in tables in the Supplementary Material.
308

309 **3. Results**

310 **3.1 Spectral measurements**

311
312
313 In Fig. 1-3 we summarize respectively the measured spectra of natrite (Fig. 1), thermonatrite
314 (Fig. 2), and natron (Fig. 3). For each mineral, the spectra corresponding to the measured
315 temperatures in the range 93-279 K are shown separately for the three analyzed grain sizes:
316 the fine one (36-50 μm) in the top panel, the medium one (75-100 μm) in the central panel,
317 and the coarse one (125-150 μm) in the bottom panel. In each plot, the top spectrum (dashed
318 line) is the first spectrum acquired at room temperature (279 K), then all the spectra are
319 shown in order of increasing temperature from bottom to top: from 93 (always the second
320 acquired spectra) back to 279 K, from bottom to top. The spectra are offset by 0.1 in
321 reflectance for clarity.
322

323 *3.1.1 Anhydrous Sodium carbonate (natrite)*

324
325 The spectra of anhydrous sodium carbonate (Fig. 1) are characterized by combinations and
326 overtones of CO_3^{2-} absorption bands located near 2.2, 2.35 and 2.55 μm (Gaffey, 1986, Clark et
327 al., 1990), whose fundamental vibrational transitions are located in the 7-14- μm region. A
328 very weak feature appearing near 1.75 μm could also be due to CO_3^{2-} absorptions (Gaffey,
329 1986), although we did not analyze it. Some $\text{H}_2\text{O}/\text{OH}^-$ could be responsible for the faint
330 absorption at 1.55 μm and for the band at 2.0 μm , although the latter overlaps with a CO_3^{2-}
331 absorption (Gaffey, 1986, Clark et al., 1990). The 3-4 μm spectral region is characterized by
332 the two strong CO_3^{2-} absorptions appearing around 3.4 and 3.9 μm , which are diagnostic of
333 anhydrous carbonates (Buijs & Schutte, 1961a; Hunt & Salisbury, 1971). In particular, the 3.4
334 μm feature (2900 cm^{-1}) is assigned to the overtone $2\nu_3$ of the fundamental vibration ν_3
335 occurring at 6.9 μm (1451 cm^{-1}), while the 4 μm feature (2500 cm^{-1}) is assigned to a
336 combination $\nu_1+\nu_3$ of the fundamental vibrations ν_1 at 9 μm (1079 cm^{-1}) and ν_3 (Buijs &
337 Schutte, 1961a; Nuevo et al., 2014). Both features are characterized by two separate minima
338 that appear as doublets at 3.4-3.5 and 3.8-4.0 μm , whose relative strength varies as a function
339 of temperature. In the 3 μm region the broad absorption band is likely due to absorption by
340 ambient water molecules adsorbed on the sample (Farmer, 1974). A very faint and narrow
341 feature appears near 2.65 μm in almost all spectra, although it remains unassigned. It could be
342 in principle due to water vapor present along the external optical path. A narrow absorption
343 also appears at 3.1 μm at cryogenic temperatures, putatively due to some water condensation
344 (see Discussion Section below). It must be noted that the preparation and manipulation in the
345 laboratory of the anhydrous sample result in moderate hydration of natrite, which in fact is
346 unavoidable due to the hygroscopic nature of the compound. The overall reflectance level at

347 the continuum background (near 1 μm) does not show any clear correlation with
348 temperature, for the anhydrous as well as for the hydrated forms. Fluctuations in the
349 reflectance level of the order of <10% occur as the temperature change. Instead a correlation
350 is seen with the hydration state; we examine this aspect in section 4.4.

351

352 3.1.2 Sodium carbonate monohydrated (*thermonatrite*)

353

354 Spectra of thermonatrite are shown in Fig. 2. These spectra are characterized both by an
355 increased complexity and by an overall notable reduction of the reflectance longward of 1.5
356 μm , because of the presence of water molecules bonded within the crystal structure of the
357 mineral. Several hydration bands due to vibrational transitions in H_2O molecules appears in
358 several locations, most of which combine and overlap with the absorption features due to
359 CO_3^{2-} ions. In spectra acquired at room temperature, the main recognizable absorption bands
360 occur at 1.25, 1.6 μm , 1.8 μm , 2.0 μm , 2.5 μm , 2.65 and 3.0 μm . The bands at 2.0 and 2.5 μm
361 display a composite structure that becomes more complex as the temperature decreases. At
362 room temperature, the 2.35- μm CO_3^{2-} absorption appears as a shoulder within the 2.55 μm
363 carbonate band, while at the lowest temperatures the 2.5- μm band splits in three separate
364 narrow minima. In the 3-4 μm region, the intense water absorption generally gives a very low
365 reflectance level while the carbonate bands are greatly attenuated; the broad 3- μm H_2O band
366 becomes more defined at low temperatures, while the reflection peak near 3.8 μm becomes
367 more evident and shifts towards shorter wavelengths. At room temperature, strong
368 absorption by water produces saturation in the 3- μm region. This saturation is stronger in the
369 spectra of the sample with grain size 75-100 μm and even more evident in spectra of the
370 samples at 125-150 μm , where the 3- μm band is almost flat. On the contrary, the 3- μm band
371 in 36-50 μm spectra is evident also in measurements acquired at room temperature.
372 Furthermore, in the finest grain size a change in the spectral slope at 3.5 μm is likely the result
373 of the nearby 3.4 μm absorption due to CO_3^{2-} .

374

375 3.1.3 Sodium carbonate decahydrate (*natron*)

376

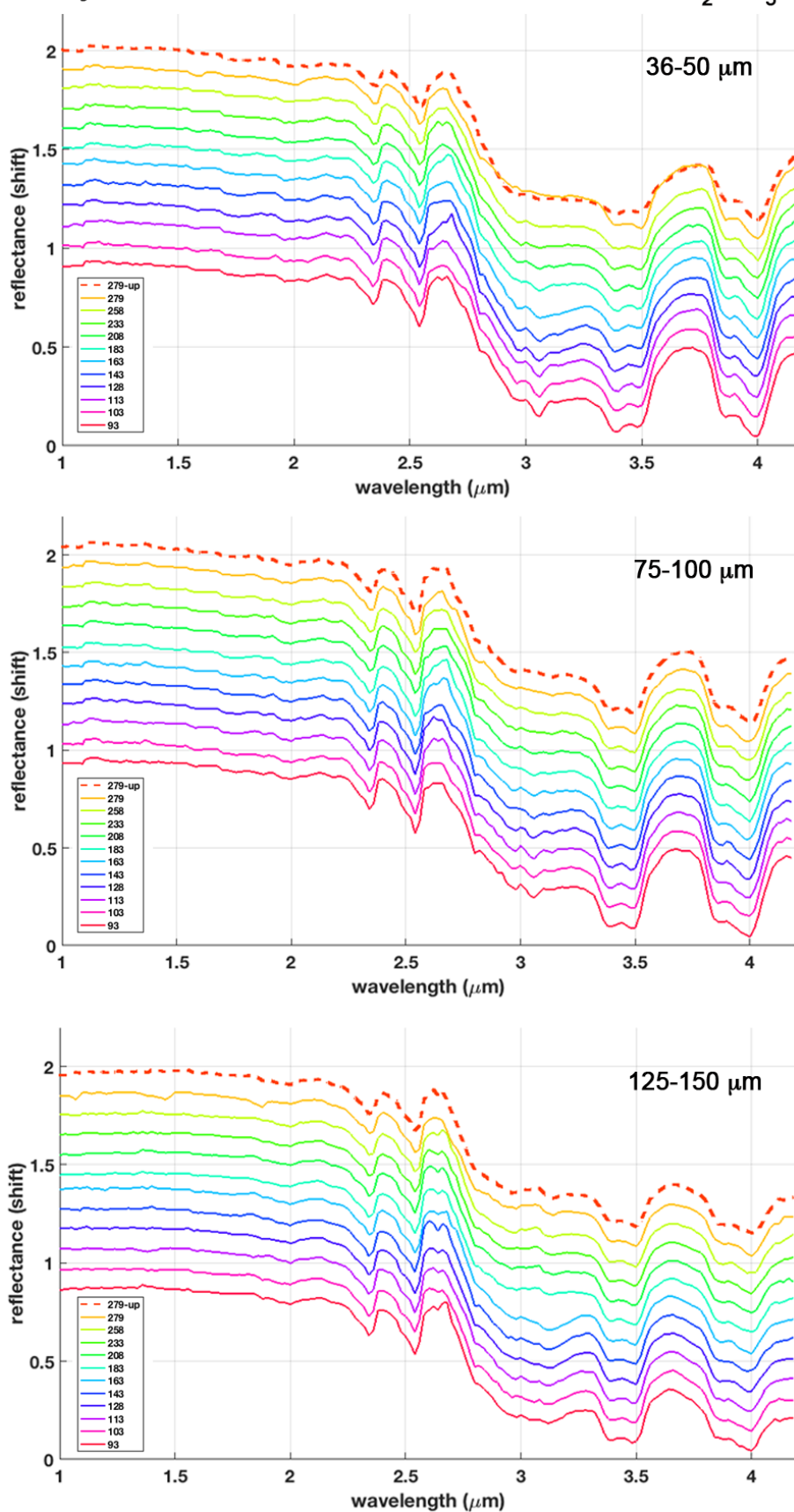
377 Figure 3 shows the spectra of sodium carbonate decahydrate, or natron. The high water
378 content is responsible for most of the absorption features. The bands occurring at 1.0, 1.25,
379 1.5, 2.0 and 3.0 μm are due to combinations and overtones of the water molecule (Farmer,
380 1974; Clark et al., 1990). The CO_3^{2-} transitions are responsible for an absorption close to 2.45
381 μm , for an absorption near 1.75-1.8 μm , although comprised within the broad 1.5- μm band,
382 for the change in the spectral slope near 3.5 μm and for the drop in reflectance towards 4 μm .
383 With respect to the thermonatrite spectra, the higher hydration state of natron results in H_2O
384 bands at 1.5 and 2 μm being very strong and broad and characterized by a less complex fine
385 structure, due to the overlap of various bands corresponding to as many transition modes.

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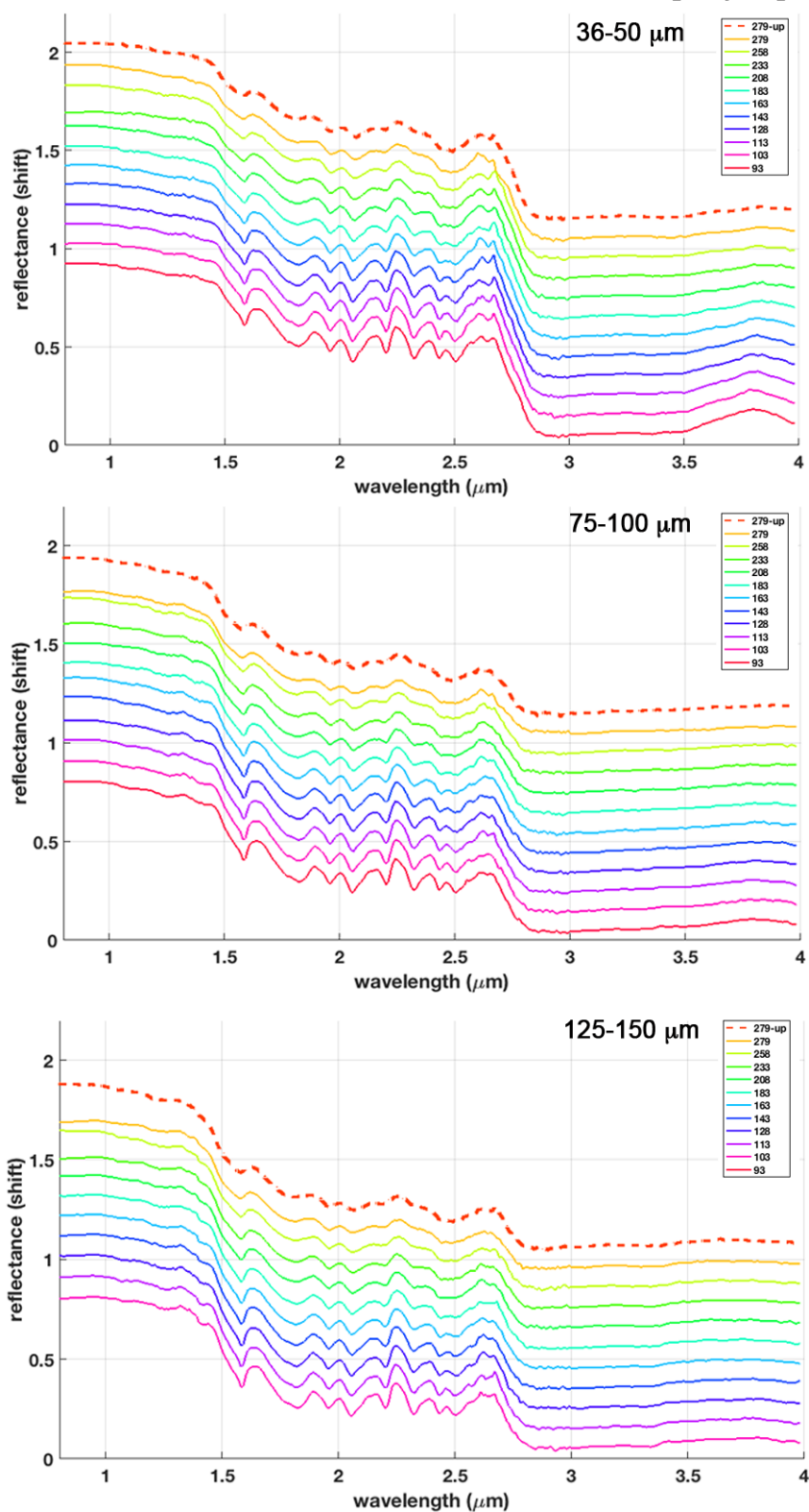
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Anyhydrous Sodium Carbonate - Natrite Na_2CO_3



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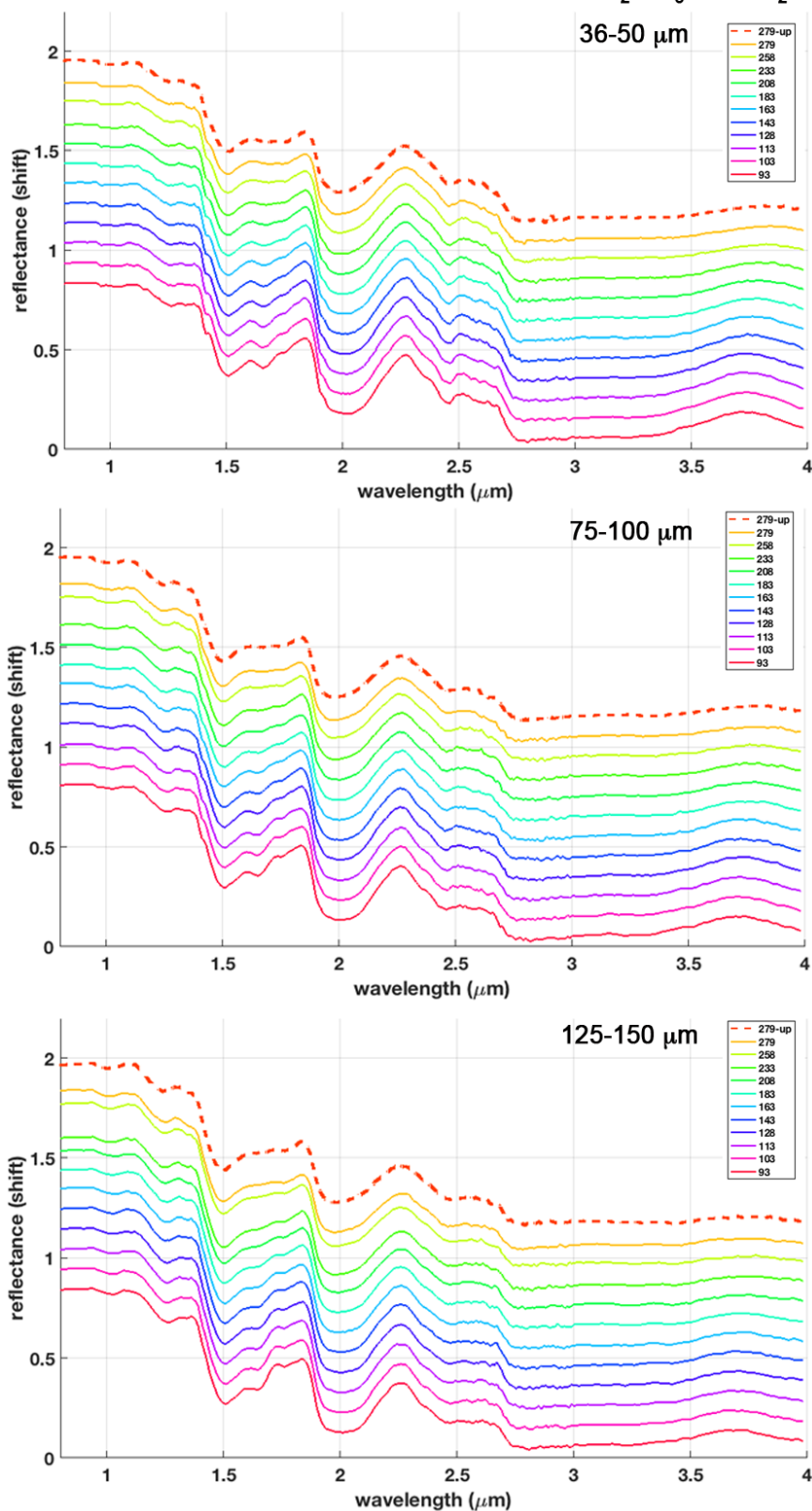
Figure 1. Spectra of anhydrous sodium carbonate (Na_2CO_3) acquired at different temperatures in the range 93-279 K. Measurements at 279 K have been acquired both at the beginning and at the end of the sequence. An arbitrary offset of 0.1 in reflectance is applied to all spectra for clarity. The bottommost spectrum corresponds to the true reflectance value, ≈ 0.9 at $1 \mu\text{m}$.

Sodium Carbonate Mono-Hydrate - ThermoNatriite $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ 

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Figure 2. Spectra of monohydrated sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) acquired at different temperatures in the range 93-279 K. Measurements at 279 K have been acquired both at the beginning and at the end of the sequence. An arbitrary offset of 0.1 in reflectance is applied to all spectra for clarity. For the 125-150 μm grain size the $T=113$ K spectrum has not been measured. The bottommost spectrum corresponds to the true reflectance value, ≈ 0.9 at $1 \mu\text{m}$.

Sodium Carbonate Deca-Hydrate - Natron $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$



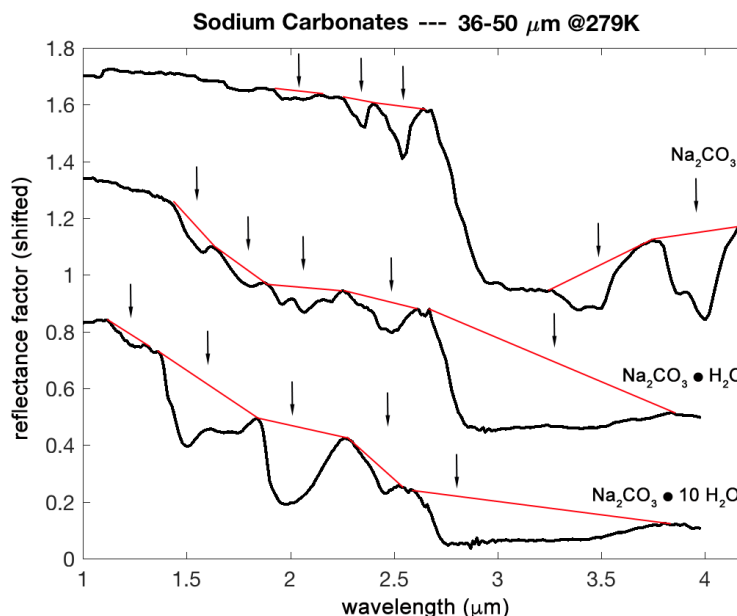
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Figure 3. Spectra of decahydrate sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$) acquired at different temperatures in the range 93-279 K. Measurements at 279 K have been acquired both at the beginning and at the end of the sequence. An arbitrary offset of 0.1 in reflectance is applied to all spectra for clarity. The bottommost spectrum corresponds to the true reflectance value, ≈ 0.8 at $1 \mu\text{m}$.

409 3.2 Spectral analysis

410

411 Spectral indices have been analyzed for each sample grain size and for all the resolved
 412 absorption bands. The analyzed features for the three compounds are indicated by the arrows
 413 in Fig. 4 and listed in Table 1. For each absorption band, the position, depth, area and width
 414 have been computed following the procedure described in Section 2.3. Linear fits have been
 415 computed for each spectral index as a function of temperature. In the next sections we
 416 describe the results of the spectral analyses. Taking into account the spectral sampling and
 417 the resolution of the instrument, here we only report trends for those band positions showing
 418 substantial shifts.



419

420

421 *Figure 4. The three analyzed compounds, at 279 K (up), 36-50-μm. The arrows indicate the analyzed*
 422 *bands. See Table 1. The red lines indicate the continuum applied (removed by division). The spectra of*
 423 *Na₂CO₃ and Na₂CO₃•H₂O are respectively offset by 0.8 and 0.4 for clarity.*

424

Compounds	Bands (μm)	Analyses	Process	Intensity
Na ₂ CO ₃	1.55		OH/H ₂ O	vw
	1.75		CO ₃	w
	2.0	X	H ₂ O+ CO ₃	w
	2.2		CO ₃	w
	2.34	X	CO ₃	m
	2.54	X	CO ₃	m
	2.65		H ₂ O (vapor)	vw
	3.0		Adsorbed H ₂ O	s
	3.40 (I), 3.49 (II)	X	CO ₃	s
3.88 (I), 3.99 (II)	X	CO ₃	vs	
Na ₂ CO ₃ •H ₂ O	1.25		H ₂ O	vw
	1.57	X	H ₂ O	m
	1.78	X	H ₂ O	m
	1.96 (I), 2.06 (II), 2.20 (III)	X	H ₂ O+ CO ₃	m
	2.32 (I), 2.44 (II), 2.50 (III)	X	CO ₃ (+ H ₂ O)	w/m
	2.65		H ₂ O (vapor)	vw
2.9	X	H ₂ O (+CO ₃)	vs	
Na ₂ CO ₃ •10H ₂ O	1.0		H ₂ O	w

	1.23	X	H ₂ O	w
	1.50 (I), 1.64 (II)	X	H ₂ O	s/m
	1.75		CO ₃	w
	1.99	X	H ₂ O (+ CO ₃)	s
	2.45	X	CO ₃	m
	2.8	X	H ₂ O (+CO ₃)	vs

425 *Table 1. List of the analyzed bands for the three compounds, indicated by X. Multiple minima within each*
426 *analyzed band are denoted by roman numerals and their spectral position presented in the text. Intensity*
427 *labels, referred to the continuum reflectance level, are: vw = very weak ($B_D < 5\%$), w = weak ($B_D < 10\%$), m*
428 *= medium ($B_D < 30\%$), s = strong ($B_D < 50\%$), vs = very strong ($B_D > 50\%$).*

430 3.3 Anhydrous sodium carbonate

432 3.3.1 2.0- μm band

434 The band parameters of the 2.0- μm feature (position, depth, area, width) are shown in Fig. 5A.
435 This feature likely results from the combination of H₂O and CO₃²⁻ absorptions. The band depth
436 and band area tend to decrease with increasing temperature values, assuming slightly higher
437 values at lower temperatures, although our measurements display large fluctuations. The
438 maximum depth is assumed by the intermediate grain size (75-100 μm). The band position
439 and band width do not show any clear correlation with temperature. The band position
440 moves to longer wavelengths (2.01-2.02 μm) for the smaller grain size (36-50 μm) compared
441 to the two larger grain sizes (1.98-1.99 μm). Here we must stress that this feature (and all
442 other relative to natrite) display shifts in position that are theoretically below the instrument
443 spectral resolution, although comparable with the spectral sampling. At the same time, we can
444 state that, because we used a consistent method all along our data analysis, we are able to
445 detect relative shifts of positions with a better accuracy, of the order of a few nm.

447 3.3.2 2.34- μm band

449 Spectral indices computed for the 2.35 μm CO₃²⁻ absorption feature are shown in Fig. 5B. The
450 band position slightly shifts towards shorter wavelengths as the temperature decreases. The
451 band depth and band area clearly increase almost linearly as the temperature drops down.
452 The band width does not show a clear temperature-dependent behavior, although it appears
453 to be increasing only for the smallest grain size. Both depth and area have maximum values
454 for the intermediate grain size (75-100 μm), whereas they show minimum values for the
455 coarse grain size (125-150 μm).

457 3.3.3 2.54- μm band

459 In Fig. 5C we show the 2.55- μm CO₃²⁻ band parameters. Again, the band position very slightly
460 shifts towards shorter wavelengths (2.544-2.540 μm) as the temperature decreases (below
461 spectral resolution), whereas the depth and area have higher values at lower temperatures.
462 The bandwidth is approximately constant. It should be noted that the instrument spectral
463 resolution is 19 nm longward of 2 μm . Again, maximum values of depth and area are found for
464 the intermediate grain size, whereas minimum values occur for the coarse grain size.

466 3.3.4 3.40-3.49 μm band

468 The 3.4- μm band, which shows up only in the anhydrous sodium carbonate sample, is
469 characterized by a doublet, with two separate minima occurring near 3.40 μm (I) and 3.49 μm

470 (II). The band parameters are shown in Fig. 6A, respectively. The position of band I appears to
471 be independent of temperature (Fig. 6A), while the position of band II shows some slight shift
472 towards shorter wavelengths as the temperature decreases (Fig. 6A). Both features display
473 band depth increasing with decreasing temperature; for the 36-50- μm grain size the depth
474 shows an increase of about 25-30%. The area and width are the same for band I and II, having
475 been computed considering the same short wavelength (3.3 μm) and long wavelength (3.7
476 μm) shoulders of the whole carbonate feature. The area shows an almost linear increase as
477 the temperature decreases, especially for the 36-50 and 75-100- μm grain sizes. In the fine
478 (36-50 μm) and coarse-grained sample (125-150 μm) there is some change occurring at ~ 160
479 K. This may be an indirect variation, triggered by the change in strength and shape of the 3
480 μm band above 163 K: it increases the continuum level at 3.3 μm resulting in an increase of
481 depth and area of the nearby 3.4-3.49 μm bands. The band clearly becomes narrower
482 (decreasing width) towards cryogenic temperatures.

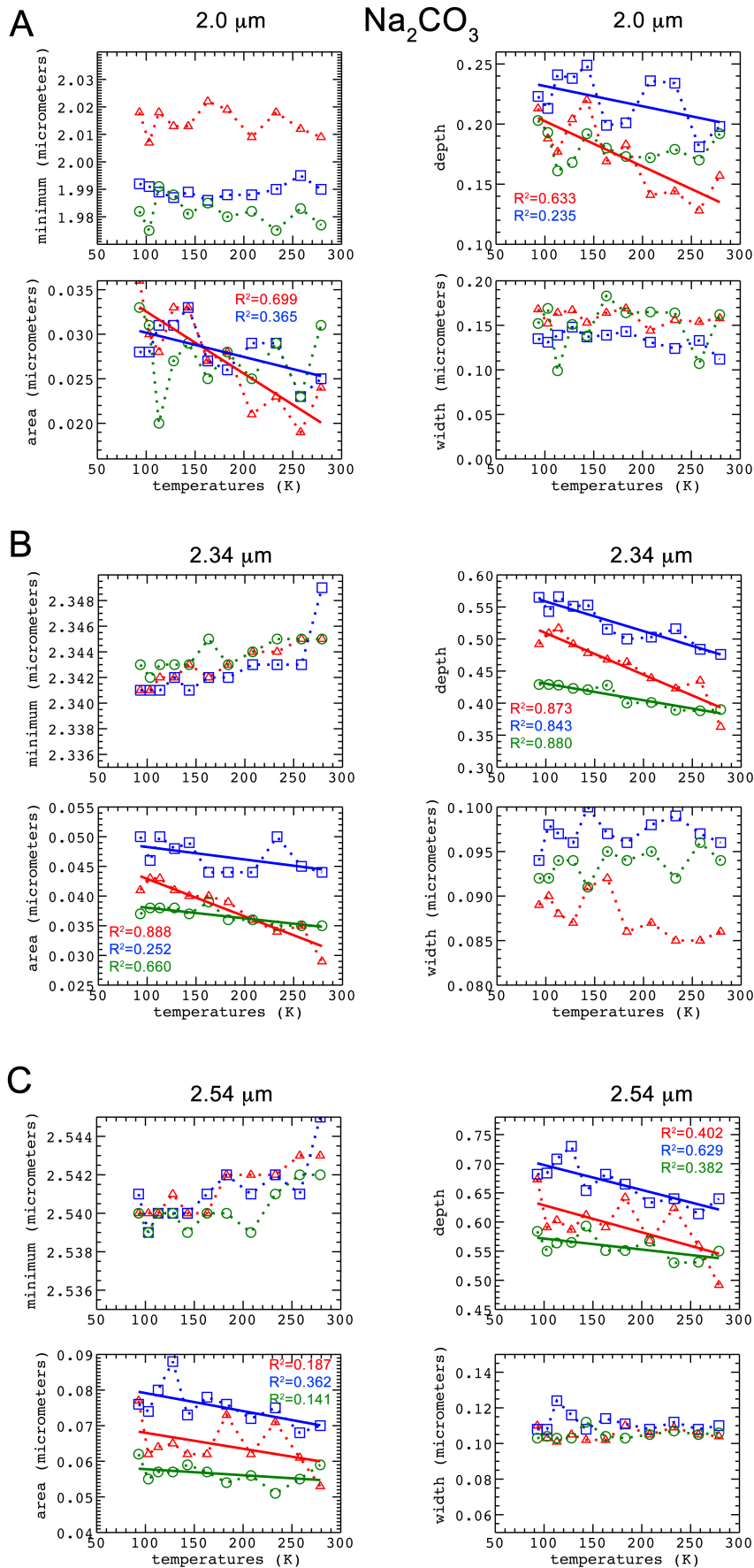
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484 *3.3.5 3.88-3.99 μm band*

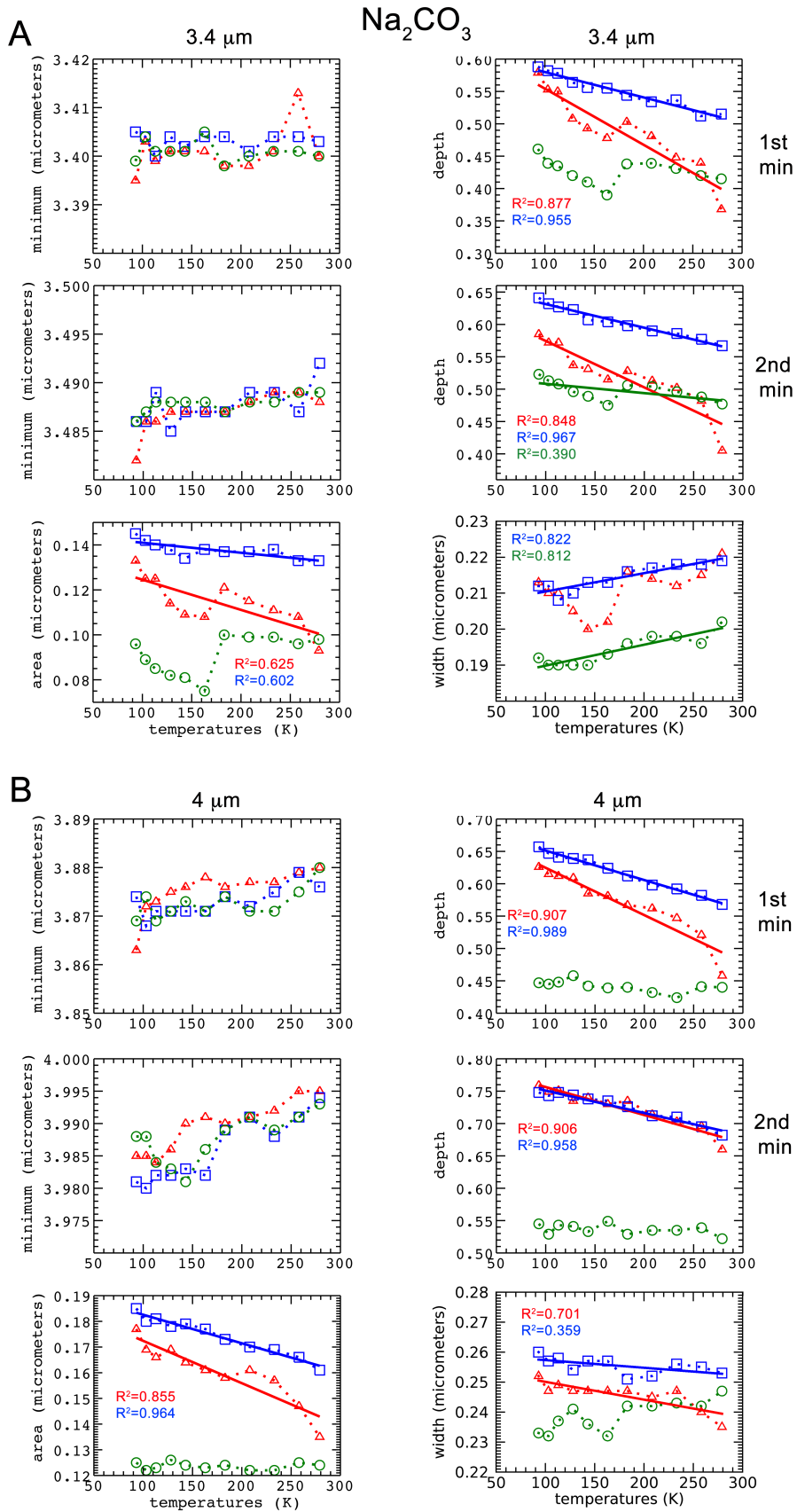
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486 The 4- μm carbonate band, as well as the 3.4- μm band, shows up only in the anhydrous
487 compound, as there is no saturated 3.0- μm water band. Spectral indices are shown in Fig. 6B.
488 Also this band is characterized by a doublet, with two minima occurring around 3.88 and 3.99
489 μm . The position of both minima shifts towards the shorter wavelengths as the temperature
490 decreases to cryogenic values, while the band depth increases linearly, by 20-30%, especially
491 for the 36-50- μm and 75-100- μm grain sizes. Conversely, this band is more influenced by
492 water absorption in the coarse 125-150- μm grain size, and its variation is not equally clear,
493 although a slight increase seems to occur. A similar behavior is found in the band area, which
494 linearly increases with decreasing temperature, notably for the 36-50 and 75-100- μm grain
495 sizes. The width does not show an unambiguous temperature dependence for all the three
496 grain sizes: it shows an increase towards low temperatures for the 36-50 and 75-100- μm
497 grain sizes, and a decrease for the coarse grain size, likely due to the greater influence of
498 water absorption. The 3.4 and 4 μm carbonate bands both have maximum depth and area
499 values for the intermediate grain size, and minimum values in correspondence of coarse grain
500 size.

501



502
 503 *Figure 5. Na_2CO_3 , band parameters of 2, 2.34 and 2.54- μm features. Red triangles: 36-50 μm . Blue*
 504 *squares: 75-100 μm . Green circles: 125-150 μm .*



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Figure 6. Na₂CO₃, band parameters of 3.40 μm (I) and 3.49 μm (II), and 3.88 μm (I) and 3.99 μm (II) features. Red triangles: 36-50 μm . Blue squares: 75-100 μm . Green circles: 125-150 μm .

510 3.4 Sodium carbonate monohydrate (thermonatrite)

511

512 3.4.1 1.57- μm band

513

514 The spectral indices of the 1.57- μm water absorption feature are shown in Fig. 7A. The band
515 position shifts towards longer wavelengths by as much as ~ 20 nm (1.56-1.58 μm) as the
516 temperature decreases. Both the depth and area linearly increase, by about 70-75%, towards
517 low temperatures, becoming very definite and intense. The bandwidth shows a clear and
518 systematic decrease with decreasing temperature, i.e. the band gets narrower, for all the three
519 grain sizes. At 93 K the fine grain size (36-50 μm) presents the maximum band depth. This is
520 true for the 1.57- μm band as well as for all other features occurring in the monohydrate
521 sample.

522

523 3.4.2 1.78- μm band

524

525 Spectral indices are shown in Fig. 7B for the 1.78 μm feature. The first three parameters show
526 trends similar to the previous band. The band position shifts towards longer wavelengths by
527 about 20-30 nm (1.77-1.80 μm) while the temperature decreases. The band depth and area
528 are both subject to a strong increase (more than 100%) as the temperature drops down. The
529 bandwidth slightly increases towards lower temperatures, for all of the three grain sizes.

530

531 3.4.3 1.96-2.2 μm band complex

532

533 The 2- μm feature (Fig. 8) is likely due to the combination H_2O and CO_3^{2-} absorptions occurring
534 in the same spectral region. This happens because in sodium carbonate monohydrate the
535 CO_3^{2-} ions are bonded to H_2O molecules through hydrogen bonding (Farmer et al., 1974). In
536 room temperature spectra (Fig. 2) this feature, with shorter and longer wavelength edges at
537 1.89 and 2.24 μm respectively, is composed of three separate minima, located at 1.96 (I), 2.06
538 (II) and 2.2 μm (III). These three relative minima become more defined (V-shape) and intense
539 (larger depth) as the temperature decreases towards cryogenic values. The position of feature
540 I (Fig. 8A) and also the position of feature II (Fig. 8B) shift as the temperature decreases
541 towards shorter wavelengths (1.961-1.957 μm , about 4 nm, and 2.067-2.056 μm , about 11
542 nm, respectively; the latter is slightly above our spectral sampling). Both features are
543 characterized by an increasing depth, by more than a factor of 2, as the temperature drops
544 down to cryogenic values. The feature III displays an inverse shift, the position moves
545 towards longer wavelengths (2.187-2.201 μm , about 14 nm, Fig. 8C) for lower values of
546 temperature. The band depth of feature III also becomes even more intense as the
547 temperature decreases. The area of the whole 2- μm band increases linearly towards
548 cryogenic temperatures, while the width decreases, notably for the 75-100 and 125-150- μm
549 grain sizes.

550

551 3.4.4 2.3-2.5- μm band complex

552

553 In room temperature spectra, this feature appears as a single asymmetric broad band located
554 at 2.47 μm , with a shoulder on the left side near 2.4 μm . At cryogenic temperatures the fine
555 structure of the band becomes evident, with three well-defined narrow features occurring
556 approximately at 2.32 μm (I), 2.44 μm (II), and 2.50 μm (III). The feature III is well visible in
557 all spectra in the range 93-279 K, the feature I appears clearly below 233 K, and the feature II
558 is clearly discernible only below 183 K. The band parameters are shown in Fig. 9. The position

559 of feature I displays a shift towards shorter wavelengths by about 5-10 nm (2.333-2.321 μm),
560 depending on the grain size, as the temperature decreases, while the depth increases by more
561 than a factor of 3 (Fig. 9A). This value is comparable with our spectral sampling, but is below
562 our spectral resolution. Similarly, the feature II shifts towards shorter wavelengths of as much
563 as 20-40 nm (2.47-2.43 μm), and the corresponding band depth increases by more than 50%
564 (Fig. 9B) while the temperature drops down. The feature III shows an opposite behavior, with
565 its position having a shift towards longer wavelengths by 20-35 nm (2.47-2.505 μm); the
566 depth again increases at lower temperatures (Fig. 9C). The area of the whole 2.3-2.5- μm band
567 becomes larger by more than a factor of 2 with decreasing temperature. The band width is
568 calculated as full width half maximum, due to the fact that this band splits in several minima,
569 which poses some difficulty in computing an unambiguous parameter. Compared to the
570 previous spectral parameter, this one does not seem to display any strong correlation with
571 temperature.

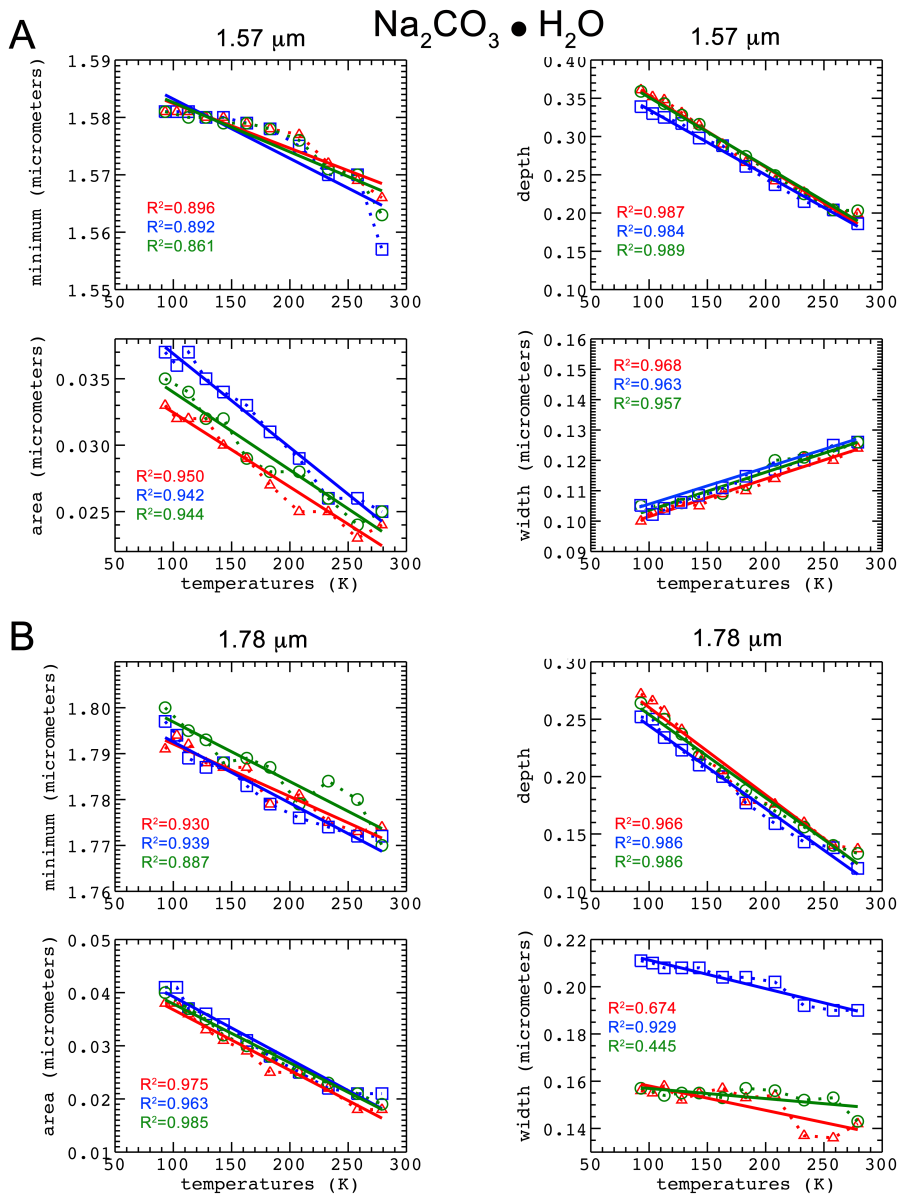
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573 *3.4.5 3- μm band*

574

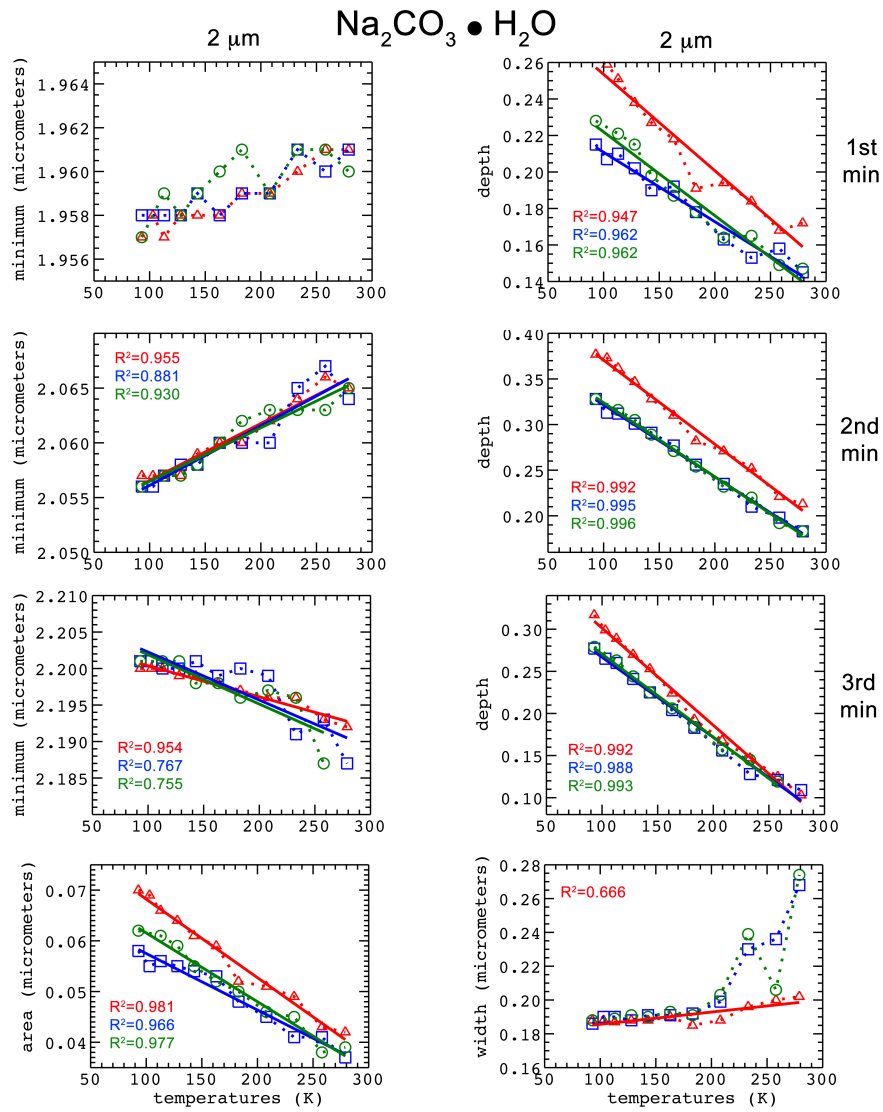
575 The position of the 3- μm water absorption band (around 2.9 μm) is characterized by a shift
576 towards longer wavelengths by 20-30 nm, especially for the 36-50 and 75-100 μm grain sizes,
577 as the temperature decreases (Fig. 9D). This band is almost saturated in 125-150 μm spectra,
578 therefore the retrieved positions are not strongly correlated with temperature for the coarse
579 grains (Fig. 9D, green circles). An analogous behavior is displayed by the bandwidth: it slightly
580 increases for lower temperatures and for the 36-50 and 75-100 μm grain sizes, whereas no
581 substantial correlation is seen for the coarse grain size. The band depth and area increase
582 clearly and linearly as the temperature decreases.

583



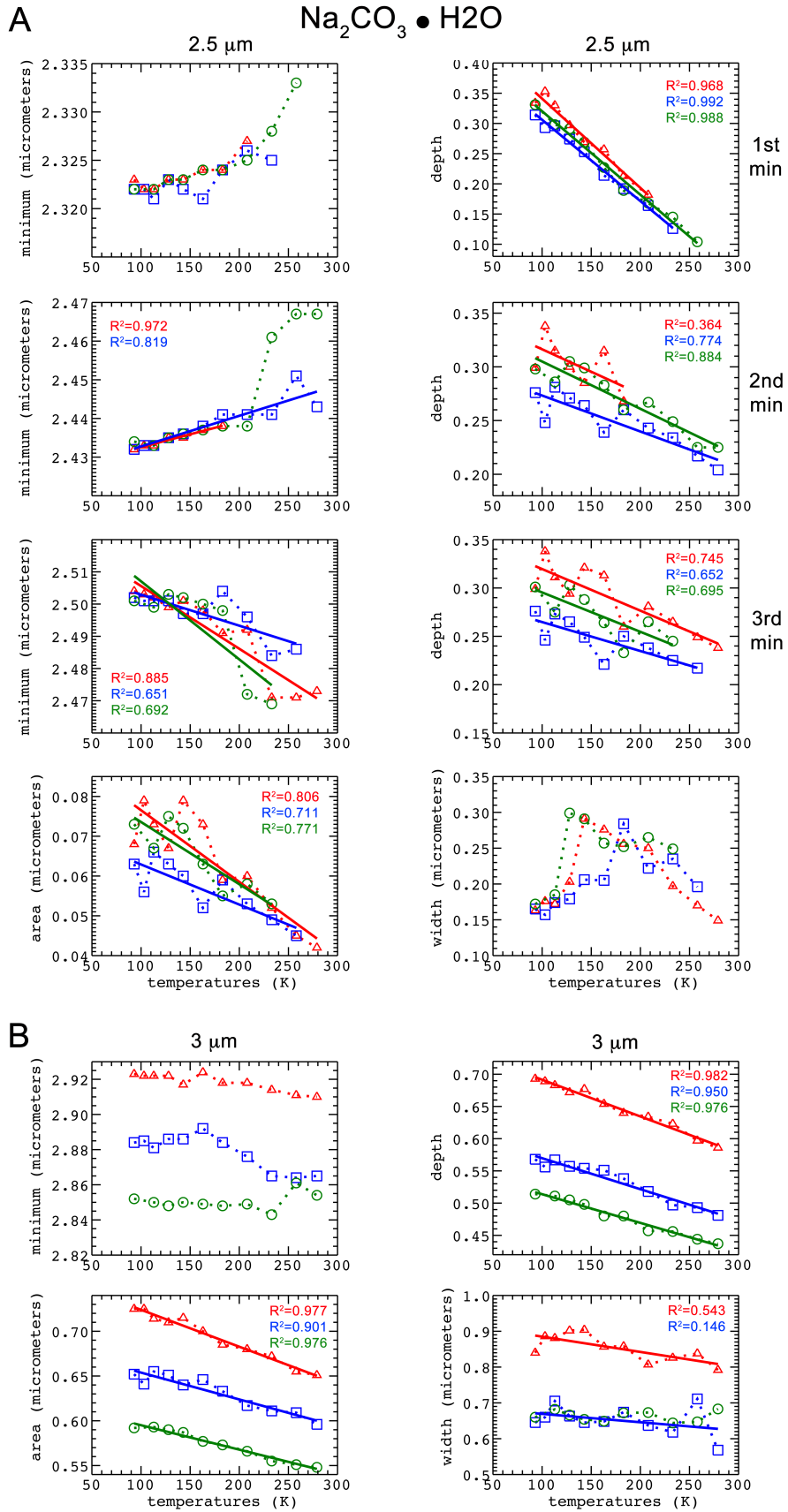
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Figure 7. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ band parameters of 1.57- μm and 1.78- μm features. Red triangles: 36-50 μm . Blue squares: 75-100 μm . Green circles: 125-150 μm .



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Figure 8. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ band parameters of 1.96 μm (I), 2.06 μm (II) and 2.20 μm (III) features. Red triangles: 36-50 μm. Blue squares: 75-100 μm. Green circles: 125-150 μm.



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Figure 9. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ band parameters of 2.32 μm (I), 2.44 μm (II) and 2.50 μm (III) features and 3.0- μm band. Red triangles: 36-50 μm . Blue squares: 75-100 μm . Green circles: 125-150 μm .

599 3.5 Sodium carbonate decahydrate (natron)

600

601 3.5.1 1.23- μm band

602

603 The water absorption at 1.23 μm shows dependencies from the temperature, as seen in Fig.
604 10A. The position shifts linearly towards longer wavelengths, by 20-30 nm, as the
605 temperature decreases (1.215-1.245 μm). The depth and area also display an increase for
606 lower temperatures, although with more fluctuations. The bandwidth does not show a clear
607 correlation with temperature. The band depth also increases linearly with grain size from fine
608 to coarse.

609

610 3.5.2 1.5- μm band complex

611

612 The 1.5- μm water band at room temperature occurs with a main minimum near 1.5 μm and a
613 secondary minimum near 1.58-1.65 μm . This secondary minimum is more pronounced in
614 finer grained size spectra and becomes a shoulder in coarser spectra (Fig. 3). At cryogenic
615 temperature the band displays a fine structure, being composed by three minima located at
616 1.50 (I), 1.65 (II) and 1.75 μm (III). Here we analyzed only the features I and II, the third
617 minimum being too weak and poorly resolved. The position of band I shifts towards longer
618 wavelengths (1.485-1.505 μm) as the temperature decreases from 279 K to 93 K, and the
619 depth increases by about 20%. The band II also shifts to longer wavelengths (1.58-1.65 μm)
620 with decreasing temperature in the range 279-93 K, for the 36-50- μm grain size; it becomes
621 visible only below 200 K for the 75-100- μm grain size, and below 150 K for the 125-150- μm
622 grain size. The depth also increases with decreasing temperature, by 65% for the finest class.
623 Finally both area and width, with respect to the whole 1.5- μm feature, display a strong
624 increase towards lower temperatures. The band depths at 1.5 and 1.65 μm both increase with
625 grain size, attaining the maximum values for the coarse grains.

626

627 3.5.3 2- μm band

628

629 The 2- μm band appears as a unique broad band in the whole temperature range 93-279 K. All
630 spectral indices reported in Fig. 11A display a strong correlation with temperature. The band
631 position shifts towards longer wavelengths by about 20-25 nm (1.97-2.00 μm) with
632 decreasing temperature. The band becomes even more intense (increasing depth), broad and
633 wide as the temperature decreases. This band shows an opposite behavior with respect to the
634 previous bands: the smaller the grain size (36-50 μm), the greater the depth.

635

636 3.5.4 2.45- μm band

637

638 The band parameters of the 2.45- μm absorption, likely related to CO_3^{2-} , are shown in Fig. 11B.
639 The position of this feature shifts towards shorter wavelengths by 15 nm (2.455-2.440 μm)
640 with decreasing temperature. The band depth and area both increase by more than a factor 2
641 as the temperature decreases. Similarly to the 2- μm band above, the maximum depth for this
642 band also occurs for fine grains. The bandwidth becomes broader for lower temperatures,
643 although the rate of broadening decreases for decreasing grain size.

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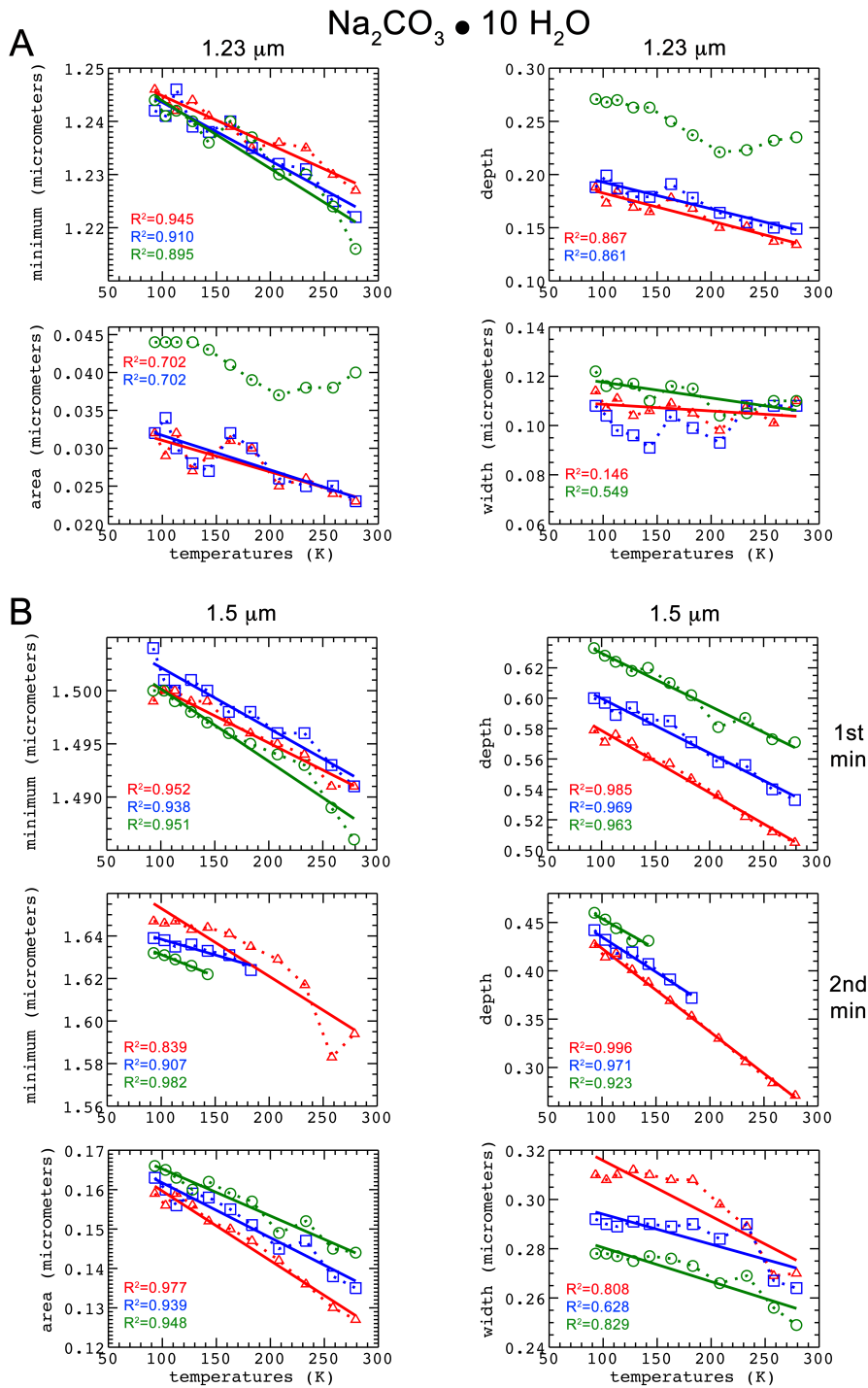
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648 *3.5.5 3- μ m band*

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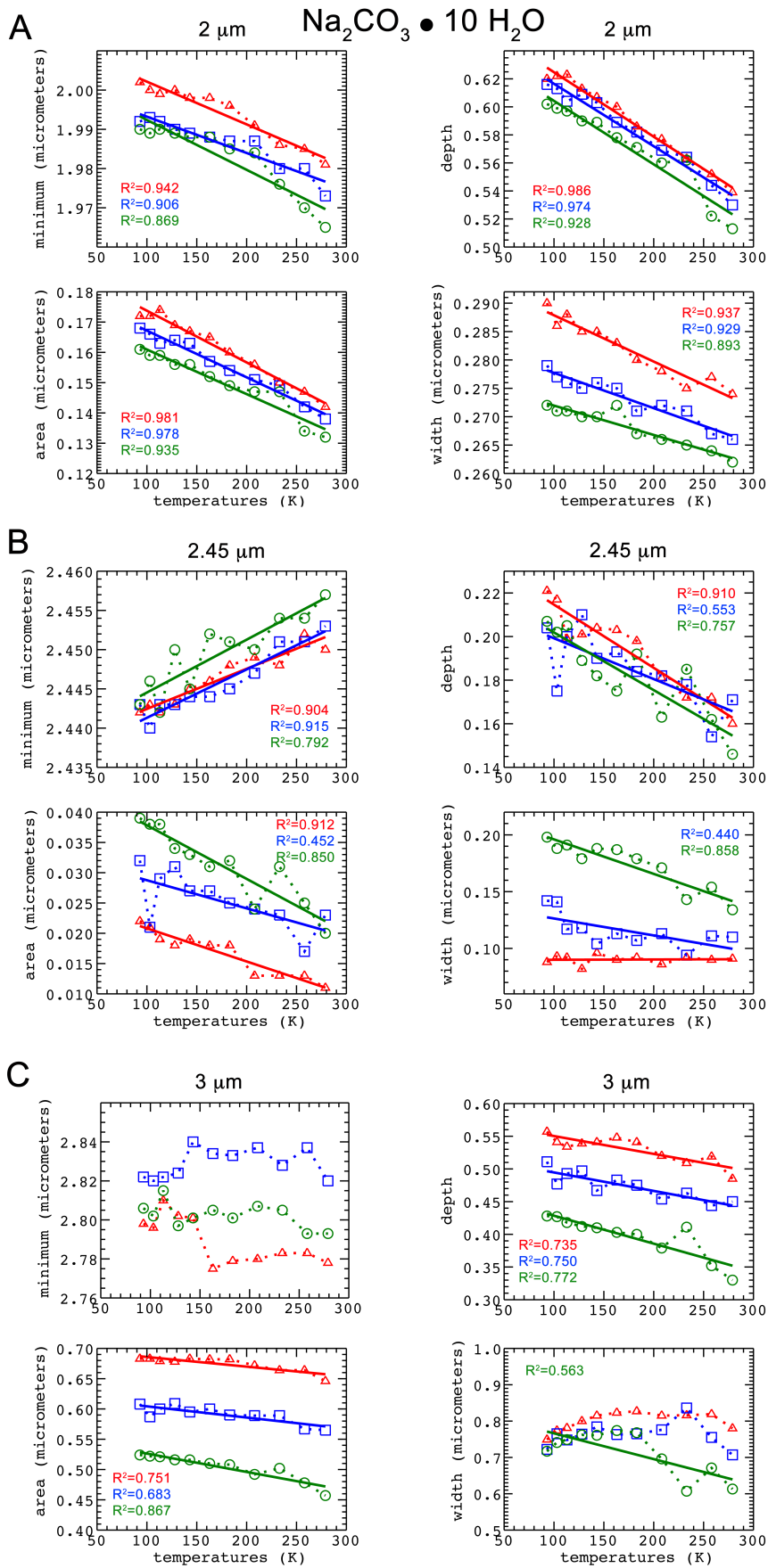
650 In Fig. 11C we show the band parameters for the 3- μ m water absorption feature. The position
651 displays a negative correlation with temperature (moving towards longer wavelengths as the
652 temperature decreases, by 20-30 nm) notably for the 36-50 and 125-150- μ m grain sizes.
653 However, this strongly saturated band is characterized by a very broad and flat minimum, so a
654 large uncertainty is associated to the retrieved central wavelength. The depth and area both
655 increase with decreasing temperature. For a fixed temperature, area and depth assume larger
656 values for the smallest grains size (36-50 μ m) and clearly decrease moving to the medium and
657 coarse grain size. The bandwidth displays different trends for the three grain sizes, although
658 with large fluctuations. Concerning the dependence on grain size, the 3- μ m water band depth
659 again decreases linearly with increasing grain size.

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Figure 10. Na₂CO₃•10H₂O band parameters of 1.23-μm, 1.50 μm (I) and 1.65 μm (II) features. Red triangles: 36-50 μm. Blue squares: 75-100 μm. Green circles: 125-150 μm.



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Figure 11. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ band parameters of 2.0- μm , 2.45- μm and 3.0- μm features. Red triangles: 36-50 μm . Blue squares: 75-100 μm . Green circles: 125-150 μm .

669 **4. Discussion**

670

671 4.1 Natrite carbonate bands at 3-4 μm

672

673 The 3.4- and 4- μm carbonate bands of natrite, both characterized by two close narrow
674 minima, show a change in relative intensity as a function of temperature. One explanation for
675 doublet bands (with split minima) is that a coupling of vibrational modes, related to different
676 molecular ions located in equivalent (symmetric) sites in the unit cell, can occur (Brooker &
677 Bates, 1971). Another explanation is the “two-site effect”, in which a particular group (for
678 example the CO_3^{2-} ion) occupies two different sites (Brooker & Bates, 1971). Here we find that
679 the relative strength of double minima of each band changes with temperature. We computed
680 the band depth ratios of the two minima of each band: the 3.4- μm band has two minima, I and
681 II, respectively centered near 3.40 and 3.49 μm , while the 4- μm band has two minima, I and II,
682 centered near 3.88 and 3.99 μm , respectively. The depth ratios are given by:

683

$$BR_{3.4} = \frac{B_{\text{depth}_{3.40}}}{B_{\text{depth}_{3.49}}}$$

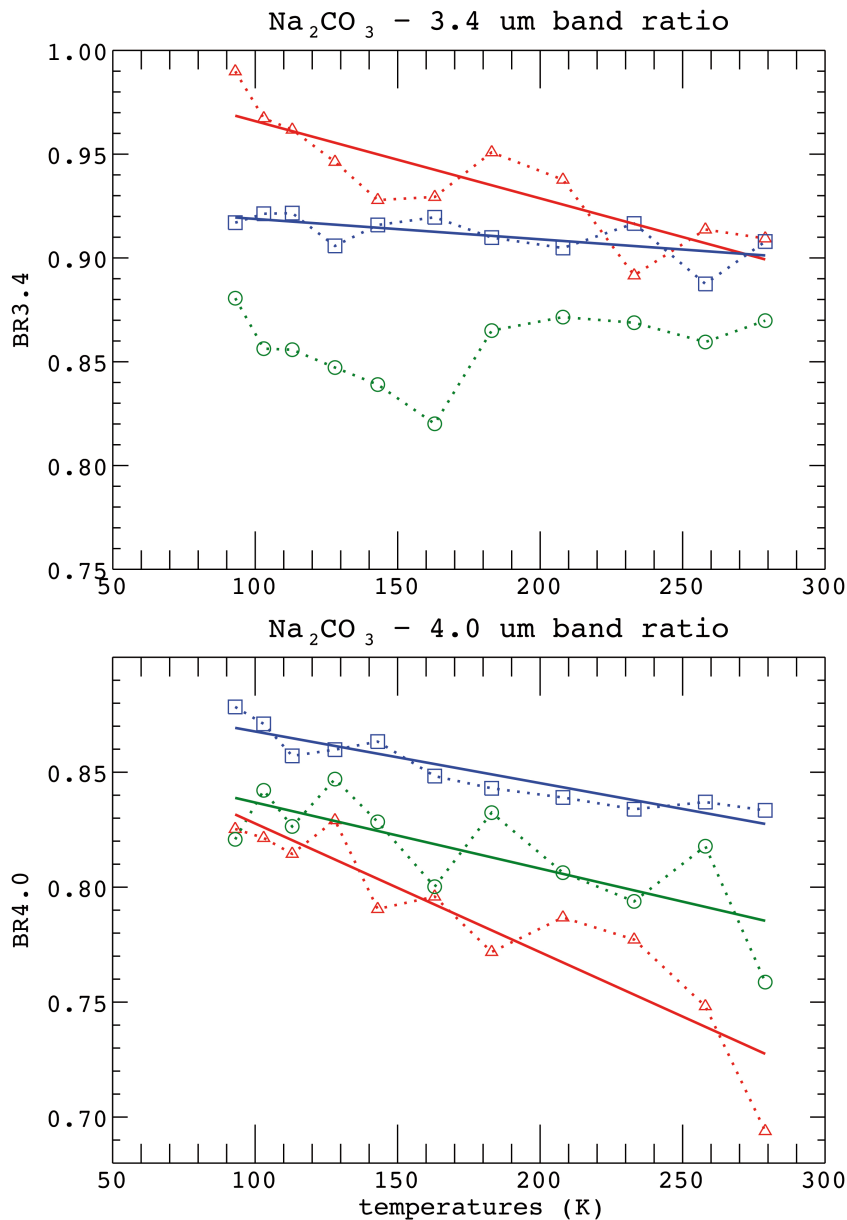
684

$$BR_{4.0} = \frac{B_{\text{depth}_{3.88}}}{B_{\text{depth}_{3.99}}}$$

685

686 The retrieved band depth ratios are shown in Fig. 12. The band depth ratio for 3.4 μm band
687 minima (Fig.12A) shows a slightly different behavior as a function of temperature, depending
688 on the grain size. Starting from room temperature, the depth ratio displays an increase
689 towards low temperatures, especially for the 36-50 μm grain size. The depth ratio rate tends
690 to reduce as the grain size becomes coarser. However this may not be an intrinsic behavior,
691 because for the coarser grain size (125-150 μm) the 3.4- μm band shape could be substantially
692 affected by the 3- μm water absorption; this is due to some adsorbed water on the grains of
693 the anhydrous sample. The depth ratio for the 4- μm band shows a more consistent behavior.
694 In all of the three grain sizes, the ratio displays a net increase as the temperature goes down
695 from 279 K to 93 K. A general explanation could be that the changes observed in band depths
696 and band depth ratios are due to changes in the reflectance of the spectral continuum (where
697 the continuum is drawn) with temperature and grain size. The effect on the continuum could
698 be enhanced when viewing at close bands (such as 3 and 3.4 μm).

699



700

701

702 *Figure 12. Natrite, band depth ratios for relative minima of carbonate bands. A: 3.4 micron band. B: 4.0*

703 *micron band. Red triangles: 36-50 μm . Blue squares: 75-100 μm . Green circles: 125-150 μm .*

704

705

706 4.2 Differences between hydration bands among thermonatrite and natron

707

708 The spectra of the three analyzed compounds appear markedly different in terms of bands
 709 shapes and positions. The main differences among them occur between the hydration
 710 absorption bands, specifically for thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).
 711 The less hydrated species, thermonatrite, at room temperature displays numerous narrow
 712 absorption bands that tend to become separate in even more and narrower features at
 713 cryogenic temperatures. All these features reflect the energy levels corresponding to the
 714 possible vibration states of the H_2O molecule. Nevertheless the features (energies) tend to
 715 remain separate because of the low number of water molecules. In the heavily hydrated
 716 species, i.e. natron, a higher number of energy levels is the result of many vibrational states
 717 allowed for the numerous (10) water molecules per structure unit. Furthermore, the cohesive

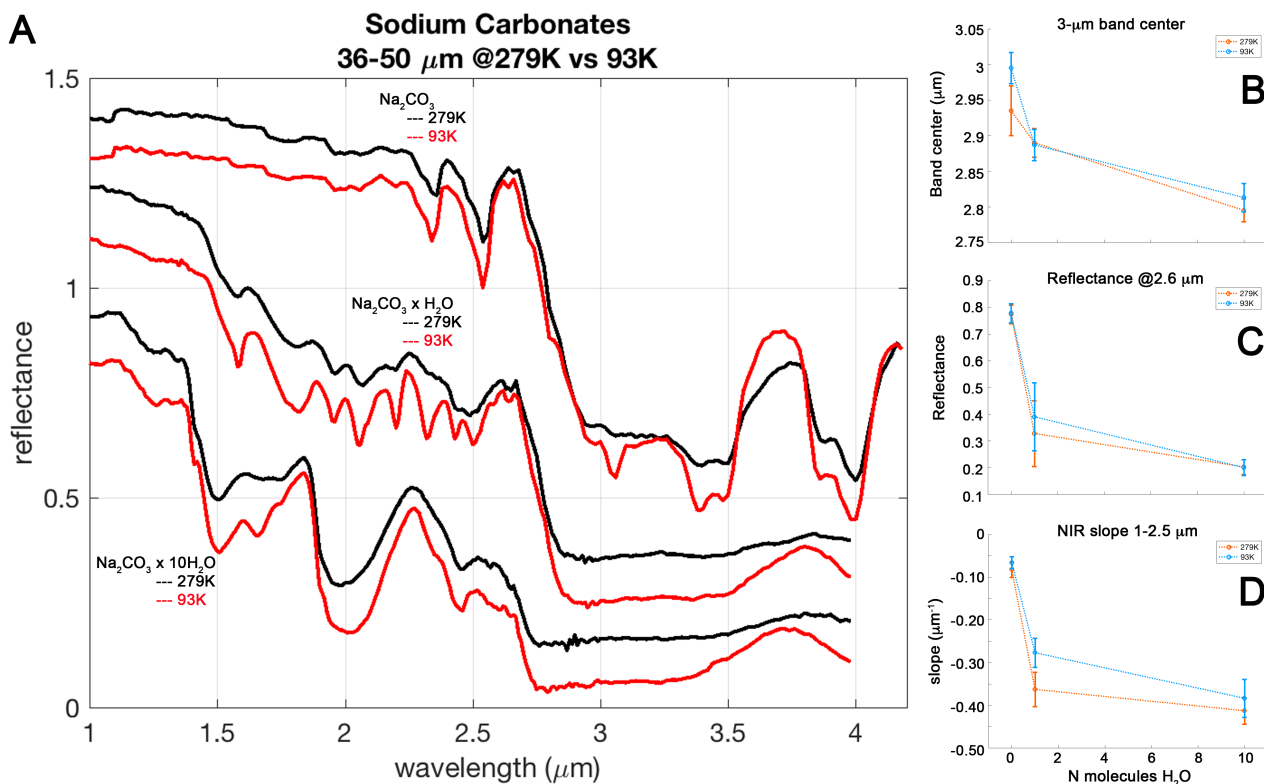
718 forces in the crystal lattice are mainly due to the hydrogen bond (Buijs & Schutte, 1961b).
719 This in turn produces a few broad and large absorption bands, especially at 1.5 and 2 μm ,
720 constituted by the overlapping/combination of numerous undistinguishable features (Farmer
721 et al., 1974). Finally, as pointed out by Buijs & Schutte (1961b), the 3- μm band in
722 monohydrate is likely most related to carbonate–water hydrogen bonding, while the 3- μm
723 band in decahydrate is mostly due to water–water hydrogen bonding.

724 4.3 Hydration state and 3- μm band variability

725 The increasing level of hydration in the sequence natrite \rightarrow thermonatrite \rightarrow natron (0 \rightarrow 1 \rightarrow
726 10) also implies clear changes in the 3- μm spectral region of water absorption. In Fig. 13A we
727 show the 279 K and 93 K spectra for the three samples at 36-50- μm , for direct comparison.
728 Three more factors characterize the sequence of hydration, beyond the already discussed
729 absorption bands: (i), a shift towards shorter wavelengths of the 3- μm band position, (ii) a
730 decrease of the overall reflectance, and (iii) a progressive increase in the NIR slope (1-2.5 μm ;
731 negative) as the number of water molecules increases. The 3- μm band position has been
732 computed for each species, averaged among the three grain sizes and plotted against the
733 number (N) of H₂O molecules (Fig. 13B); error bars are obtained by calculating the standard
734 deviation after varying the band edges for continuum removal. The position clearly shifts
735 towards shorter wavelengths as the water content of the species increases. The spectral
736 continuum has been retrieved at 2.6 μm , following the same approach as for the 3- μm
737 position; this parameter is plotted as a function of water molecules in Fig. 13C. The continuum
738 reflectance level is characterized by a net decrease as the water content of the mineral
739 increases. Finally the NIR slope has been computed in the range 1-2.5 μm . The absolute value
740 of the slope displays a net increase (the negative slope decreases) as the number of water
741 molecules increases (Fig. 13D).

742 A narrow minimum at 3.1 μm in natrite, which does not show up in the starting 279 K-
743 spectrum (Fig. 1, red line, bottom) appears in the 93 K-spectrum (orange line) and then
744 weakens and disappears as the temperature increases up to 279 K (red line, top). This
745 absorption could be due to the formation of some very finely grained water frost on the
746 sample. In the 75-100- μm grain size spectra the appearing and disappearing of two minima at
747 2.99-3.1 μm at the lowest temperatures could be evidence of the same phenomenon. In
748 general, in the 3- μm region of thermonatrite and natron, we observe a global change, as
749 discussed, mainly consisting in the reduction of the reflectance level at cryogenic
750 temperatures and in the formation of a well defined large absorption band; this is as also
751 evidenced by the more pronounced shape of the 3.75- μm reflectance maximum, whose
752 position shifts towards shorter wavelengths, while the 2.75- μm position shifts in the opposite
753 direction (e.g. Fig.12A). The general narrowing of the whole band as the temperature
754 decreases is consistent with a lower number of allowed vibrational modes (due to changes in
755 thermal population) at cryogenic temperatures.

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761 *Figure 13. A. Spectra acquired for the three species for 36-50 μm grain size, at 279 K (black) and 93 K*
 762 *(red). Spectra of Na_2CO_3 and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ are shifted in reflectance by 0.2 and 0.1 for clarity, respectively.*
 763 *B. Band minimum of the 3 μm band, as a function of number of water molecules. C. Reflectance @2.6 μm*
 764 *as a function of water molecules. D. NIR slope (1-2.5 μm) versus water molecules. For each species, the*
 765 *spectral parameters have been averaged over the three grain sizes.*
 766

767 4.4 Temperature dependence of H_2O and CO_3^{2-} species.

768

769 Table 2 schematically synthesizes with arrows the behavior of each analyzed parameter, as a
 770 function of decreasing temperature. For all the absorption features, regardless of the
 771 originating chemical species, the depth and area increase as the temperature decreases. The
 772 bandwidth does not display a unique behavior, mainly because it is difficult to define an
 773 unambiguous width parameter for multi-minima and fine structured bands. The band
 774 minimum displays the following behavior: the band minimum regularly shifts towards
 775 shorter wavelengths, as the temperature decreases, when related to CO_3^{2-} vibrations; on the
 776 contrary the minimum appears to shift towards longer wavelengths when the band is
 777 assigned to H_2O transitions. The H_2O transitions are mostly related to hydrogen bonds in
 778 water-water interactions. The strength of hydrogen bond increases as the temperature
 779 decreases, and its effect is to shift the band minimum towards lower frequencies (longer
 780 wavelengths). In some cases the behavior is mixed, that is relatively to overlapping
 781 absorption bands due to both H_2O and CO_3^{2-} (bands with fine structure at 2.0 and 2.5 μm in
 782 thermonatrite). Our finding of CO_3 absorption shifting towards shorter wavelengths (higher
 783 wavenumbers) as temperature decreases however is consistent with the results of Harris &
 784 Salje (1992), and can be explained with an increasing and strengthening of CO_3 -Na
 785 interactions, as discussed above (Harris & Salje, 1992; Arakcheeva & Chapuis, 2005).
 786 Concerning the shift in position of H_2O transition features, instead, our opposite results are
 787 consistent with findings of Grundy & Schmitt (1998). They found, in Near-IR transmission

788 spectra of water ice, that H₂O absorptions move towards longer wavelengths with decreasing
789 temperature.
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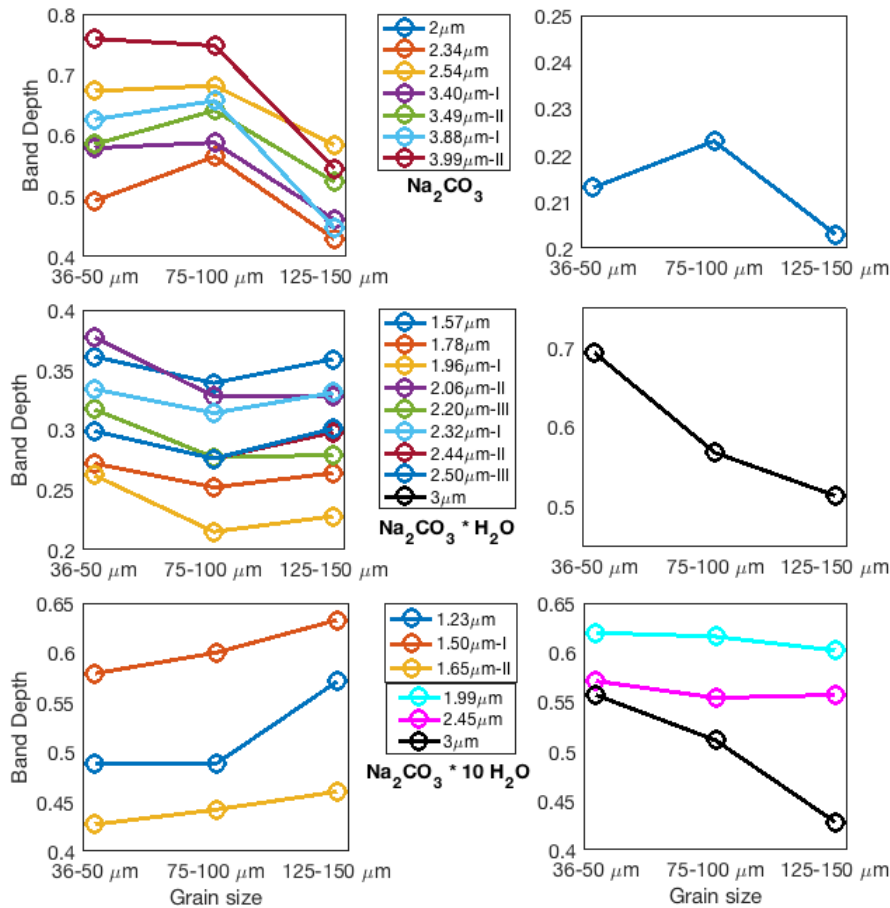
Sample	B (μm)	Absorption	B _C vs decreasing T	ΔB _C	B _D vs decreasing T	ΔB _D	B _A vs decreasing T	ΔB _A	B _W vs decreasing T	ΔB _W
Na ₂ CO ₃	2.0				↑	+30%	↑	+75%		
	2.34	CO ₃ ²⁻	← (short λ)	-10 nm	↑	+43%	↑	+50%		
	2.54	CO ₃ ²⁻	← (short λ)	-4 nm	↑	+40%	↑	+33%		
	3.40 (I)	CO ₃ ²⁻			↑	+71%	↑	+40%	↓	-4.5%
	3.49 (II)	CO ₃ ²⁻	← (short λ)	-5 nm	↑	+50%			↓	-4.5%
	3.88 (I)	CO ₃ ²⁻	← (short λ)	-15 nm	↑	+44%	↑	+38%		
	3.99 (II)	CO ₃ ²⁻	← (short λ)	-15 nm	↑	+15%				
Na ₂ CO ₃ •H ₂ O	1.57 (II)	H ₂ O	→ (long λ)	+25 nm	↑	+75%	↑	+60%	↓	-23%
	1.78	H ₂ O	→ (long λ)	+30 nm	↑	+116%	↑	+100%	↑	+10%
	1.96 (I)	H ₂ O+CO ₃ ²⁻	← (short λ)	-3 nm	↑	+62%	↑	+75%	↓	-36%
	2.06 (II)	H ₂ O+CO ₃ ²⁻	← (short λ)	-10 nm	↑	+100%				
	2.20 (III)	H ₂ O+CO ₃ ²⁻	→ (long λ)	+15 nm	↑	+200%				
	2.32 (I)	H ₂ O+CO ₃ ²⁻	← (short λ)	-14 nm	↑	+200%	↑	+100%		
	2.44 (I)	H ₂ O+CO ₃ ²⁻	← (short λ)	-40 nm	↑	+35%				
	2.50 (III)	H ₂ O+CO ₃ ²⁻	→ (long λ)	+30 nm	↑	+28%				
	3.0	H ₂ O	→ (long λ)	+20 nm	↑	+17%	↑	+8%	↑	+12%
Na ₂ CO ₃ •10 H ₂ O	1.23	H ₂ O	→ (long λ)	+20 nm	↑	+36%	↑	+33%		
	1.50 (I)	H ₂ O	→ (long λ)	+15 nm	↑	+16%	↑	+23%	↑	+17%
	1.65 (II)	H ₂ O	→ (long λ)	+60 nm	↑	+72%				
	1.99	H ₂ O	→ (long λ)	+25 nm	↑	+15%	↑	+23%	↑	+5.5%
	2.45	CO ₃ ²⁻	← (short λ)	-15 nm	↑	+37%	↑	+100%	↑	+30%
	3.0	H ₂ O	→ (long λ)	+10 nm	↑	+31%	↑	+15%		

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793 *Table 2. Band parameters variations (vs temperature decrease) for the analyzed spectral features.*
794 *Abbreviations are: B = band, B_C = band position, B_D = depth, B_A = area and B_W = width. Maximum percent*
795 *changes are listed in columns on the left side of each corresponding parameter.*
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797 4.5 Variations with grain size

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800 In Fig. 14 we show the band depths at 93 K for each sample and for all of the considered grain
801 sizes. The band depth displays a different behavior, as a function of grain size, for the different
802 types of samples. Concerning the anhydrous sample (natrite, Fig. 14, top) the band depth
803 value reaches a maximum at intermediate grain size (75-100 μm) for nearly all the absorption
804 bands. In the monohydrate sample (Fig. 14, center) the band depth assumes maximum values
805 for the fine grain size (36-50 μm), in all the absorption bands except the 3-μm band. Finally,
806 regarding the decahydrate sample (Fig. 14, bottom) the band depths at 1.23, 1.50 and 1.65 μm
807 increase with increasing grain size, while the band depths at 1.96-2.20, 2.45 and 3 μm
808 decrease with increasing grain size. It has to be noted that the 3-μm feature has the same
809 behavior (maximum BD for fine particles) for mono- and decahydrate: this is because this
810 water feature readily saturates also for fine particles. The general behavior is explained
811 considering that different materials (and different absorption features) are characterized by
812 optimal grain sizes that maximize the absorption relative to the nearby continuum levels and
813 the corresponding band depth (Hapke, 1993; Harloff & Arnold, 2001). When the grain size
814 increases, first the reflectance at band center decreases faster than its continuum, then the
815 band starts to saturate and the spectral continuum in between two bands decreases faster
816 than the one at band center. The onset between these two behaviors occurs at lower grain
817 size for stronger bands. However, overlapping of band wings may modify this general

818 behavior. Thus, in the anhydrous sample a “critical” grain size is reached at 75-100 μm . In the
 819 decahydrate sample, this is the grain size at which the band depth reaches its maximum value,
 820 decreases as passing from weak absorptions (1.23 μm) to more intense absorptions (i.e.
 821 towards the 3- μm band) (Hapke, 1993). In the case of monohydrate sample, the situation is
 822 complicated by the high concentration of closely spaced absorption bands and by the fact that
 823 absorption features are complex combinations of CO_3^{2-} and $\text{OH}^-/\text{H}_2\text{O}$ transitions.
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 827 *Figure 14. Band depth values at 93 K for the absorption bands of the three samples, as a function of the*
 828 *sample grain size. Top: natrite. Center: thermonatrite (monohydrate). Bottom: natron (decahydrate).*
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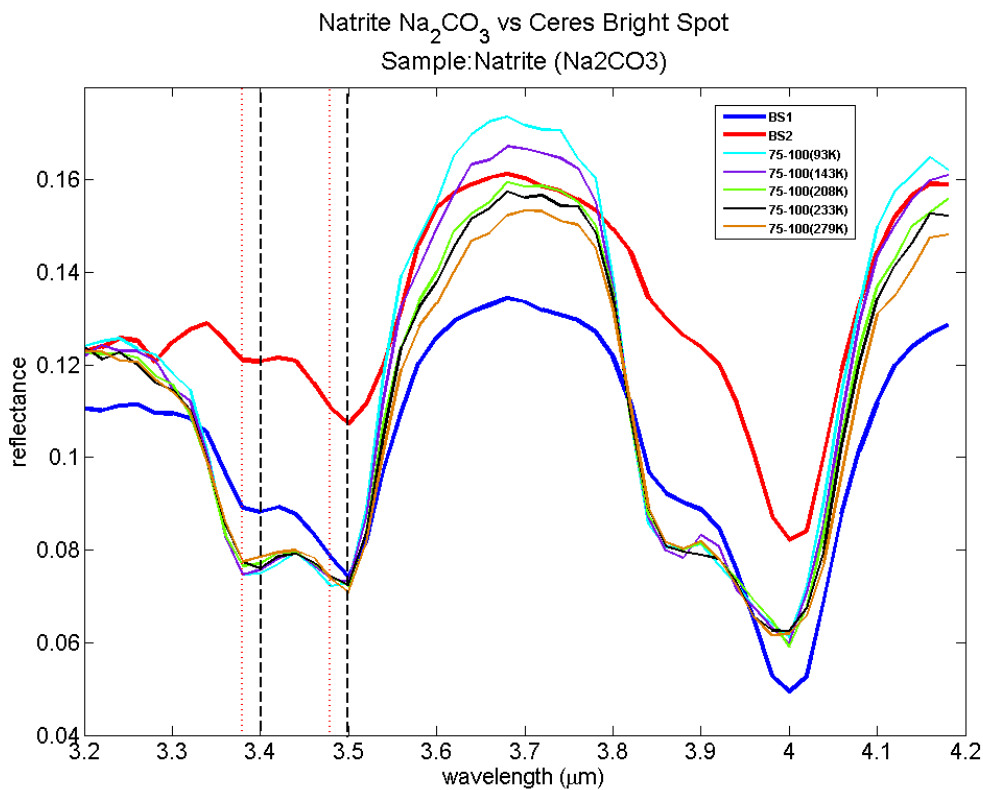
830 4.6 Comparison with Ceres

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 832 As discussed in Section 1, natrite has been invoked as the main component of some of the
 833 high-albedo geologic features observed on Ceres. Here we report a comparison of the 3-4- μm
 834 region between Dawn-VIR spectra of Cerealia Facula, i.e. the brightest feature found in the
 835 middle of the floor of crater Occator (De Sanctis et al., 2016) and our natrite spectra. In
 836 particular, we compare the VIR-measured spectra of two locations within Cerealia Facula
 837 (hereafter BS1, BS2 from Raponi et al., 2018; Fig. 15), with five different spectra of medium
 838 grain-sized natrite acquired at 93, 143, 208, 233 and 279 K. In particular, this has been
 839 inferred observing the behavior of the 3.40 μm (I) and 3.49 μm (II) minima. The 3.40 μm (I)
 840 position shifts towards shorter wavelengths in the 93 K, 143 K and 208 K spectra, compared
 841 to the bright spot (red dotted line); the 3.49 μm (II) position shifts towards shorter
 842 wavelengths in the 93 K spectrum (red dotted line). The 233 K spectrum has both I and II
 843 positions matching the same positions of the BS1 and BS2 spectra (black dashed lines, located
 844 at 3.40 and 3.50 μm). From this analysis, given the shift in position as a function of

845 temperature, we can infer that a temperature around 230K can be associated with bright
846 spots.

847 The shape of the 4- μm feature can further support this conclusion. At the three lowest
848 temperatures in Fig. 15 (93, 143 and 208 K), the two minima at 3.88 and 3.99 μm in natrite
849 spectra are clearly separated by a relative maximum. In the spectra of bright spots BS1 and
850 BS2, instead, the 3.88- μm feature appears as a shoulder on the left side of the 3.99- μm
851 minimum. The best matching spectrum, despite the difference in intensity, is the one acquired
852 at 233 K, in which again the 3.88- μm feature appears as a shoulder of the 3.99- μm minimum.
853 The 279K spectrum has the short-wavelength minimum of the 3.4 μm band shifted at 3.38
854 μm ; the short-wavelength side of the 4 μm band again appears as a separated minimum
855 rather than as a shoulder.

856 The 233K temperature value is consistent with maximum daytime temperature values
857 retrieved on Ceres by VIR using its long-wavelength region between 4.5 μm and 5.1 μm ,
858 where thermal emission from the surface dominates the measured signal (Tosi et al., 2016).
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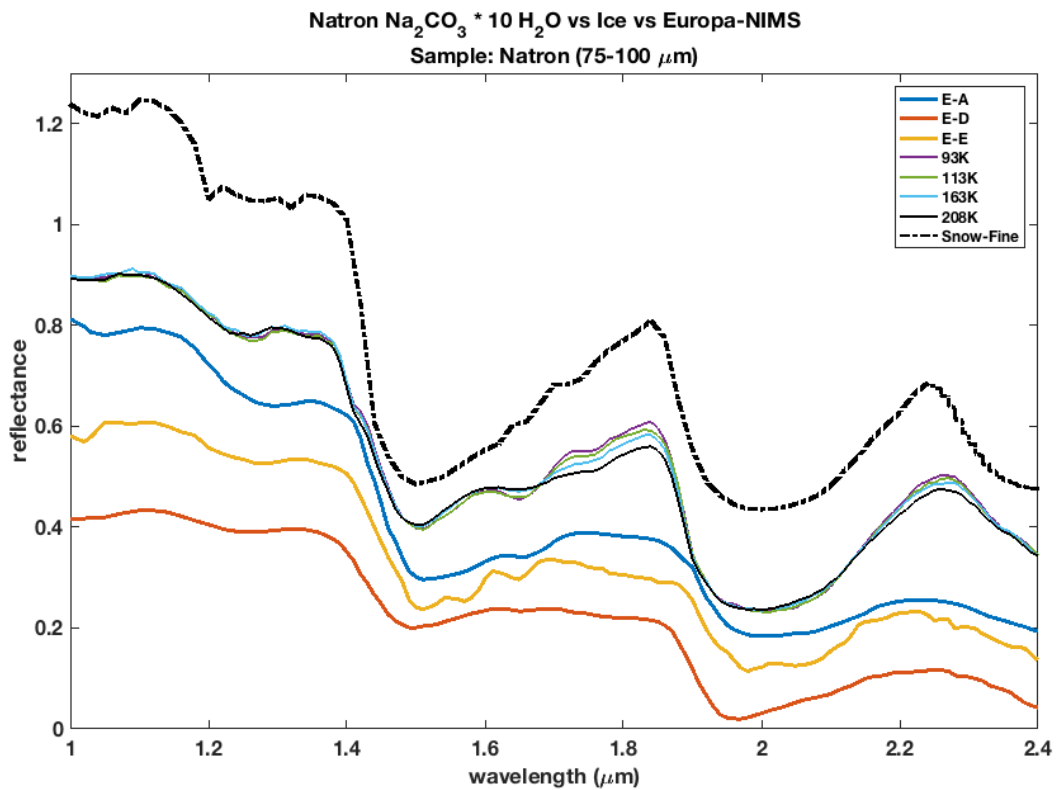
861
862 *Figure 15. Spectra of Natrite sample with 75-100 μm grain size at 5 temperatures compared to two*
863 *spectra of Ceres Bright Spots (BS1 and BS2). VIR data have been resampled on the same set of*
864 *wavelengths used in the lab (the average VIR spectral sampling is ~ 10 nm in the infrared range 1-5 μm ,*
865 *De Sanctis et al., 2011). The two red-dotted lines indicate the positions of minima in the 93K spectrum.*
866 *The two black-dashed lines indicate the positions of band minima of BS1 and BS2: they both match with*
867 *the minima in the 233K spectrum.*

868 4.7 Comparison with Europa

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871 In Fig. 16 we compare four spectra of natron of intermediate grain size, respectively acquired
872 at 93, 113, 163 and 208 K, to three spectra of Europa corresponding to as many locations
873 observed by Galileo-NIMS (from McCord et al., 2010), and to pure water ice (fine snow, from
874 ENVI spectral library) for reference. The spectra from McCord et al. (2010, Fig. 3b) refer to

875 different pixel areas: spectrum “A” is interpreted to be water ice-like, spectrum “D” in
 876 interpreted as heavily hydrated terrain, whereas spectrum “E” is an area intermediate
 877 between “A” and “D”. From a comparison between our measurements and NIMS data it
 878 appears that our spectra display a better agreement with NIMS spectra labeled as “water ice-
 879 like” (spectrum A), or at least are intermediate between A and E. By looking at the 1.5- μ m
 880 region, the 113-163 K spectra seem the most similar, given that the 93 K-spectrum displays
 881 too strong 1.75- μ m feature, while the 208 K spectrum has a too weak 1.65- μ m feature.
 882 However, in NIMS-measured spectra of Europa, water-related bands are shifted to longer
 883 wavelengths compared to our natron spectra, only slightly at 1.5 μ m, but more clearly for the
 884 1.25 and 2 μ m bands. This, combined with a redder near-IR slope as observed in Europa,
 885 suggest that non-ice materials other than natron should be better candidates to fit the Europa
 886 spectra in the near infrared .

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 892 *Figure 16. Laboratory spectra of natron with 75-100 μ m grain size at four different temperatures,*
 893 *compared to three spectra of Europa-NIMS (From McCord et al., 2010; spectra pixel A, D, E) and with*
 894 *pure water ice (fine snow, ENVI JHU-Johns Hopkins University Spectral Library, Baldrige et al., 2009).*
 895

896 4.8 Implications for MAJIS-JUICE

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 898 The MAJIS spectrometer (Piccioni et al., 2014) onboard the ESA JUICE mission will observe
 899 Jupiter’s moons in the 0.5-5.54- μ m range, with unprecedented spectral sampling: on average,
 900 3.6 nm/band in the 0.5-2.35- μ m channel and 6.5 nm/band in the 2.25-5.54- μ m channel. A
 901 legitimate question is whether this instrument in principle would be able to reveal the same
 902 temperature-dependent spectral changes we retrieved for the sodium carbonate samples. We
 903 focus on the absorption features that show the largest displacements in position.

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Natrite:

- the bands at 2 and 2.35 μm show shifts by about 10 nm, that are comparable with our spectral sampling
- the 3.88 μm I and 3.99 μm II features show a shift in minimum of 10-15 nm, again comparable with actual spectral sampling, but well above the spectral detection threshold of MAJIS.

Thermonatrite:

- the band at 1.57 and 1.78 μm shift by 20-30 nm
- the 2.06 μm II band has a shift of about 10 nm; the 2.20 μm III band shifts by 8-14 nm
- the 2.5- μm bands display shifts of 5-11 nm, 20-35 nm and 20-35 nm, relatively to the three features at 2.32, 2.44 and 2.50 μm .
- the 3- μm feature minimum varies by about 15-20 nm.

Natron:

- the 1.23 μm band minimum varies by 20-30 nm
- the minimum of 1.5- μm band shifts by about 15 nm and 20-60 nm for the two occurring features at 1.50 and 1.65 μm
- minimum changes by about 20-25 nm and 15 nm relatively to 2- μm and 2.45- μm bands, respectively.

In the case of bright spots found on Ceres, whose surface composition sometimes is compatible with the presence of sodium carbonates, a direct comparison with our laboratory spectra allowed us to confirm that the anhydrous form (natrite) provides the best spectral match and to infer the temperature that provides the best agreement with the measured spectra.

In principle, temperature-dependent spectral shifts in sodium carbonates, if present on the surface of the icy Galilean moons, should be observable with JUICE-MAJIS. The most sensitive bands (~ 0.2 nm/K) may allow one to determine the surface temperature with an accuracy better than 10-15 K, provided that the material unit is in relatively pure form and the signal-to-noise ratio is large enough. Future comparisons with the band shapes and the relative band intensities may further improve this accuracy. Concerning the band intensity, the depth and area values for most of the bands vary by a minimum of 5-10% up to a factor of 2 or 3 for many absorption bands.

5. Conclusions

In this paper, we measured three sodium carbonates, i.e. natrite, thermonatrite and natron, in the infrared range 1-4.0 / 1-4.2 μm , in a range of cryogenic temperatures and in three different grain sizes, demonstrating that they show clear temperature-dependent behaviors. As the temperature decreases from 279 K down to 93 K, we can safely identify a number of spectral characteristics that are common to all the samples and grain sizes, namely:

- A fine structure of absorption bands appears and becomes more defined at lower temperatures. Some new features become visible at low temperatures, others increase their strength.
- The band depth and area values typically increase as the temperature decreases.
- The bandwidth show contrasting behavior, depending on the particular absorption band.

953 As the water content increases, in the sequence: natrite → thermonatrite → natron (0 → 1 →
954 10 H₂O molecules), we observe that:

955

- 956 - the 3- μ m water absorption becomes more intense and saturates, and its short-wave
957 wing moves towards shorter wavelengths: i.e., the saturation region becomes larger
958 and starts at even shorter wavelengths as the water content increases.
- 959 - For higher water content the average continuum reflectance level lowers, and the 1-
960 2.6- μ m VNIR negative slope becomes steeper.

961

962 The band positions almost systematically display a different behavior with temperature,
963 which depends on the absorbing molecule they are related to, provided that evaluable shifts
964 are greater than the spectral resolution. Absorption features corresponding to vibrational
965 modes involving H₂O molecules (especially in natron spectra) typically shift towards longer
966 wavelengths as the temperature decreases. This is explained by an increasing strength of
967 hydrogen bonding as the temperature decreases. Conversely, the absorption bands
968 corresponding to vibrations occurring in CO₃ carbonate ion (bands of natrite) tend to shift
969 towards shorter wavelengths as the temperature decreases, possibly due to phase transition
970 occurring in natrite. An intermediate behavior characterizes the thermonatrite spectrum.

971 The MAJIS spectro-imager onboard the JUICE mission will closely observe the surface of
972 Jupiter's icy moons with high spectral resolution. In this regard, these laboratory spectra will
973 aid the interpretation of future hyperspectral data in highlighting variations in composition,
974 texture and temperature.

975

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977

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