



**HAL**  
open science

## Reflectance spectra of mascagnite and salammoniac minerals with varying viewing geometry

M. Fastelli, B. Schmitt, P. Beck, O. Poch, A. Zucchini, F. Frondini, P. Comodi

► **To cite this version:**

M. Fastelli, B. Schmitt, P. Beck, O. Poch, A. Zucchini, et al.. Reflectance spectra of mascagnite and salammoniac minerals with varying viewing geometry. *Icarus*, 2023, 403, pp.115633. 10.1016/j.icarus.2023.115633 . hal-04281445

**HAL Id: hal-04281445**

**<https://hal.science/hal-04281445>**

Submitted on 12 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# 1 Reflectance spectra of mascagnite and salammoniac minerals 2 with varying viewing geometry.

3 Fastelli M.<sup>a\*</sup>, Schmitt B.<sup>b</sup>, Beck P.<sup>b</sup>, Poch O.<sup>b</sup>, Zucchini A.<sup>a</sup>, Frondini F.<sup>a</sup> and Comodi P.<sup>a</sup>

4 a Department of Physics and Geology, University of Perugia, I-06123, Perugia, Italy

5 b Univ. Grenoble Alpes, CNRS, IPAG, 38000 Grenoble, France

6 \*Email: maximiliano.fastelli@unipg.it

## 7 Highlights

- 8 • Mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and salammoniac-NH<sub>4</sub>Cl minerals were characterized by means of  
9 BRDF spectroscopy with varying viewing geometries in term of incidence (*i*) and emergence  
10 (*e*) angles.
- 11 • Relationship between the viewing geometry variations and the spectral feature parameters  
12 (band area, depth, slope) of NH<sub>4</sub><sup>+</sup> features were observed.
- 13 • High spectral variability was observed for *i* ≥ 30° and *e* ≥ 60° angles.
- 14 • Results from such investigation will be useful to interpret occurrence of ammonium salts on  
15 planetary surfaces, especially small bodies.

## 16 Abstract

17 We analyse the quantitative effects of viewing geometry variations on the near-infrared reflectance  
18 spectra of mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and salammoniac-NH<sub>4</sub>Cl samples. Bi-directional reflectance  
19 spectra are collected in the 1 - 4.2 μm range considering a set of 3 incidence (*i*) angles (*i* = 0°; 30°;  
20 60°) and 9 emergence (*e*) angles between -70° and 70° at room temperature and computed with  
21 respect to the normal direction. The NH<sub>4</sub><sup>+</sup> overtone and combinations bands located at ~ 1.09, 1.32,  
22 1.62, 2.04, 2.2 and 3.05 μm are experimentally investigated. The bidirectional reflectance spectra  
23 of these samples show significant variations with the observation geometry in terms of reflectance  
24 values, spectral slope, and absorption bands parameters. The band positions remain essentially  
25 unchanged by varying the incident and emergence angles. On the other hand, bands' area and depth  
26 show the highest variability for *i* ≥ 30° and *e* greater than ±40° (up to a factor 2.3 in relative mean  
27 variation). The area and depth parameters of these bands show a dual behaviour: (i) for the weak-  
28 medium spectral features below 2 μm the area and depth decrease as the phase angle increases.  
29 (ii) The strong spectral features above 2 μm increase their values only at phase angles above 90°,  
30 but also at low phase angles for high incidences, *i* ≥ 30°. This behaviour is linked both to the non-  
31 linear radiative transfer in particulate media and to the way the band depth and area are defined,  
32 relative to the local continuum. We observe important dependence (up to ~60% relative mean  
33 variation) of band depth and area on the incidence angle, up to 60°, compared to moderate variation  
34 with emergence angles (up to ~20% relative mean variation). Furthermore, the ~ 3 μm features  
35 becomes more saturated at ± 70° emergence angles. A general trend of spectral bluing with change  
36 in observation geometry is observed. The current dataset is a contribution in the framework of  
37 present and future space missions focused on understanding the nature and quantification of  
38 ammonium-bearing minerals on icy bodies. The NH<sub>4</sub><sup>+</sup> – bearing minerals identification could provide

39 information on: (i) ocean/brine compositions, (ii) possible explanations of geological phenomena  
40 and (iii) implications for biological activity.

41 **Keywords:** mascagnite, salammoniac, reflectance spectra, icy bodies, viewing geometry.

## 42 **1 Introduction**

43 Planetary surface remote sensing by visible and near-infrared reflectance spectroscopy (0.4 -5  $\mu\text{m}$ ),  
44 from telescopic observations and spacecrafts, is a widely applied technique for investigating and  
45 deciphering their composition. One way to resolve and identify which are the best candidates to  
46 represent surface compositions of planetary bodies is to collect mineral spectra in the laboratory  
47 and compare them with planetary data. In addition, by varying different physical parameters we can  
48 extend the existing spectral libraries such as temperature, granulometry and observation geometry  
49 on these minerals. In planetary sciences, reflectance spectroscopy in the visible and near-infrared  
50 has proven its considerable power to disclose the mineralogy of Solar System bodies (Bishop et al.,  
51 2019; Pelkey et al., 2007; Singer et al., 1979).

52 The reflectance spectra of minerals in the near infrared and part of mid infrared region (1 -5  $\mu\text{m}$ ,  
53 SWIR 1-3 $\mu\text{m}$  + LWIR 3-5 $\mu\text{m}$ ) have diagnostic absorption features, due to electronic and vibration  
54 transitions, that are essential in determining surface mineralogy and consequently to understand  
55 planetary formation and evolution (Mustard and Glotch, 2019). Mineral spectral bands are closely  
56 linked to the different configurations of atoms and molecules inside the crystal structure, but they  
57 can vary in terms of positions and shapes also as a function of different environmental conditions  
58 such as temperature or pressure (e.g. (Comodi et al., 2017, 1990) which affect the structural  
59 evolutions, sometimes in anomalous way (Gatta et al., 2005). Furthermore, grain size and  
60 observation geometry strongly influence the spectral features (e.g. Beck et al., 2012; Comodi et al.,  
61 2021; De Angelis et al., 2021).

62 Regarding the viewing geometry, the reflectance spectra collected by spacecraft missions are  
63 generally bidirectional, that is, the incidence of the sun light has a specific angle relative to the  
64 normal direction of the surface and the reflected light has itself a proper emergence direction  
65 (Pommerol and Schmitt, 2008a). Numerous bidirectional radiative transfer models have been  
66 created that take into account the physical properties of the surface of planetary bodies, e.g.,  
67 particle size and shape, roughness of the surface (Hapke, 2012, 1981); however, as surfaces are  
68 complex systems and often difficult to model, these models need to be tested with experimental  
69 data to confirm their reliability and suggest how they can be improved. For this reason, it is essential  
70 to collect laboratory Bidirectional Reflectance Distribution Function (BRDF) spectra of well-  
71 characterised samples. Furthermore, with the creation of hyperspectral cameras with increasingly  
72 high spatial resolution, the effect of surface roughness and observation geometry can be also  
73 considered.

74 Given the presence of surface roughness, topography and variations in morphology, the surface  
75 reflectance spectra of every Solar System bodies are affected by observation geometries, some  
76 examples include Mercury (Warell and Bergfors, 2008), Uranus' moons (Nelson et al., 1987) and  
77 asteroids (Clark et al., 2002; Magrin et al., 2012). For example on icy bodies, chaos terrain on  
78 Europa's surface, that represents resurfacing process, can be mostly identified at incidence angles  
79  $> 70^\circ$  (Neish et al., 2012). On Pluto's surface, the changes in viewing geometry during the New

80 Horizons flyby generated significant spectral changes in the N<sub>2</sub>, CO and CH<sub>4</sub> absorption bands  
81 (Cruikshank et al., 2015). The dwarf planet Ceres displays a negative slope in the 0.5-2.5 μm spectral  
82 region at fresh impact craters which is related to possible changes in physical properties and  
83 composition (Stephan et al., 2017).

84 Up to now, several laboratory studies have analysed in detail ammonium bearing minerals using  
85 visible and near-infrared spectroscopy at various temperatures and considering different particle  
86 sizes (e.g., (Berg et al., 2016; Ciarniello et al., 2017; De Angelis et al., 2021a; Ehlmann et al., 2018;  
87 Fastelli et al., 2020; Krohn and Altaner, 1987). In all these works, the variation in viewing geometry  
88 has not been examined for the here reported samples. Exception made for the work of Ciarniello et  
89 al., 2017 that examined the BRDF effect of NH<sub>4</sub>Cl sample. Thus, reflectance spectra of NH<sub>4</sub><sup>+</sup> minerals  
90 with different observation geometries seem to be lacking in the bibliographic record and a  
91 systematic work, dedicated to a comparative study of different effects of emergence and incidence  
92 angles on NH<sub>4</sub><sup>+</sup> features, is here proposed.

93 Ammonium bearing minerals have been hypothesised on the surface of primordial objects, such as  
94 comets (Poch et al., 2020), on evolved telluric planets such as Mars (Quinn et al., 2011), in some icy  
95 bodies like Ceres and Pluto (Dalle Ore et al., 2019; King et al., 1992) and asteroids, like Ryugu  
96 (Pilorget et al., 2022). The interest and identification of these minerals is linked to the possible  
97 emergence of life. Nitrogen is a key element in many biological compounds and in providing  
98 explanations for evolution and geological phenomena as they are potential environmental markers.  
99 The unambiguous detection and quantification of ammonium bearing minerals on icy bodies and  
100 small object like comets has a significant impact on the presence of either liquid salt water or  
101 phenomena such as cryovolcanism (Kargel, 1992) but also in the incorporation and evolution of  
102 nitrogen in the early Solar System (Füri and Marty, 2015). Salammoniac-NH<sub>4</sub>Cl was identified on the  
103 surface of Ceres in relation to the absorption feature at ~2.21 μm in a bright spot area (De Sanctis  
104 et al., 2016). The genesis of this mineral is linked to the presence of either ancient brine reservoirs  
105 or brines induced by impact heating (De Sanctis et al., 2020). In fact, the formation of salammoniac  
106 is strictly related to the presence of liquid water combined with hydrothermal activity. Ammonium  
107 spectral signatures, at 1.65 and 2.2 μm, were also identified on Pluto, in a region of past extensional  
108 tectonic activity called Virgil Fossae (Cruikshank et al., 2019). These bands can be attributed to the  
109 presence of ammonium chloride salts in analogy to the one reported by Cook et al. (2018) who  
110 modelled the surface of Charon, Nyx and Hydra Pluto's satellites, observed by New Horizons, using  
111 NH<sub>4</sub>Cl as endmembers.

112 Mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> has been suggested to be one of the rock forming minerals of the interior of  
113 Titan generated by the interactions of primordial aqueous ammonia with sulphate solutions leaking  
114 from the rocky core (Fortes et al., 2007). The Titan's internal model, from outside to inside, consists  
115 of a shell of methane clathrate, a layer of aqueous ammonium sulphates and a serpentinite core  
116 overlaid by a high pressure icy mantle (Fortes et al., 2007). Furthermore, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was proposed  
117 on Mars Iano Chaos area due to the presence of absorption bands at ~1.07, 1.31 and 1.57 μm  
118 consistent with its spectrum (Sefton-Nash et al., 2012). Salammoniac and mascagnite minerals are  
119 known for their low temperature phase transitions characterized by a reordering of hydrogen bonds  
120 inside the crystal structure. Salammoniac undergoes to a λ-transition defined as order-disorder type  
121 at ~242K (Levy and Peterson, 1952). After the phase transition, the mineral has a disordered CsCl-  
122 type crystal structure in which the NH<sub>4</sub><sup>+</sup> ions are distributed arbitrarily between two energy-

123 equivalent orientations (Wang and Wright, 1974). Mascagnite, on the other hand , undergoes a  
124 phase transition upon cooling at  $\sim 224\text{K}$  from a para-electric crystal structure with space group  $Pnma$   
125 towards a ferro-electric crystal structure with space group  $Pna2_1$  (Hasebe, 1981). In the para-electric  
126 phase, H-bonds are bifurcated and trifurcated while in the ferro-electric phase they turn in a classic,  
127 much stronger, hydrogen bond. The presence of these phase transitions may have a strong effect  
128 on the convective flow and consequently on the results of internal planetary models (Fortes and  
129 Choukroun, 2010). The two selected ammonium bearing minerals were previously characterised  
130 and tested in Fastelli et al. (2022), where the low temperature spectral behaviour was discussed.  
131 The two samples analysed in this work could represent the two most promising candidates as  
132 ammonium-bearing minerals. Also their sensitivity to solar ray alterations (Dalle Ore et al., 2019)  
133 and phase transitions should have direct consequences on the internal structure and dynamic of the  
134 bodies. If ammonium-bearing minerals are detected at the surface of icy bodies, they can play a key  
135 role as freezing compounds, depending on their abundance, that reduce the solidification  
136 temperature of water, allowing it to remain liquid in the conditions beneath the crust of frozen  
137 bodies (Neveu et al., 2017). Ammonium bearing minerals mixed with liquid  $\text{H}_2\text{O}$  can also participate  
138 in potential prebiotic reactions (e.g; Burcar et al., 2016). In addition, the spectra shown and analysed  
139 in this work will be used for future interpretation of reflectance spectra of Pluto's surface as well as  
140 on other planetary bodies such as icy satellites, asteroids, Kuiper Belt Objects (KBOs) and comets.

141 In this work the BRDF spectra of salammoniac and mascagnite minerals were collected with a set of  
142 three incidence angles  $i = 0^\circ, 30^\circ$  and  $60^\circ$  and nine emergence angles in the  $e = \pm 70^\circ$  range, to  
143 investigate how the observation geometries influence the  $\text{NH}_4^+$  signatures: what is the behaviour of  
144 band parameters such as their area, full width at half maximum (FWHM) and depth under varying  
145 observation geometries. The effect of geometry variation on the spectral slope was also described.

## 146 2 Materials and Methods

### 147 2.1 Ammonium bearing minerals

148 The two selected mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and salammoniac-NH<sub>4</sub>Cl samples were checked and  
149 characterized using X-ray powder diffraction (XRPD) technique at the Department of Physics and  
150 Geology, University of Perugia (Italy), using a Philips PW 1830 diffractometer, with a graphite  
151 monochromator, and using the CuK $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Data were taken with a step scan of  
152 0.02°/step and a step time of 20 s/step. Quantitative phase analysis were performed using the  
153 Rietveld method (Rietveld, 1969) through EXP-GUI GSAS software (Larson and Von Dreele, 1987;  
154 Toby, 2001) following the procedure described in (Guidobaldi et al., 2018). The results show that  
155 the salammoniac sample is 100 wt% pure while the mascagnite sample contains a small percentage  
156 of mohrite mineral [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] about 6.4 wt% (Fastelli et al., 2022), see table 1 for details.  
157 Particle size, for the analysed samples, ranges between 32 – 80  $\mu\text{m}$ . Samples were first finely ground  
158 with an agate mortar and then dry sieved.

159

160 Table 1: Compositional data, source and description for selected samples used in this study from  
161 Fastelli et al., 2022.

Mineral Name	Chemical Formula	Purity	Source
Mascagnite / Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	XRPD checked: small amount of mohrite 6.4 wt% [(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O]	Pozzuoli, Italy
Salammoniac / Ammonium chloride	NH <sub>4</sub> Cl	XRPD checked: 100 wt%	Pozzuoli, Italy

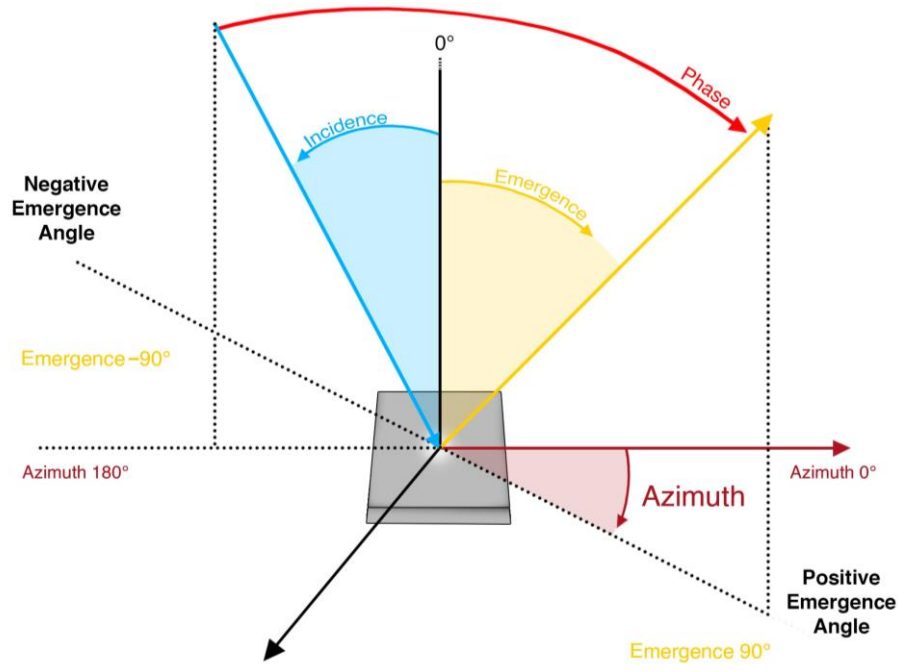
162

### 163 2.2 Bidirectional Reflectance Distribution Function spectra

164 The reflectance spectra analysed in this study were collected using the custom-made bidirectional  
165 reflectance spectro-gonio-radiometer SHINE (SpectroHotometer with variable INcidence and  
166 Emergence) (Brissaud et al., 2004) at the Cold Surface Spectroscopy facility (CSS) of the IPAG  
167 laboratory (<https://cold-spectro.sshade.eu>). This set up permits the collection of spectra in the  
168 visible (VIS) and near-infrared (NIR) ranges (0.35 – 4.5  $\mu\text{m}$ ) over a wide set of illumination (0 – 80°)  
169 and emergence angles ( $e = 0\text{--}80^\circ$ ). We recorded spectra over the 1 – 4.2  $\mu\text{m}$  range with a spectral  
170 sampling of 10 nm up to 3.2  $\mu\text{m}$  and 20 nm above with effective spectral resolution varying in 3  
171 steps (3 gratings with fixed slit width) between 7.5 and 30 nm over the range. The illumination spot  
172 was 7.5 mm in diameter. The illumination is monochromatic and modulated (~970 Hz) with a  
173 synchronous detection so thermal emission from the sample and surrounding (not modulated) did  
174 not contribute to the reflected light (modulated) measurement (Bonney 2001, Brissaud et al.,  
175 2004).

176 Measurements were taken in the principal plane considering a set of 3 incidence angles  $i = 0^\circ, 30^\circ,$   
177  $60^\circ$  and 9 emergence angles  $e = -70^\circ, -60^\circ, -40^\circ, -20^\circ, 0^\circ, 20^\circ, 40^\circ, 60^\circ, 70^\circ$  at room temperature.  
178 Both illumination and emergence angles are zenithal angles (measured from the normal direction  
179 to the surface) and the emergence is positive in the same quadrant as illumination in the principal  
180 plane (i.e, this corresponds to azimuth = 0° for positive emergence values, and 180° for negative

181 values). The phase angle  $g$  is thus simply:  $g = |i - e|$ . Furthermore, we define ( $i=0^\circ, e=20^\circ$ ) as our  
 182 reference configuration and compare the spectra measured at all other configurations with the  
 183 spectrum measured at this configuration. Figure 1 presents a schematic view of the different  
 184 geometrical parameters analysed.



185

186 Fig. 1: Schematic representation of the different geometrical parameters analysed in this work.  
 187 Pictures modified from Potin et al., 2019.

188 Approximately 2 g of powdered samples were put in an aluminum sample holder cup, 34 mm in  
 189 diameter and 4 mm deep. The density (0.54 and 0.64 g/cm<sup>3</sup>, respectively) and porosity (~64% for  
 190 both) of the salammoniac and mascagnite samples were calculated using the measured volume and  
 191 mass of the samples and the bulk density of the minerals.

192 The surfaces were accurately prepared, as the macroscopic structure (roughness) of the surface has  
 193 a significant effect on the collected spectra and particularly on the reflectance changes between  
 194 different measurement geometries (Cord et al., 2003; Pommerol and Schmitt, 2008a).

### 195 2.3 Data reduction

196 The recorded spectra were firstly calibrated in reflectance factor (i.e. relative to a perfectly  
 197 Lambertian surface) by measuring the BRDF of a Spectralon© 99% reference target at the same set  
 198 of geometries as well as an Infragold© reference target measured under the standard calibration  
 199 geometry ( $i=0, e=30^\circ$ ) of the instrument (spectrally equivalent to the directional-hemispheric ( $i=8^\circ$ )  
 200 calibration provided by Labsphere). The reflectance is obtained by dividing the sample  
 201 measurement by the Spectralon© measurement at the same geometry and by multiplying by the  
 202 value of the spectral reflectance of Spectralon© at that geometry, from a previously calibrated  
 203 absolute BRDF evaluation of the reference target (Bonneyoy, 2001). The spectral behavior of the  
 204 part of the spectrum above 1.3  $\mu\text{m}$  is obtained by dividing by the Infragold© measurement at the  
 205 standard calibration geometry ( $i=0, e=30^\circ$ ) of the instrument and by multiplying by its spectral  
 206 directional-hemispheric reflectance. The absolute reflectance of this part of the spectrum is then

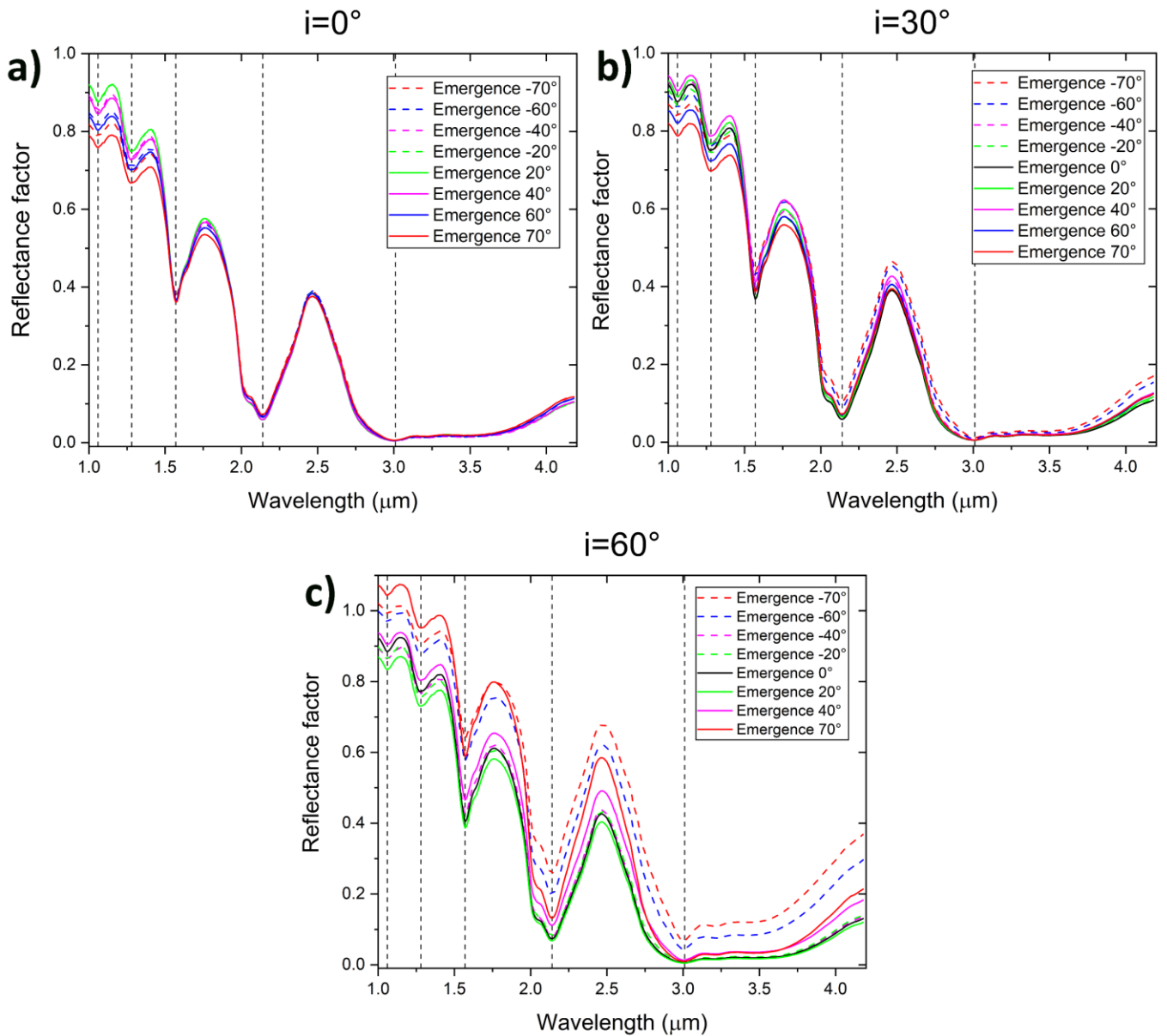
207 obtained by adjusting (with a multiplying factor) the value of the spectrum at 1.3  $\mu\text{m}$ , to that of the  
208 spectrum absolutely calibrated with Spectralon.

209 Regarding the study of band parameters in relation to angle variations, the procedure used to  
210 homogenize the data is detailed in the following. For each examined band, the removal of the  
211 continuum was taken equal and kept constant (same anchor point for the continuum) for all spectra.  
212 The position of the absorption bands was then measured using a second-order polynomial fit around  
213 the minimum. The depth of the band was calculated according to the following equation of:  $D = (R_c$   
214  $- R_b)/R_c$  in which  $R_b$  is the reflectance at the centre of the band and  $R_c$  is the reflectance of the  
215 continuum at the centre of the band (Clark and Roush, 1984). The band area was determined by  
216 numerical integration over the band after continuum removal. The full width at half maximum  
217 (FWHM) was derived by cross cutting the band removed from the continuum with a horizontal line  
218 that passes through mid-depth. The band area and depth were computed for the entire band  
219 complex and not for all relative minima. More detailed information on the spectral parameter  
220 analysis procedure can be found in Comodi et al. (2021) and Fastelli et al. (2021). The spectra  
221 reduction was performed for the selected absorption bands of interest for remote sensing  
222 identification of  $\text{NH}_4^+$ - bearing minerals located at  $\sim 1.07$ ,  $\sim 1.3$ ,  $\sim 1.58$ ,  $\sim 2.07$ ,  $\sim 2.17$  and  $\sim 3.03$   $\mu\text{m}$

### 223 **3 Results**

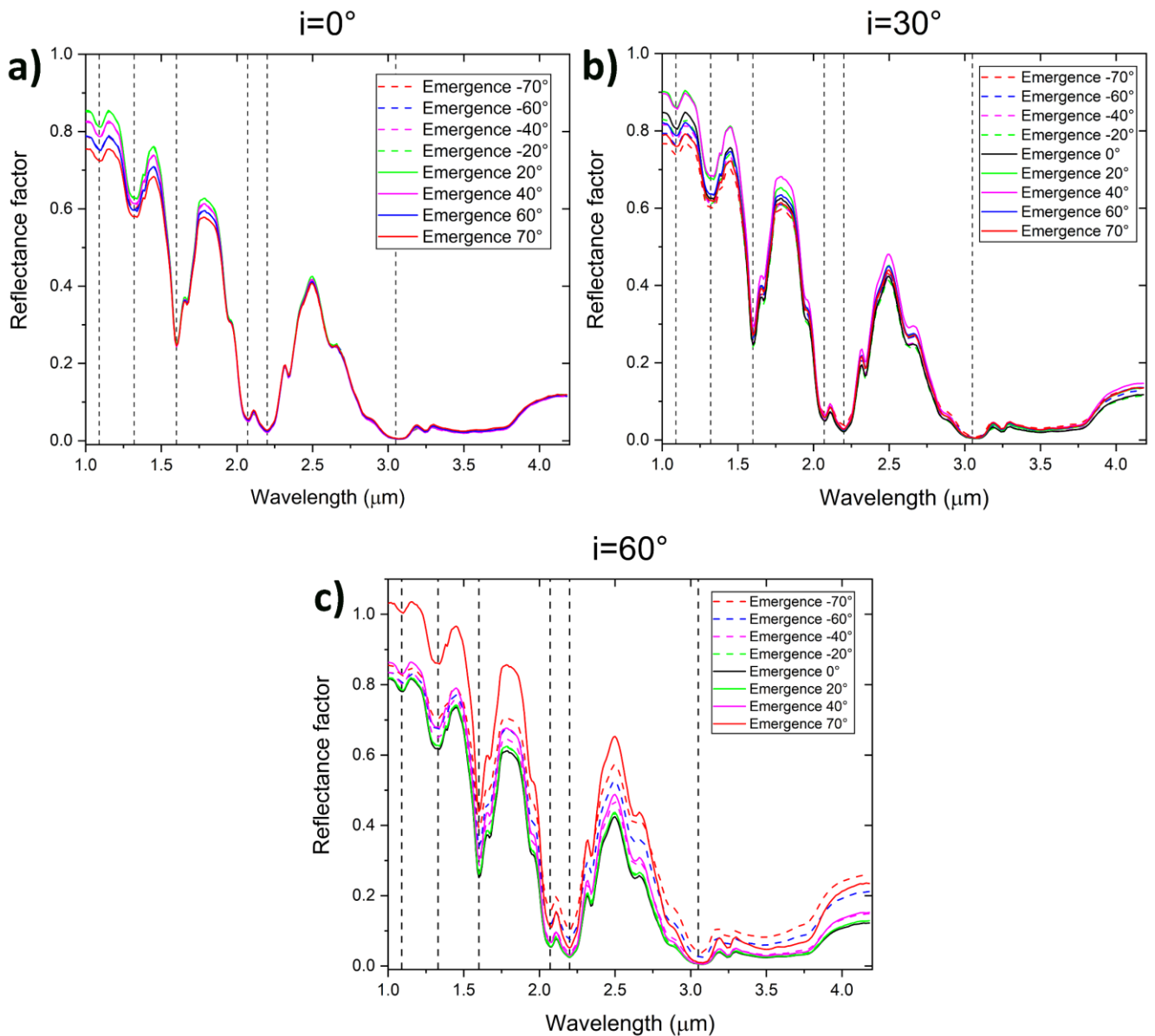
224 Figures 2 and 3 report the bi-directional reflectance spectra of the two selected ammonium bearing  
225 minerals mascagnite and salammoniac, respectively, collected at different illumination-emergence  
226 geometries. Table 2 provides the absorption bands positions at reference geometry for this work  
227 ( $i=0^\circ$ ,  $e=20^\circ$ .) analysed in this work and their assignment.





228

229 Fig. 2: BRDF spectra of the Mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> sample. Each of the three plots presents spectra  
 230 measured at zenithal incidence angle  $0^\circ$  (a),  $30^\circ$  (b) and  $60^\circ$  (c) and different emergence angles in  
 231 the  $\pm 70^\circ$  range. Spectra with negative emergence “e” angle (i.e. azimuth =  $180^\circ$ ) are reported with  
 232 dashed lines retaining the same colour for same absolute value of the positive emergence (i.e.  
 233 azimuth =  $0^\circ$ ). BRDF data at 1.06, 1.28, 1.57, 2.14 and 3.01  $\mu\text{m}$  wavelengths are analysed (marked  
 234 by vertical dash lines).



235

236 Fig. 3: BRDF spectra of the Salammoniac-NH<sub>4</sub>Cl sample. Each of the three plots presents spectra  
 237 measured at zenithal incidence angle  $0^\circ$  (a),  $30^\circ$  (b) and  $60^\circ$  (c) and different emergence angles in  
 238 the  $\pm 70^\circ$  range. Spectra with negative emergence “e” angle (i.e. azimuth =  $180^\circ$ ) are reported with  
 239 dashed lines retaining the same colour for same absolute value of the positive emergence (i.e.  
 240 azimuth =  $0^\circ$ ). BRDF data at 1.09, 1.33, 1.62, 2.06, 2.2 and 3.05 μm wavelengths are analysed  
 241 (marked by vertical dash lines).

242 Table 2: Positions and vibration mode assignments of the reflectance spectra collected with  
 243 reference geometry ( $i=0^\circ$ ;  $e=20^\circ$ ) for the selected bands analysed in this work. Intensity labels are:  
 244  $w$  = weak,  $m-s$  = moderately-strong,  $m$ =medium and  $s$ =strong. Band assignments were made  
 245 following (Berg et al., 2016; Fastelli et al., 2022; Krohn and Altaner, 1987).

Mineral	Band position ( $\mu\text{m}$ )	Vibrational modes	Intensity
Mascagnite ( $\text{NH}_4$ ) $_2$ $\text{SO}_4$	1.06	$\text{NH}_4^+ 3\nu_3$	$w$
	1.28	$\text{NH}_4^+ 2\nu_3 + \nu_4$	$w$
	1.57	$\text{NH}_4^+ 2\nu_3$	$m-s$
	2.18	$\text{NH}_4^+ \nu_3 + \nu_4$	$s$
	3.01	$\text{NH}_4^+ \nu_3$	$s$
Salammoniac $\text{NH}_4\text{Cl}$	1.09	$\text{NH}_4^+ 3\nu_3$	$w$
	1.32	$\text{NH}_4^+ 2\nu_3 + \nu_4$	$w$
	1.62	$\text{NH}_4^+ 2\nu_3$	$m-s$
	2.06	$\text{NH}_4^+ \nu_2 + \nu_3$	$s$
	2.2	$\text{NH}_4^+ \nu_1 + \nu_4$ and/or $\text{NH}_4^+ \nu_3 + \nu_4$	$s$
	3.05	$\text{NH}_4^+ \nu_3$	$s$

246

247 The absorption bands identified in the spectra of both samples in the 1-2.5  $\mu\text{m}$  range are mainly due  
 248 to overtones and combinations of the fundamental internal vibrations of the  $\text{NH}_4^+$  group. These  
 249 features are located at  $\sim 1.07$ ,  $\sim 1.3$ ,  $\sim 1.58$ ,  $\sim 2.07$ ,  $\sim 2.17$   $\mu\text{m}$ . On the right side of the spectra, between  
 250 2.8 and 3.8  $\mu\text{m}$ , we notice several saturated and overlapping  $\text{NH}_4^+$  bands except for the salammoniac  
 251 sample which shows two clear features at 3.05 and 3.25  $\mu\text{m}$ . Due to the high hygroscopicity of these  
 252 minerals, although they were kept inside a desiccator before measurement, some spectral features  
 253 of adsorbed  $\text{H}_2\text{O}$  are present at  $\sim 1.47$ ,  $\sim 1.94$ ,  $\sim 2.62$ ,  $\sim 2.83$  and  $\sim 3.0$   $\mu\text{m}$  that, in some cases, overlap  
 254 with the  $\text{NH}_4^+$  bands. In addition, the water molecules absorb in wide wavelength ranges around  
 255 each of the central wavelengths listed above. These positions refer to spectra collected with the  
 256 reference configuration geometry ( $i=0^\circ$ ,  $e=20^\circ$ ).

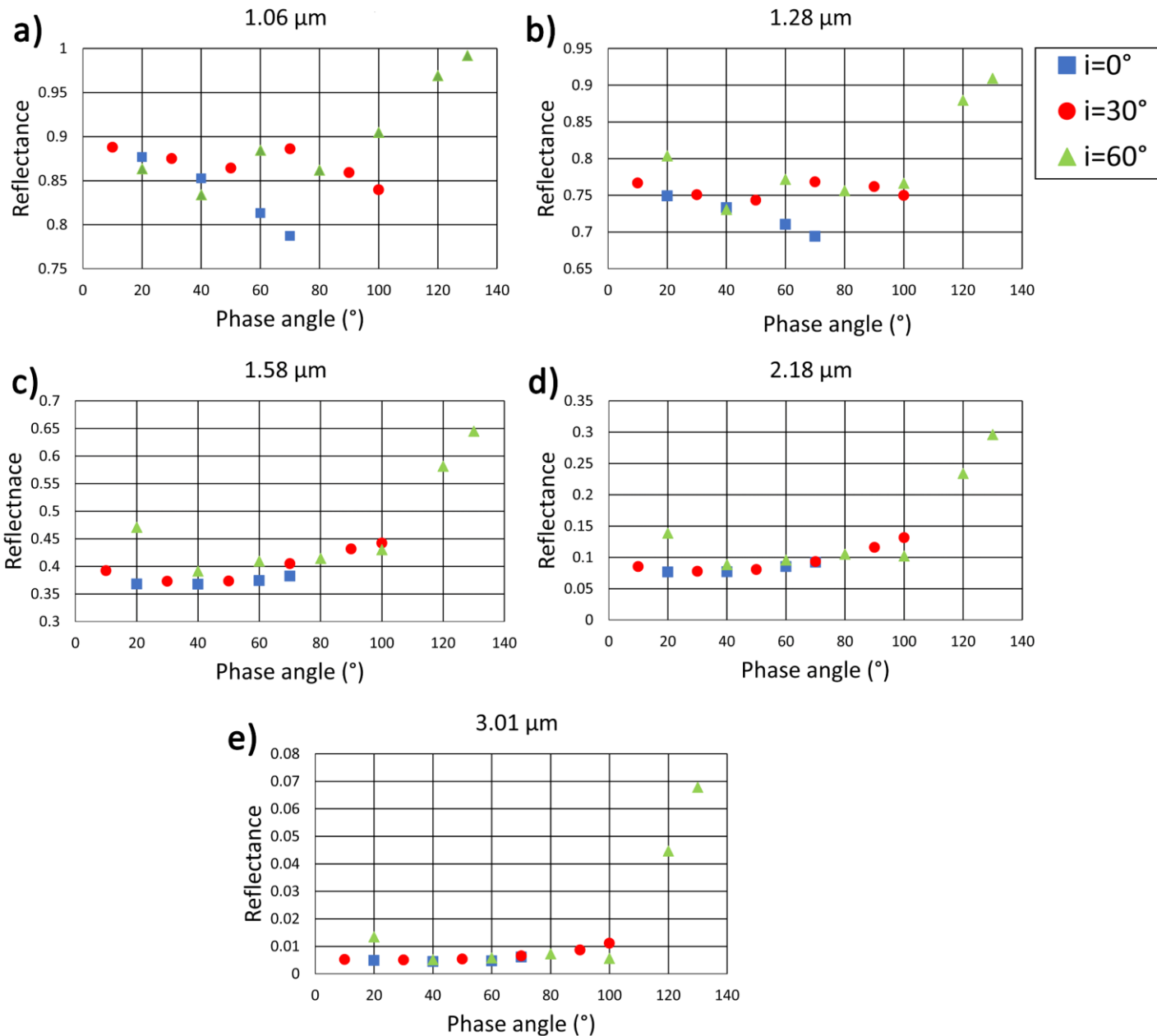
257 Ammonium sulphates  $\text{NH}_4^+$  absorption features are located near 1  $\mu\text{m}$ , at  $\sim 1.56$   $\mu\text{m}$ , and  $\sim 2.2$   $\mu\text{m}$ .  
 258 Over 3  $\mu\text{m}$ , bands are broad and saturated at reference configuration geometry. Ammonium  
 259 chloride ( $\text{NH}_4\text{Cl}$ ) presents clear absorption features in the 1.0 – 2.12  $\mu\text{m}$  range with distinct  
 260 absorption feature at 1.09, 1.33, 1.38 1.62 and 1.67  $\mu\text{m}$  and three bands in the 2- 2.4  $\mu\text{m}$  range  
 261 attributed to  $\text{NH}_4^+$  groups.

262 The selected absorption bands can be ascribed to the following detailed vibrational modes of  $\text{NH}_4^+$   
 263 group:  $\sim 1.09$   $\mu\text{m}$  ( $\text{NH}_4^+ 3\nu_3$ );  $\sim 1.3$   $\mu\text{m}$  ( $\text{NH}_4^+ 2\nu_3 + \nu_4$ );  $\sim 1.6$   $\mu\text{m}$  ( $\text{NH}_4^+ 2\nu_3$ );  $\sim 2.02$   $\mu\text{m}$  ( $\text{NH}_4^+ \nu_2 + \nu_3$ );  
 264  $\sim 2.2$   $\mu\text{m}$  ( $\text{NH}_4^+ \nu_3 + \nu_4$ );  $\sim 3$   $\mu\text{m}$  ( $\text{NH}_4^+ \nu_3$ ) (Berg et al., 2016; Fastelli et al., 2021; Krohn and Altaner,  
 265 1987).

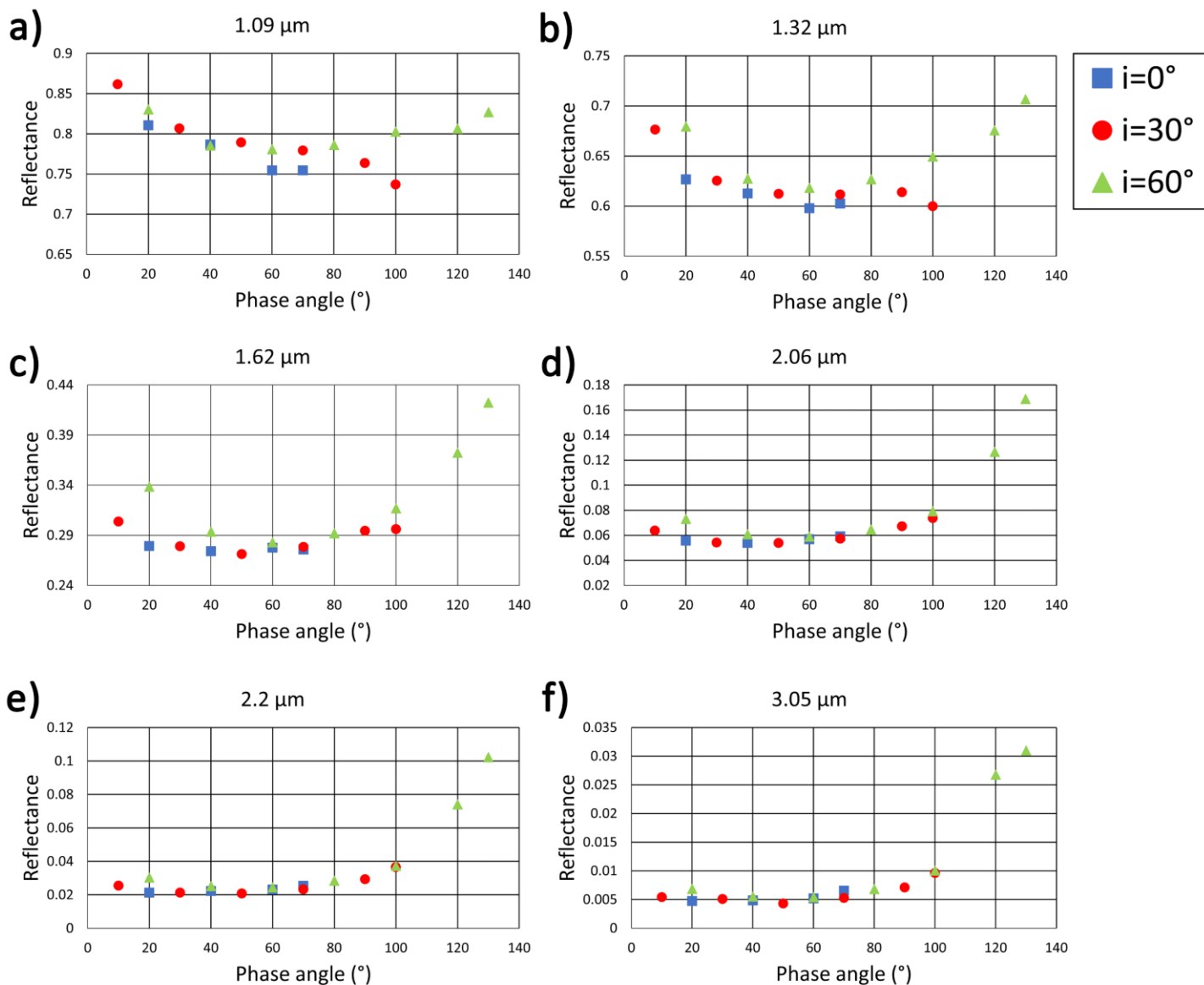
266 The effect of increase in reflectivity towards high incidence and emergence angles due to ‘forward  
 267 scattering’ is evident from the plots shown in Figures 2 and 3 for both samples. In fact, the highest  
 268 reflectance values are found at the highest incidence and negative emergence angles (high phase  
 269 angles). A second clear effect is the reduction of the negative slope with respect to wavelength in  
 270 the continuum of salammoniac and mascagnite samples at high emergence and incidence angles.  
 271 Spectra acquired at an incident angle of  $0^\circ$  are characterised by a lower variability of this parameter  
 272 relative to emergence angles. On the contrary, spectra collected at an incident angle of  $60^\circ$  show

273 significant variations depending on the angle of emergence, in particular at both low ( $g \leq 20^\circ$ , i.e.,  $e = 40 - 70^\circ$ ) and high phase angles ( $g > 100^\circ$ , i.e.,  $e < -40^\circ$ ).

275 Another interesting behaviour is shown by the  $\text{NH}_4^+$  absorption feature in mascagnite sample  
 276 located at  $\sim 3.0 \mu\text{m}$ . In particular, as the incident and emergence angles increase, these features  
 277 become less saturated and better defined (Figure 2). In order to clarify the behaviour of the selected  
 278 bands, for both samples, figures 4 and 5 show the variation in reflectance factor in relation to phase  
 279 angles ( $g$ ).



280  
 281 *Figure 4: Reflectance factor as a function of the phase angle  $g$  for mascagnite- $(\text{NH}_4)_2\text{SO}_4$  sample.*  
 282 *Colored symbols refer to each incidence angle: blue squares ( $i = 0^\circ$ ), red circles ( $i = 30^\circ$ ) and green*  
 283 *triangles ( $i = 60^\circ$ ). Panels a, b, c, d and e correspond to 1.06, 1.28, 1.58, 2.18 and 3.01  $\mu\text{m}$*   
 284 *wavelengths, respectively. Note the different scale of the y axis.*



285

286 Figure 5: Reflectance factor as a function of the phase angle  $g$  for salammoniac- $\text{NH}_4\text{Cl}$  sample.  
 287 Colored symbols refer to each incidence angle: blue squares ( $i = 0^\circ$ ), red circles ( $i = 30^\circ$ ) and  
 288 green triangles ( $i = 60^\circ$ ). Panels a, b, c, d, e and f correspond to 1.09, 1.32, 1.62, 2.06, 2.2 and 3.05  $\mu\text{m}$   
 289 wavelengths, respectively. Note the different scale of the y axis.

290 **3.1 BRDF spectra and geometry**

291 The measured reflectance factors at different incident zenithal angles are shown in polar plots in  
 292 Figures 6 and 7 for mascagnite and salammoniac, respectively, where the BRDF appears as a half of  
 293 a circle (with value of 1 for a perfectly Lambertian surface) and gives a simple overview of the  
 294 different viewing geometry effect. BRDF is plotted in polar coordinates at 1.06, 1.28, 1.57, 2.18 and  
 295 3.01  $\mu\text{m}$  for mascagnite (Figure 6) and at 1.09, 1.32, 1.60, 2.06, 2.2 and 3.05  $\mu\text{m}$  for salammoniac  
 296 (Figure 7). These wavelengths correspond to the minima positions of  $\text{NH}_4^+$  absorption bands. The  
 297 reported BRDF polar plots show a backscattering effect around the incidence quadrant (small phase  
 298 angles) and forward scattering at high phase angles. The increase of reflectance values as phase  
 299 angle decreases is due to the shadows hiding opposition effect (SHOE), *i.e.*, at angles close to  $0^\circ$  the  
 300 effect of shadows between particles is almost negligible and the reflectance in the direction of  
 301 incidence increases (Hapke, 1986). The samples analysed were manually powdered and sieved,

302 reducing the distribution of grain sizes. Thanks to the accurate sample preparation the roughness is  
303 at the level of a few grain sizes. However, the SHOE effect is affected by the intrinsic roughness of  
304 powder that creates shadowing of one particle over another (Pommerol and Schmitt, 2008a; Potin  
305 et al., 2019). Mascagnite and salammoniac present relatively similar behaviours of the BRDF and  
306 show an increase in reflectivity towards high phase angles (for  $i \geq 30^\circ$  and  $e \geq 60^\circ$ ) especially for  
307 absorption bands over  $2 \mu\text{m}$ . In fact, smaller particles compared to those with larger dimensions,  
308 producing a larger number of reflections at their interface, have more pronounced forward  
309 scattering than larger particles, except when very small particles form fluffy aggregates, which is not  
310 the case of our samples which are slightly packed to get a flat surface. Due to these phenomena, the  
311 two samples studied show a non-Lambertian behaviour.

312 The reflectance values variations for the analysed bands are reported in table 3 and 4 for mascagnite  
313 and salammoniac, respectively. For the mascagnite sample, the weak bands located at  $1.06$  and  $1.28$   
314  $\mu\text{m}$  have slightly decreased reflectance values, for  $i = 0^\circ$  and  $30^\circ$  and large emergence angles,  $e \geq$   
315  $\pm 40^\circ$ , from  $0.87$  ( $i = 0^\circ$ ;  $e = 20^\circ$ ) to  $0.75$  ( $i = 0^\circ$ ;  $e = -70^\circ$ ) (Figures 6 a-b); The moderately strong spectral  
316 feature at  $1.58 \mu\text{m}$ , shows almost no change in reflectance with emergence angle for nadir  
317 illumination ( $i = 0^\circ$ ), but at  $i = 30^\circ$  the reflectance starts to increase at high phase angle ( $> 70^\circ$ , i.e.,  $e$   
318  $< -40^\circ$ , Figure 6 c). This trend is growing with the strong band at  $2.18 \mu\text{m}$  and the very strong one at  
319  $3.01 \mu\text{m}$  which show an increase in the reflectance values for increasing phase angles at both  $i = 0^\circ$   
320 and  $30^\circ$ , a behaviour opposite to that of the  $1.06$  and  $1.28 \mu\text{m}$  features. Furthermore, at high  
321 incidence angle ( $i = 60^\circ$ ) all bands display a clear reflectance increase at both low ( $g \leq 20^\circ$ , i.e.,  $e =$   
322  $40 - 70^\circ$ ) and high phase angles ( $g > 100^\circ$ , i.e.,  $e < -40^\circ$ ).

323 At low and high phase angles the relative magnitude of the increase in reflectance (relative to values  
324 at medium phase angle) rapidly grows with the absolute band strength. For the strongest band  
325 around  $3 \mu\text{m}$  we can observe the highest increase of the reflectance values, by a factor more than  
326 3 at low phase angle, and by more than an order of magnitude at high phase angles. On the other  
327 hand the weakest  $1.06$  and  $1.28 \mu\text{m}$  features display only moderate increase in band center  
328 reflectance values, by factors of less than 1.3.

329 The BRDF spectra of salammoniac sample exhibit similar behaviour to mascagnite. The spectral  
330 features at  $1.09$ ,  $1.58$  and  $1.62 \mu\text{m}$  are those characterized by less variability, in terms of reflectance  
331 reduction, with the phase angle variation (Figures 7 a-b-c). These spectral features show the  
332 maximum reflectance value for  $i = 60^\circ$  and  $e = 70^\circ$ . The bands located at  $2.06$ ,  $2.2$  and  $3.05 \mu\text{m}$  have  
333 increased reflectance values starting from  $i = 30^\circ$  and  $e \geq 40^\circ$  (Figures 7 d-e-f). Maximum reflectance  
334 values are obtained for observation geometry configurations corresponding to  $i = 30^\circ$  and  $e = 70^\circ$ .

335 Table 3: Reflectance behaviour of the analysed bands as a function of incidence (*i*) and emergence  
 336 (*e*) angles for the mascagnite sample. The arrows indicate the increase (↑) or decrease (↓)  
 337 variations with respect to the  $e = 0^\circ$  angle. The symbol (-) indicates no variations.

Bands position ( $\mu\text{m}$ )	$i = 0^\circ$								
	$-70^\circ$	$-60^\circ$	$-40^\circ$	$-20^\circ$	$0^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$70^\circ$
1.06	↓	↓	↓	-		-	↓	↓	↓
1.28	↓	↓	↓	-		-	↓	↓	↓
1.57	↑	↑	↓	-		-	↓	↓	↓
2.18	↑	↑	↑	-		-	↑	↑	↑
3.01	↑	↑	↓	-		-	↓	↑	↑
	$i = 30^\circ$								
1.06	↓	↓	↑	↑		↑	↑	↓	↓
1.28	↓	↓	↑	-		↑	↑	↓	↓
1.57	↑	↑	↑	-		↑	↑	↓	↓
2.18	↑	↑	↑	-		↑	↑	↑	↑
3.01	↑	↑	↑	↑		↑	↑	-	↑
	$i = 60^\circ$								
1.06	↑	↑	↑	↓		↓	↑		↑
1.28	↑	↑	↑	↓		↓	↑		↑
1.57	↑	↑	↑	↑		↓	↑		↑
2.18	↑	↑	↑	↑		↑	↑		↑
3.01	↑	↑	↓	↑		↓	↑		↑

338

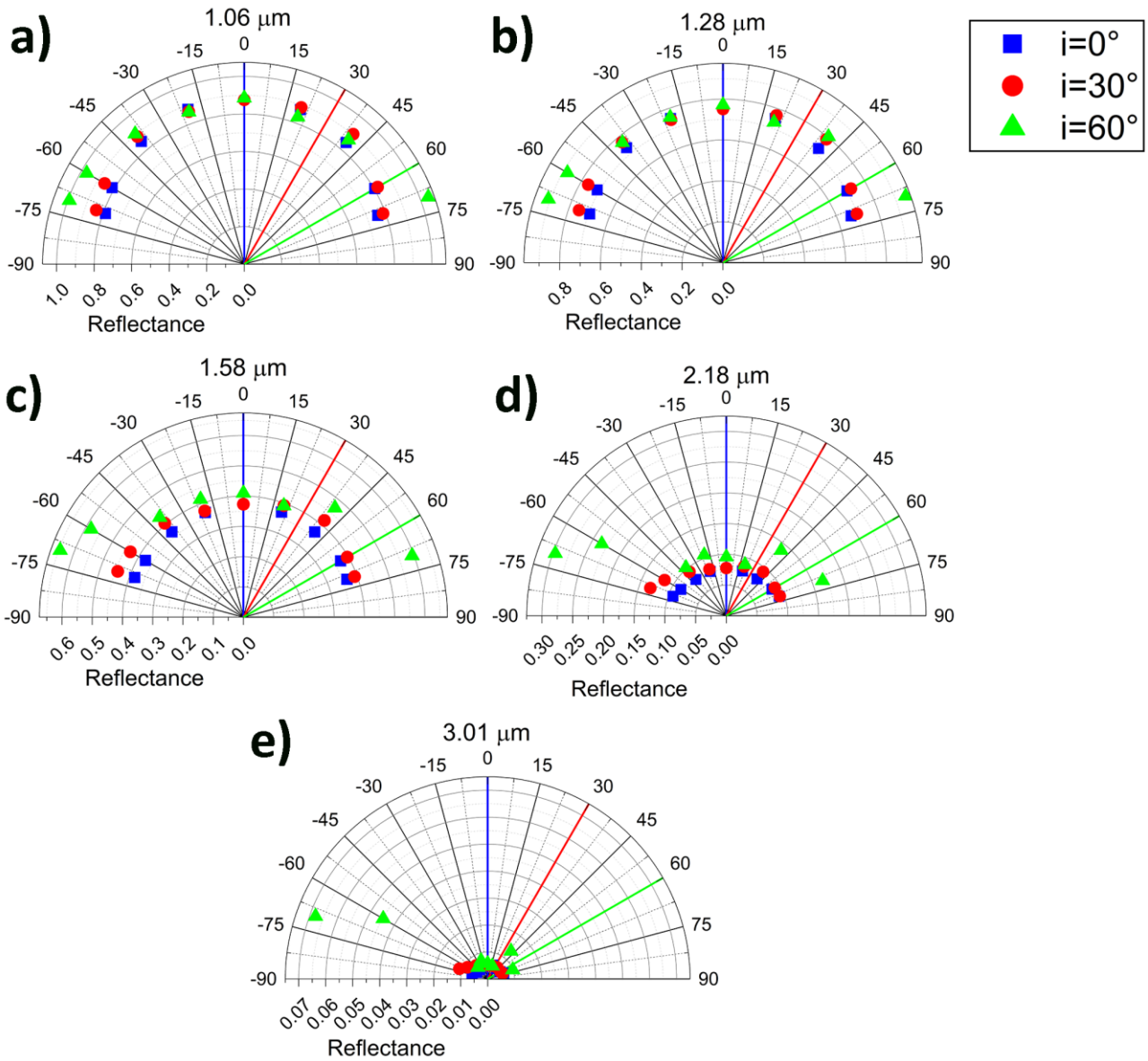
339 Table 4: Reflectance behaviour of the analysed bands as a function of incidence (*i*) and emergence  
 340 (*e*) angles for the salammoniac sample. The arrows indicate the increase (↑) or decrease (↓)  
 341 variations with respect to the  $e = 0^\circ$  angle. The symbol (-) indicates no variations.

Bands position ( $\mu\text{m}$ )	$i = 0^\circ$								
	$-70^\circ$	$-60^\circ$	$-40^\circ$	$-20^\circ$	$0^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$70^\circ$
1.09	↓	↓	↓	-		-	↓	↓	↓
1.32	↓	↓	-	-		-	↓	↓	↓
1.62	↑	↑	↓	-		-	↓	↑	-
2.06	↑	↑	↓	-		-	↓	↑	↑
2.2	↑	↑	↑	-		-	↑	↑	↑
3.05	↑	↑	↑	-		-	↑	↑	↑

	<b>i = 30°</b>									
1.09	↓	↓	↓	-		↑	↑	-	↓	
1.32	↓	↓	-	-		↑	↑	↓	↓	
1.62	↑	↑	-	↓		↑	↑	↑	↑	
2.06	↑	↑	↑	-		↑	↑	↑	↑	
2.2	↑	↑	↑	-		↑	↑	↓	-	
3.05	↑	↑	↑	↑		↑	↑	↑	↑	
	<b>i = 60°</b>									
1.09	↓	↑	↑	↑		↑	↑		↑	
1.32	↓	↑	↑	↑		↑	↑		↑	
1.62	↑	↑	↑	↑		↑	↑		↑	
2.06	↑	↑	↑	↑		↑	↑		↑	
2.2	↑	↑	↑	↑		↑	↑		↑	
3.05	↑	↑	↑	↑		↑	↑		↑	

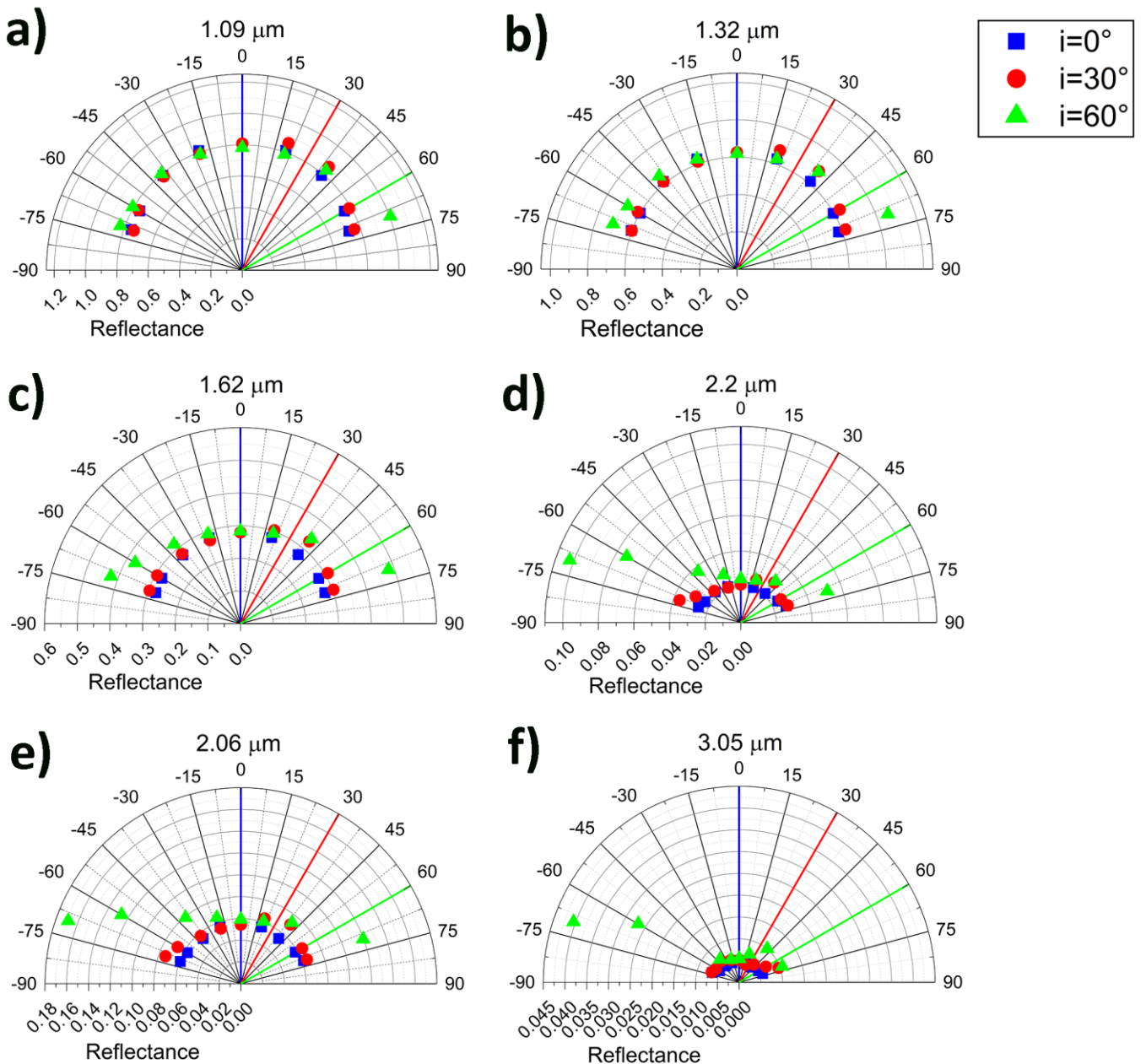
342





343

344 *Fig.6. Polar plots in the principal plane of bidirectional reflectance distribution function for*  
 345 *mascagnite-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> sample. Colored symbols and lines refer to each incidence angle: blue squares*  
 346 *( $i = 0^\circ$ ), red circles ( $i = 30^\circ$ ) and green triangles ( $i = 60^\circ$ ). Positive emergence angles correspond to*  
 347 *azimuth =  $0^\circ$  (back-scattering quadrant) and negative values to azimuth =  $180^\circ$  (forward-scattering*  
 348 *quadrant). Angles are given in degrees. Note the different scales of the axis. Panels a, b, c, d and e*  
 349 *correspond to 1.06, 1.28, 1.58, 2.18 and 3.01 μm wavelengths, respectively.*



350

351 Fig. 7: Polar plots in the principal plane of bidirectional reflectance distribution function for  
 352 mascagnite- $(\text{NH}_4)_2\text{SO}_4$  sample. Colored symbols and lines refer to each incidence angle: blue squares  
 353 ( $i = 0^\circ$ ), red circles ( $i = 30^\circ$ ) and green triangles ( $i = 60^\circ$ ). Positive emergence angles correspond to  
 354 azimuth =  $0^\circ$  (back-scattering quadrant) and negative values to azimuth =  $180^\circ$  (forward-scattering  
 355 quadrant). Angles are given in degrees. Note the different scales of the axis. Panels a, b, c, d, e and  
 356 f correspond to 1.09, 1.32, 1.62, 2.06, 2.2 and 3.05  $\mu\text{m}$  wavelengths, respectively.

### 357 3.2 Effect of observation geometry on bands parameters

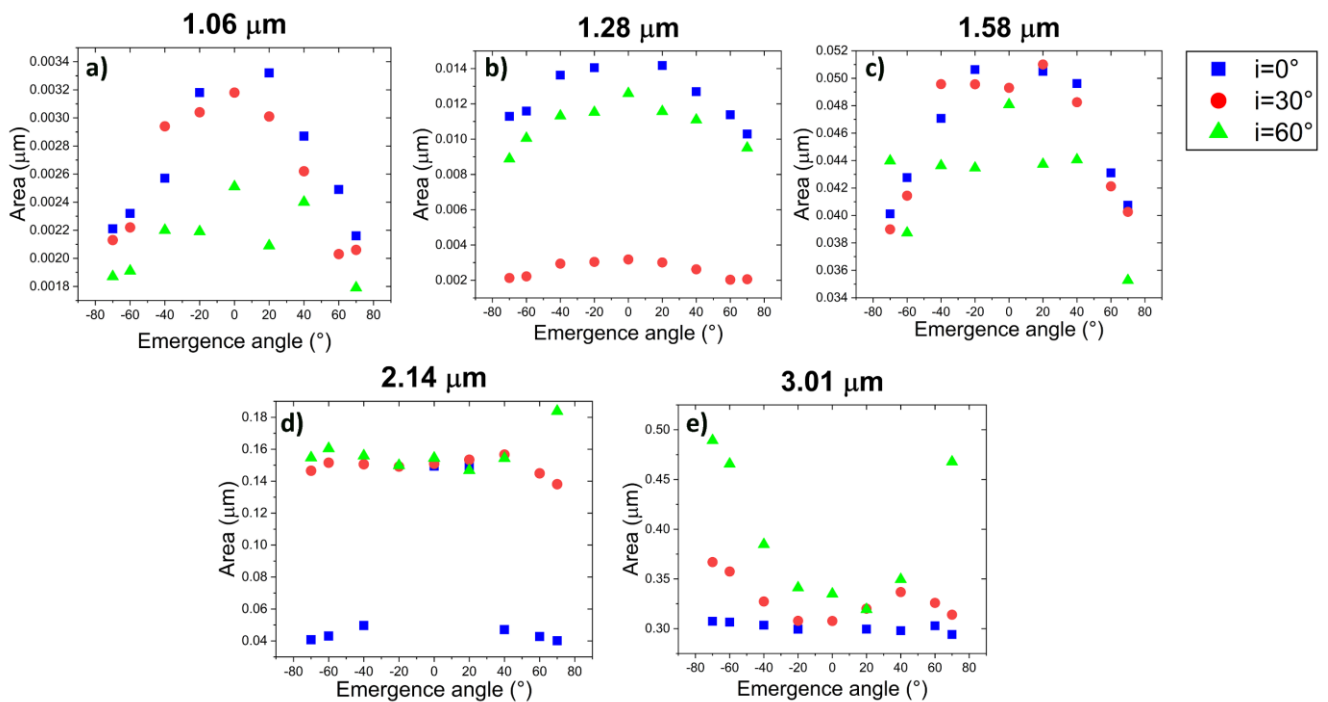
358 For the two analysed samples, the bands depth, area and FWHM were analysed following Comodi  
 359 et al. (2021) as reported in the methods section (section 2). The bands area, depth and FWHM of  
 360 mascagnite sample are reported in Figures 8, 9, and 10, respectively, whereas the bands area, depth  
 361 and FWHM of salamoniac sample are given in Figures 11, 12 and 13, respectively. The absorption

362 features detected for the mascagnite and salammoniac samples are consistent with previous  
 363 published spectra (e.g., Berg et al., 2016).

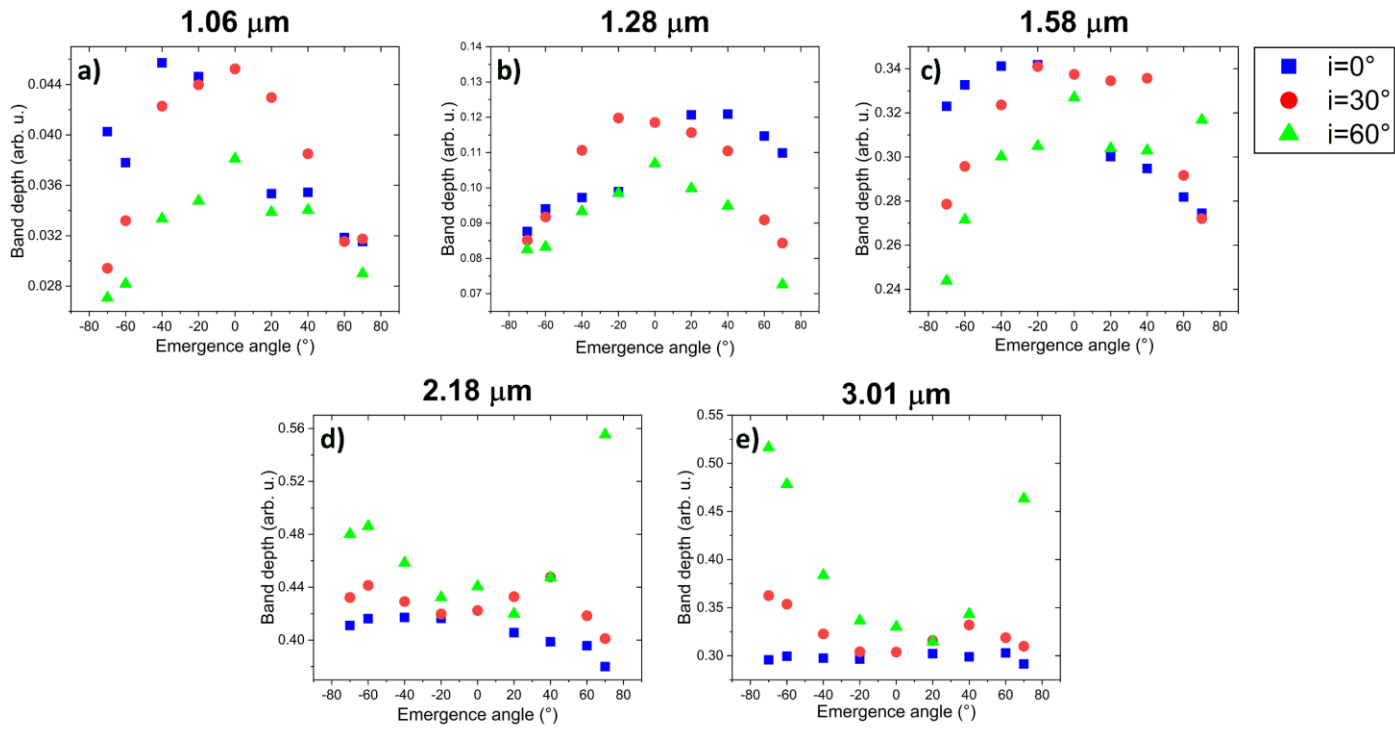
364 The collected data show that the band depth and area are strongly influenced by the viewing angle  
 365 (Figures 8, 9 and 11, 12). On the contrary, the position of the bands remains unchanged. Similar  
 366 works (e.g.; Beck et al., 2012; Pommerol and Schmitt, 2008b; Potin et al., 2019) report that variation  
 367 in the observation geometry corresponds to a decrease in band depth at higher phase angles due  
 368 to the increase in photons scattered out of the sample before penetrating a few grains deep below  
 369 the surface. Our measurements show a decrease in depth values with increasing incidence and  
 370 emergence angles as reported in literature for  $e \geq 40^\circ$ . However, an opposite trend can be observed  
 371 for the absorption bands located over  $2 \mu\text{m}$ . For both mascagnite (Figures 8 and 9) and salammoniac  
 372 samples (Figures 11 and 12), for  $i = 60^\circ$  and  $(i)$  and  $(e)$  angles greater than  $40^\circ$ , the band depth and  
 373 consequently the area tend to increase their values. This is particularly marked on the  $\sim 2.2$  ( $\nu_3 + \nu_4$ )  
 374 and  $\sim 3.0$  ( $\nu_3$ )  $\mu\text{m}$  features in both minerals.

375 Regarding the  $3 \mu\text{m}$  band, it exhibits a broad and shallow shape for variable emergence angles  
 376 collected with  $i=0^\circ$ . This spectral feature reveals a fine structure with increasing incidence and  
 377 emergence angles. For incidence angle equal to  $60^\circ$  and emergence angles  $\geq 60^\circ$ , the  $3 \mu\text{m}$  feature  
 378 is well defined and clearly detectable (Figures 6e and 7f).

379 Finally, the FWHM parameter shows no clear trend with the change in observation geometry  
 380 (Figures 10 and 13). The absence of a possible trend for this band parameter was also found when  
 381 varying other physical parameters such as temperature and particle size (e.g.; De Angelis et al., 2021,  
 382 2019). However, our data for the  $2.18 \mu\text{m}$  bands of mascagnite sample (Fig. 7d) and the  $1.62 \mu\text{m}$   
 383 bands of salammoniac (Fig. 10c) display clear trends with changing viewing geometry.  
 384

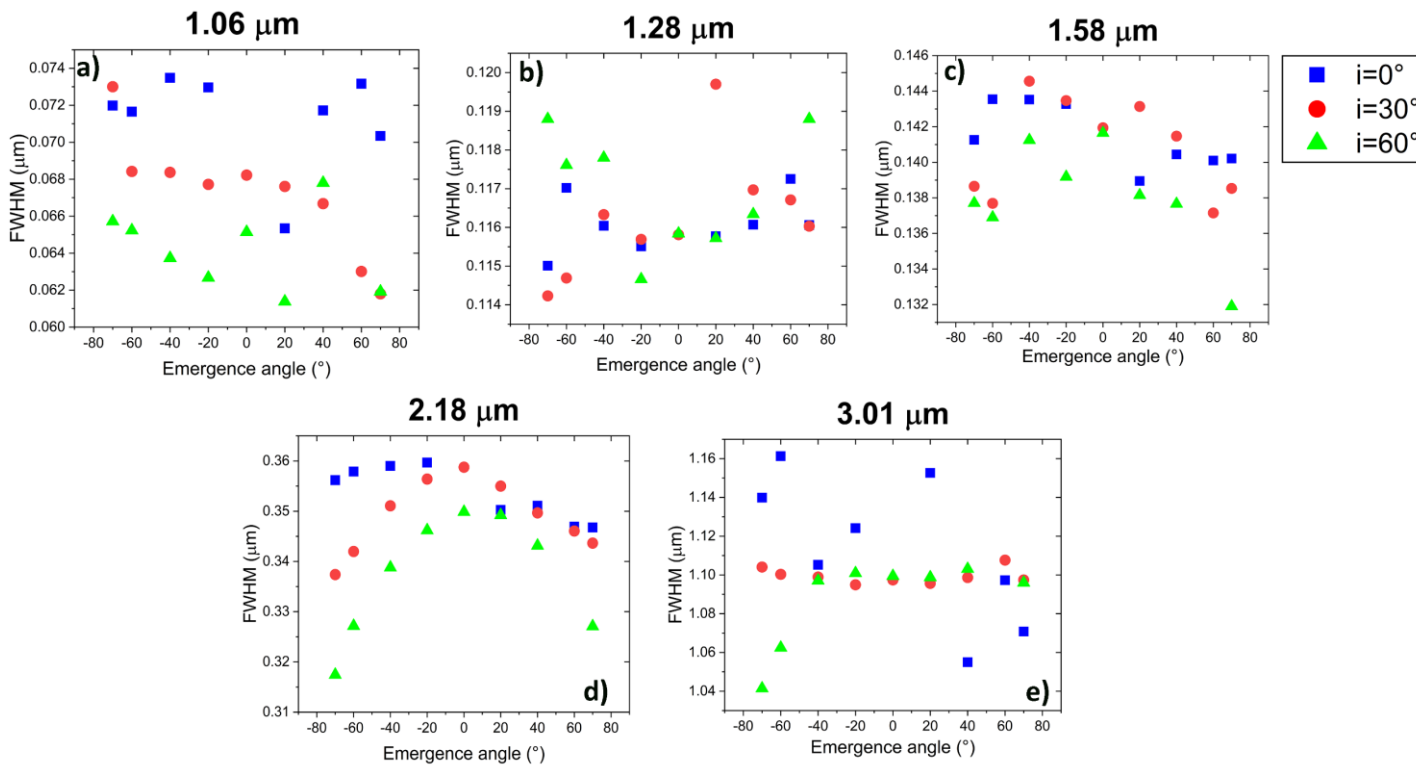


385  
 386  
 387 *Fig. 8: Band area of the 1.06 (a), 1.28 (b), 1.58 (c), 2.18 (d) and 3.01 (e)  $\mu\text{m}$  absorption features of*  
 388 *mascagnite sample for different incident and emergence angles. Note the different scales of the y*  
 389 *axis.*



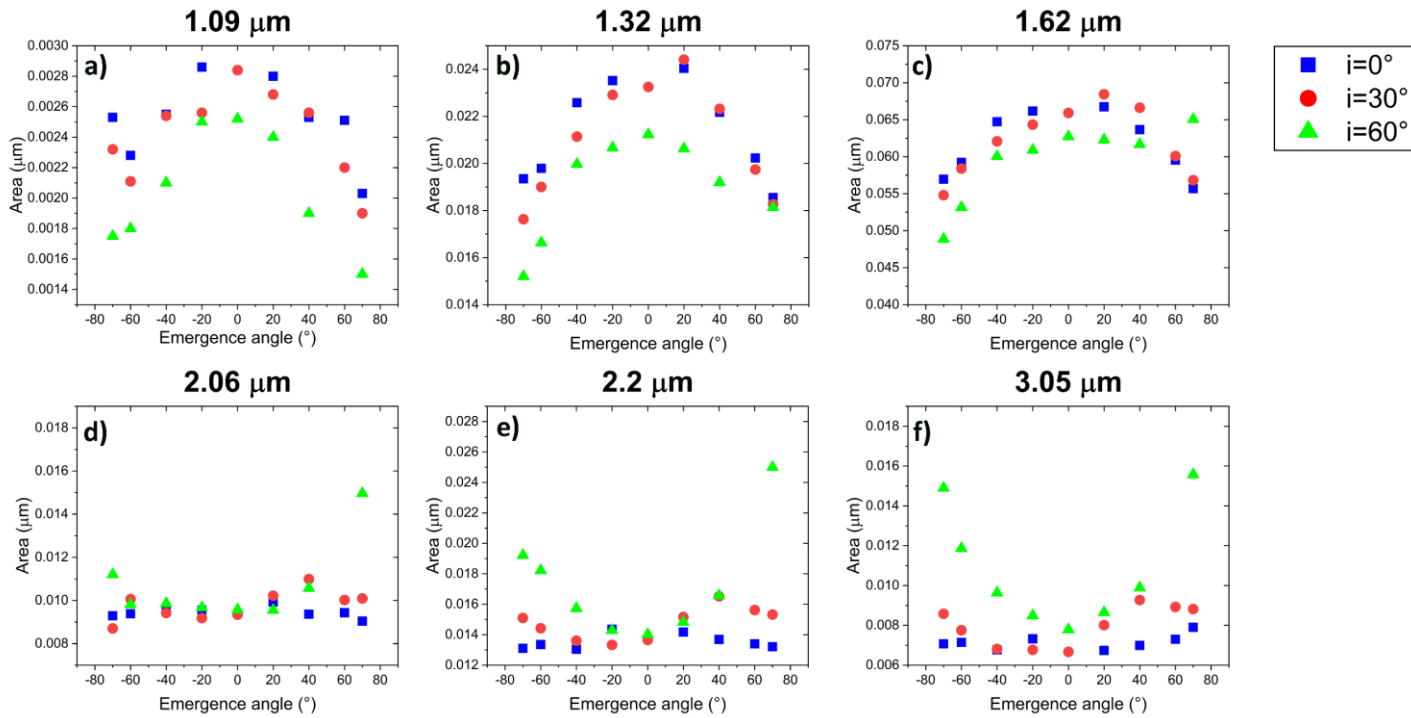
390

391 *Fig. 9: Band depth of the 1.06 (a), 1.28 (b), 1.58 (c), 2.18 (d) and 3.01 (e)  $\mu\text{m}$  absorption features of*  
 392 *mascagnite sample for different incident and emergence angles. Note the different scales of the y*  
 393 *axis.*



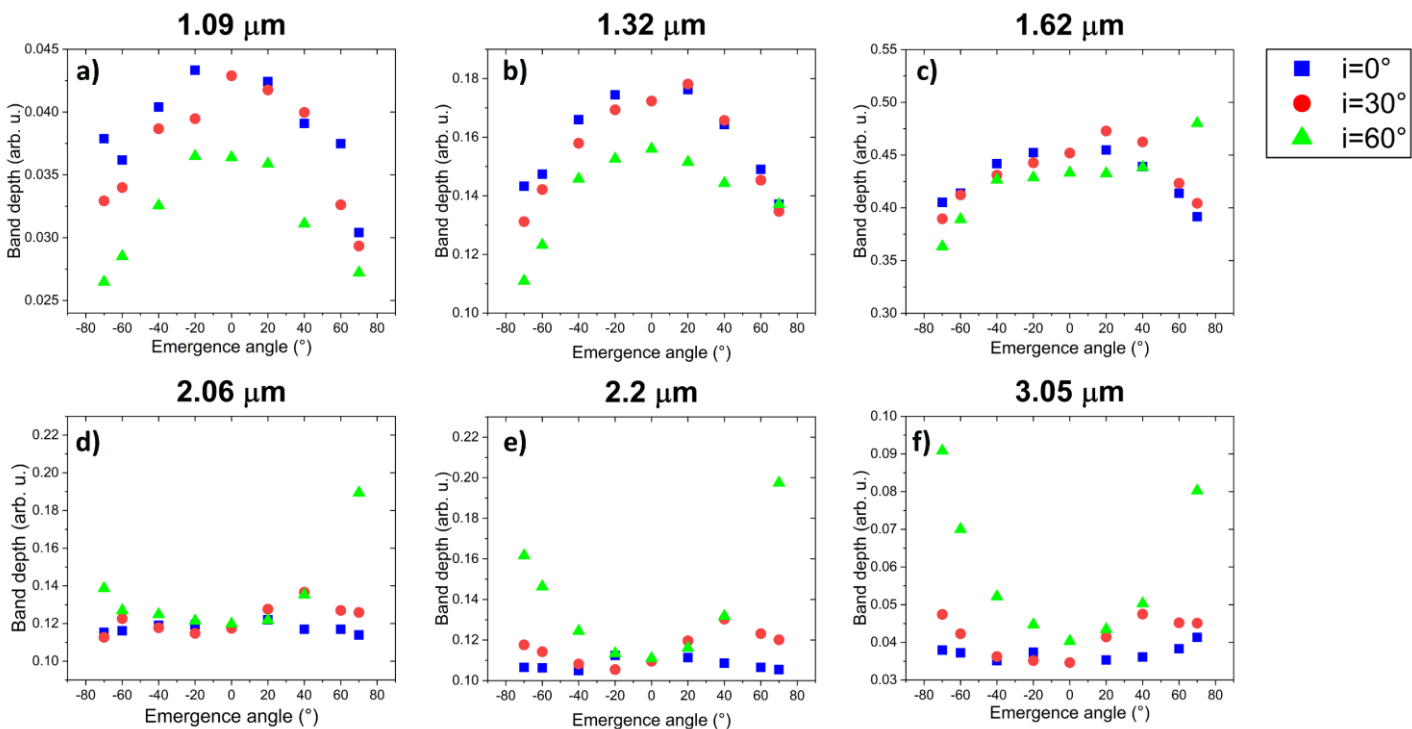
394

395 *Fig.10: Band FWHM of the 1.06 (a), 1.28 (b), 1.58 (c), 2.18 (d) and 3.01 (e)  $\mu\text{m}$  absorption features*  
 396 *of mascagnite sample for different incident and emergence angles. Note the different scales of the*  
 397 *y axis.*



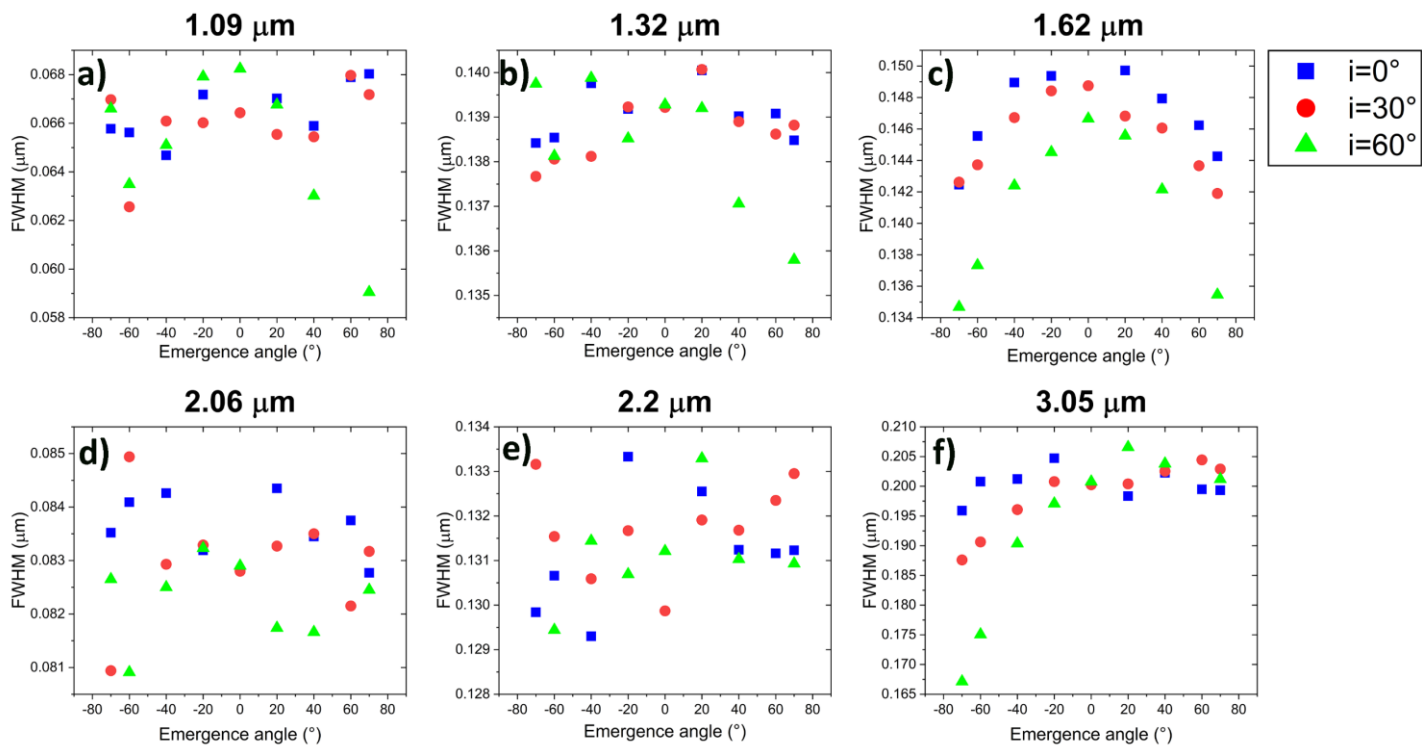
398

399 *Fig.11: Band area of the 1.09 (a), 1.32 (b), 1.62 (c), 2.06 (d), 2.2 (e) and 3.05 (f)  $\mu\text{m}$  absorption*  
 400 *features of salammoniac sample for different incident and emergence angles. Note the different*  
 401 *scales of the y axis.*



402

403 *Fig. 12: Band depth of the 1.09 (a), 1.32 (b), 1.62 (c), 2.06 (d), 2.2 (e) and 3.05 (f)  $\mu\text{m}$  absorption*  
 404 *features of salammoniac sample for different incident and emergence angles geometry. Note the*  
 405 *different scale of the y axis.*



406

407 *Fig.13: Band FWHM of the 1.09 (a), 1.32 (b), 1.62 (c), 2.06 (d), 2.2 (e) and 3.05 (f)  $\mu\text{m}$  absorption*  
 408 *features of salammoniac sample for different incident angle and emergence angles. Note the different*  
 409 *scales of the y axis.*

410 3.3 Spectral slope vs geometry

411 For the quantitative determination of the slope parameter, the methodology reported in Fornasier  
412 et al. (2015) was followed. The spectral slope can be computed as the ratio of two reflectance values  
413 given at two different wavelengths (Schröder et al., 2014). For each collected spectrum, three slopes  
414 were determined, taking into account the reflectance values located at 1.15 - 1.4  $\mu\text{m}$ , 1.4 - 1.76  $\mu\text{m}$   
415 and 1.76 - 2.46  $\mu\text{m}$ ; these three regions were chosen as no absorption feature occurs within them.  
416 The value of the normalized spectral slope is calculated as the ratio between the reflectance values  
417 at 1.4  $\mu\text{m}$  (1) and at 1.15  $\mu\text{m}$  (2) here reported as an example. The same operation was made for  
418 the other two slopes:

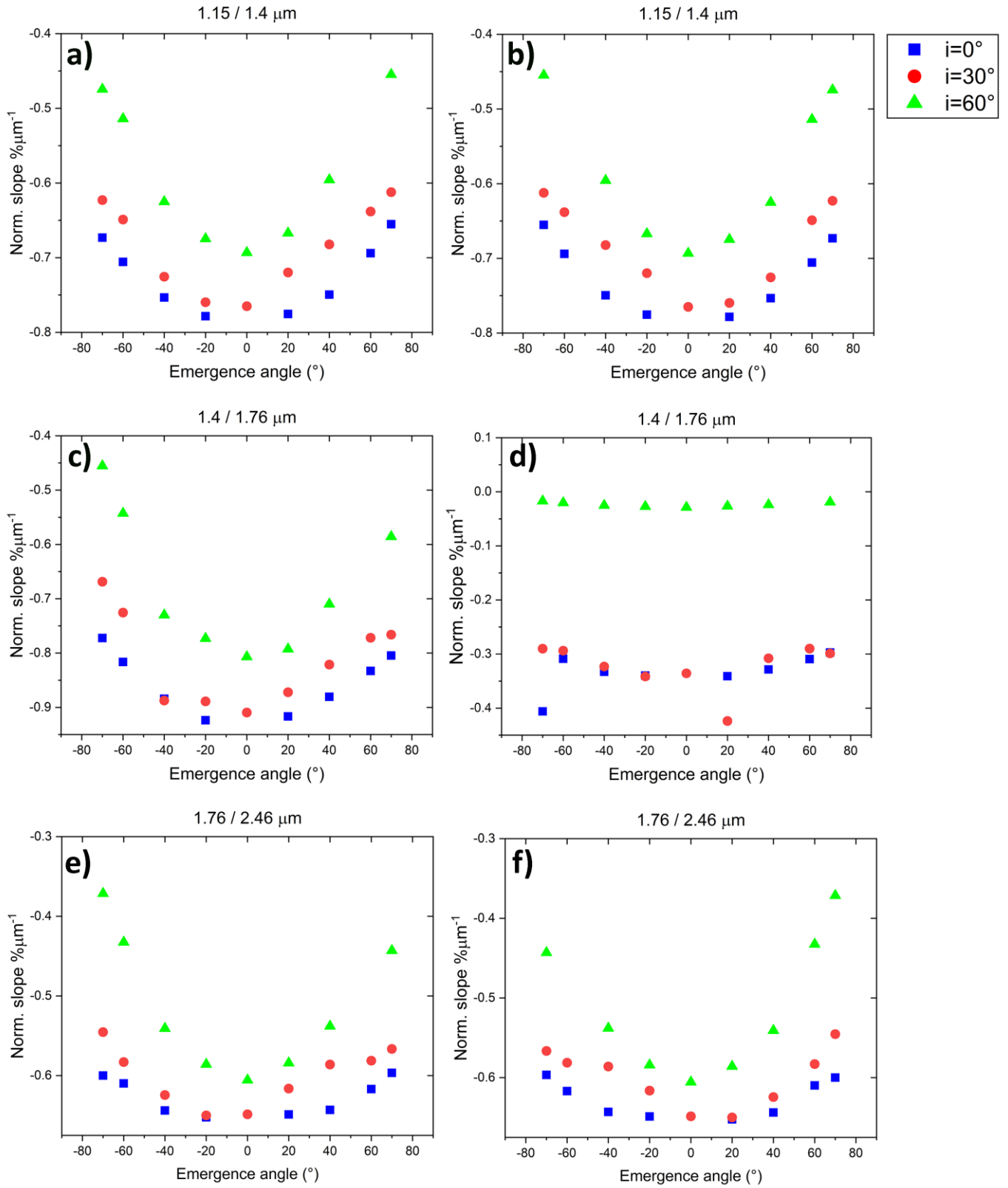
419 
$$\text{norm. slope } (\% \mu\text{m}^{-1}) = 2 * \frac{(R1-R2)}{[(R1+R2)*(\lambda1-\lambda2)]}$$

420 where  $R$  and  $\lambda$  indicate the values of reflectance and wavelength ( $\mu\text{m}$ ), respectively.

421 The variation of the spectral slope and the emergence angles is reported in Figure 14 for both  
422 salammoniac and mascagnite. The reflectance spectra of salammoniac (Figure 14a) have a similar  
423 negative slope (blueing) to those of mascagnite (Figure 14b). At low emergence angle, mascagnite  
424 spectra have slope value of  $-0.53 \% \mu\text{m}^{-1}$ , whereas salammoniac displays slope value of  $-0.77 \% \mu\text{m}^{-1}$ .  
425 At incidence ( $i = 0$ ) and emerges ( $e = \pm 70^\circ$ ) angles, the slope of mascagnite sample reaches the  
426 mean value of  $-0.30 \% \mu\text{m}^{-1}$  compared to  $-0.45 \% \mu\text{m}^{-1}$  for the salammoniac spectra. Generally, the  
427 blueing effect is linear with increasing angles of incidence and emergence. The spectral slope is  
428 strongly affected by the surface particle density and texture (Binzel et al., 2015) as well as by the  
429 different grain size distribution and chemical composition (De Angelis et al., 2014; Pisello et al.,  
430 2022a, 2022b). Regarding the variation of the slope with different grain sizes, we expect a change  
431 from positive (red) to negative (blue) values as the grain size increases.

## Mascagnite

## Salammoniac



432

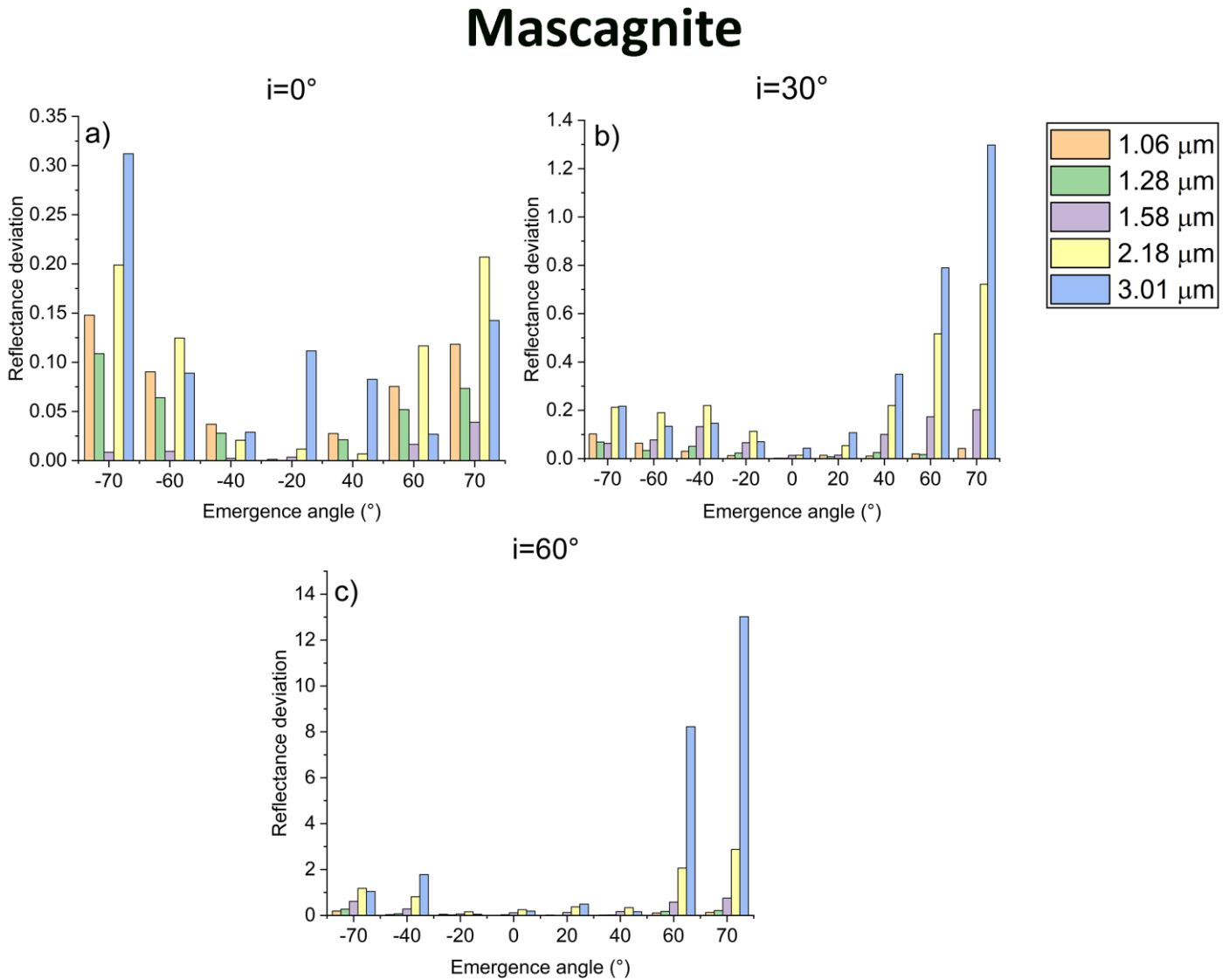
433 Fig.14: Effect of the geometry variation on the spectral slope of the reflectance spectra of mascagnite  
 434 (left column a-c-e) and salammoniac samples (right column b-d-f).



435 **4. Discussions**

436 **4.1 Quantification of viewing geometry variations**

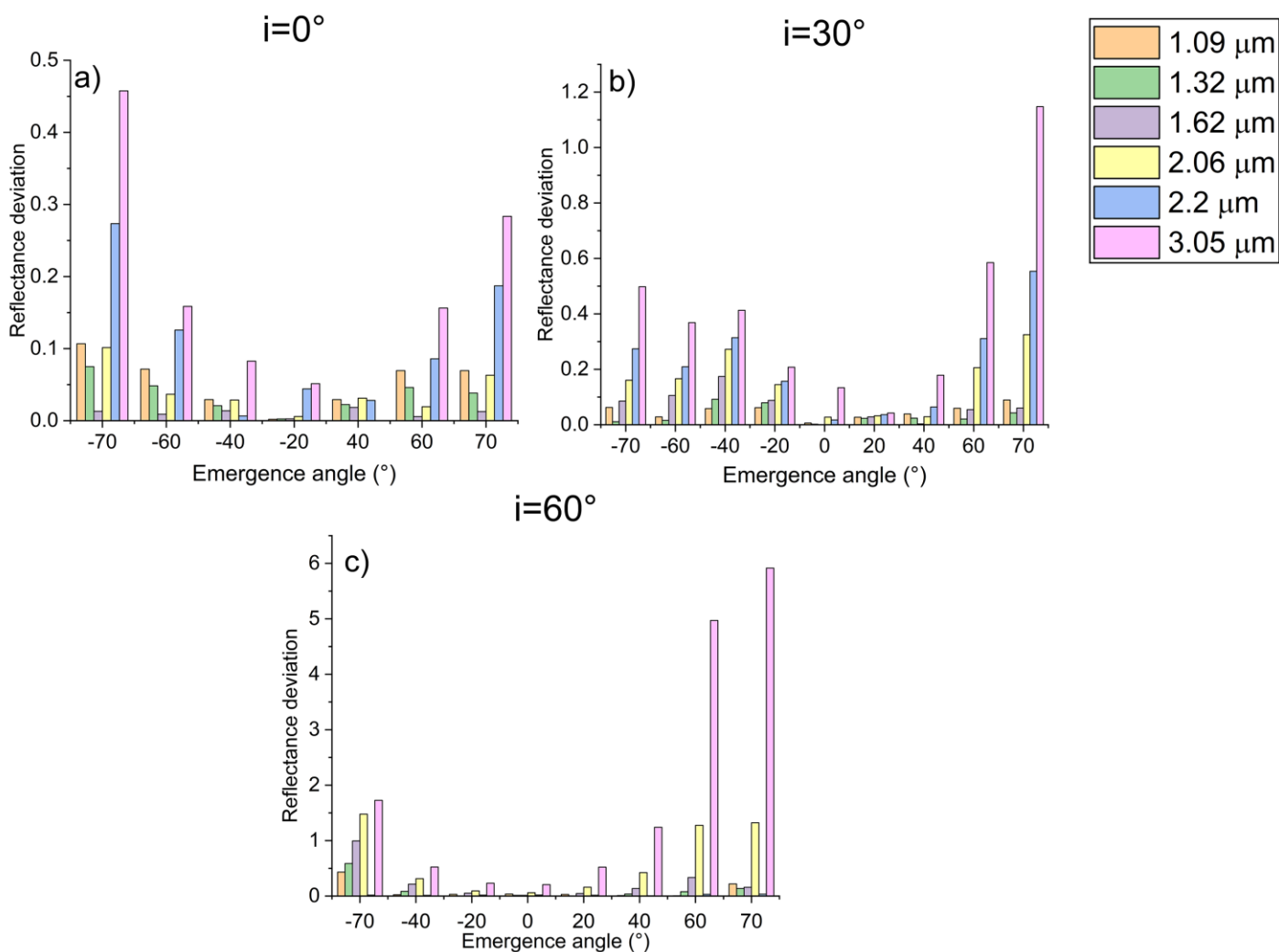
437 To numerically quantify the effect of the emergence angle variations on the measured reflectance  
438 spectra, we calculated the difference between reflectance with  $e = 20^\circ$  with respect to the other  
439 values of  $e$ . For the selected bands analysed in the previous sections, the absolute value of  $(R_e -$   
440  $R_{e=20})$  was divided by  $R_{e=20}$  to express the ratio of deviation with respect to the reference geometry  
441 observation ( $i=0^\circ$  and  $e=20^\circ$ ). Each deviation value for mascagnite e salammoniac samples is plotted  
442 in Figures 15 and 16, respectively, for  $i= 0^\circ; 30^\circ; 60^\circ$ .



443

444 Fig. 15: Histogram reports the deviation ratio relative to the spectrum collected with reference  
445 geometry ( $i=0^\circ$  and  $e=20^\circ$ ), for incidence angles equal to  $0^\circ$  (a);  $30^\circ$  (b) and  $60^\circ$  (c) and emergence  
446 angles in the  $\pm 70^\circ$  range for the mascagnite sample. Note the different scales.

# Salammoniac



447

448 Fig.16: Histogram reports the deviation ratio from relative to the spectrum collected with reference  
 449 geometry ( $i=0^\circ$  and  $e=20^\circ$ ), for incidence angles equal to  $0^\circ$  (a);  $30^\circ$  (b) and  $60^\circ$  (c) and emergence  
 450 angles in the  $\pm 70^\circ$  range for the salammoniac sample. Note the different scales.

451 In general, the relative change in reflectance values is already evident for small emergence angle  
 452 variations ( $e = \pm 20^\circ$ ). For  $e \geq 40^\circ$ , the spectral variation becomes significant and much more  
 453 appreciable as shown in Figures 6 and 7. At geometric configurations with  $i = 60^\circ$  and  $e \geq 40^\circ$  we can  
 454 notice that the reflectance spectra of the inclined geometries tend to diverge from the one  
 455 measured in nadir geometry.

456 Mascagnite sample displays a moderate monotonic increase of reflectance values, when varying the  
 457 emergence angles for the  $\text{NH}_4^+$  bands located at 1.06 and 1.28  $\mu\text{m}$  with the highest values for  $e = -$   
 458  $70^\circ$ . The bands at 2.18 and 3.01  $\mu\text{m}$  display an abrupt change when  $e \geq 60^\circ$ . These behaviours are  
 459 the same for different incidence angles but much more marked for configurations with  $i = 60^\circ$ . In  
 460 fact, the 1.06 and 1.28  $\mu\text{m}$  features with  $i=60^\circ$  more drastically change their reflectance values  
 461 (Figure 15). Salammoniac bands at 1.09 and 1.32  $\mu\text{m}$  increase reflectance values reaching the  
 462 highest ones for  $e \geq 60^\circ$  and  $i = 60^\circ$ , whereas for  $i = 30^\circ$  these two features do not show severe

463 changes (Figure 16). Regarding the bands above 2  $\mu\text{m}$ , they are the most sensitive to variations in  
464 viewing geometries with a strong increase for  $e \geq 40^\circ$ , especially also for  $i = 60^\circ$  (Figure 16).

465 The histograms in Figures 15 and 16 also show which geometric configurations and bands have the  
466 greatest variability. It is evident that the bands located at 1.58 and 1.62  $\mu\text{m}$ , attributed to  $2\nu_3 \text{NH}_4^+$   
467 vibrational modes, are the less sensitive to changes in geometry. Furthermore, when increasing the  
468 incidence angle, the deviation drastically increases (Figure 15 and 16 c). The change in observation  
469 geometry affects all the selected features, in particular the bands located at 2.18 ( $\nu_3 + \nu_4$ ) and 3.01  
470 ( $\nu_3$ )  $\mu\text{m}$  for mascagnite and 2.06 ( $\nu_2 + \nu_3$ ), 2.2 ( $\nu_3 + \nu_4$ ) and 3.05 ( $\nu_3$ )  $\mu\text{m}$  for salammoniac. Finally, high  
471 incidence and negative emergence angles (forward scattering quadrant) have the highest  
472 reflectance deviation compared to positive equivalents (backward scattering quadrant) due to the  
473 shallow penetration depth of the light in the forward grazing geometries. The highest deviation is  
474 confirmed for incidence angles  $\geq 30^\circ$  and emergence angles  $\geq 60^\circ$ .

475 The results obtained in this work show that observation geometry can have a strong impact on band  
476 parameters, such as depth and area, in both ammonium-bearing minerals, in terms of shape of  $\text{NH}_4^+$   
477 absorption features. Incidence and emergence angles changes affect absorption bands and spectral  
478 slope. The different geometry configurations variously affect the continuum and absorption bands,  
479 especially for high incidence and emergence angles.

480 Although in literature (Beck et al., 2012, 2011) the variation in observation geometry is followed by  
481 a decrease in depth at larger phase angles, we notice a different trend related to the variations in  
482 both emergence and incidence angles. Considering angles of incidence close to nadir ( $0^\circ$  and  $30^\circ$ ), a  
483 twofold trend can be observed as the angle of emergence changes. An initial increase in area and  
484 depth values for small emergence angles up to about  $20^\circ$  and then its gradual decreases, especially  
485 for bands located above 2  $\mu\text{m}$ . On the other hand, for  $i = 60^\circ$ , we notice that for bands located at  
486  $\sim 1.05$ ,  $\sim 1.3$ ,  $\sim 1.56$   $\mu\text{m}$ , depth and area generally decrease while the features at  $\sim 2.02$ ,  $\sim 2.2$  and  $\sim 3.0$   
487  $\mu\text{m}$  have an opposite trend. This difference in behaviour between weak-medium bands and strong-  
488 to-nearly saturated bands is linked to the fact that at high incidence and phase angles the light  
489 penetrates to a shallower depth than for near normal incidence and consequently escapes with less  
490 absorption (smaller path through the medium). For the weak-medium bands it will thus increase  
491 their reflectance at band centre but to a smaller extent the continuum wavelengths around the band  
492 which are already weakly absorbing and have high reflectance. This effect reduces the depth and  
493 area of these bands with increasing phase angle. For strong-to-nearly saturated bands the reverse  
494 occurs. The continuum wavelengths around the band, which have medium reflectance levels, will  
495 significantly decrease their absorption and increase their reflectance, while the almost saturated  
496 band centres see only a moderate increase of their reflectance. Consequently, the band contrast  
497 ('relative' band depth and area) strongly increases when approaching grazing geometries. This  
498 interpretation is thus linked both to the non-linear radiative transfer in particulate media and to the  
499 way the individual band depth and area are defined, i.e. relative to their nearby reflectance maxima,  
500 called 'continuum', which have the tendency to have lower reflectance for strong bands than for  
501 weaker ones.

502 Finally, to summarise the behaviour of the band area and depth parameters, we calculated the  
503 relative percentage change from the reference observation configuration  $i=0^\circ$  and  $e=20^\circ$ . In order  
504 to provide a semi-quantitative relative percentage variation, we used the following normalisation:

505  $[(\Delta_e - \Delta_{emin}) / (\Delta_{emax} - \Delta_{emin})] * 100$

506 where,

- 507 -  $\Delta_e = X_0 - X_e$ , meaning  $X_0$  the value of band parameters, either area or depth, at reference  
508 observation configuration ( $i=0^\circ$  and  $e=20^\circ$ ) and  $X_e$  the value of band parameters at each  
509 emergence angle in the  $\pm 70^\circ$  range.  
510 -  $\Delta_{emax}$ , meaning the maximum values of  $\Delta_e$  in the studied dataset.  
511 -  $\Delta_{emin}$ , meaning the minimum values of  $\Delta_e$  in the studied dataset.

512 This calculation was made for each absorption band analysed in this work. The results obtained  
513 show that the relative percentage change in area and depth, considering the angle of incidence  $i=0$ ,  
514 varies from  $\sim 10\%$  ( $e=-20^\circ$ ) to  $\sim 37\%$  ( $e=\pm 70^\circ$ ). Variations are significant at angles of incidence equal  
515 to  $60^\circ$  and emergence  $\pm 70^\circ$  with an average variation of  $\sim 70\%$ . Both mascagnite and salammoniac  
516 samples display single values of band area and depth percentage change of  $\sim 90\%$  for  $i=0^\circ$  and  $e=-$   
517  $70^\circ$ . The main difference between the two samples, in terms of relative percentage change, was  
518 found for the  $i=0^\circ$  configuration. In the mascagnite samples the percent variation is greater (from  
519  $\sim 20\%$  at  $e=-20$  to  $\sim 55\%$  at  $e=70^\circ$ ) than salammoniac (from  $\sim 5\%$  at  $e=-20$  to  $\sim 20\%$  at  $e=0^\circ$ ).

520 Our results indicate that variations of incidence and emergence angles generate changes in band  
521 parameters and reflectance values with a band strength change non directly related to the  
522 abundance of the presumed mineralogical phase. This supports the relevance of measuring the  
523 BRDF of minerals and BRDF surfaces over wide wavelength ranges, both in the laboratory and for  
524 the surfaces of Solar System objects.

#### 525 4.2 Implications for icy bodies

526 The surface absorption feature of Ceres at  $2.21 \mu\text{m}$ , in the remotely collected reflectance spectra,  
527 has been attributed to the presence of  $\text{NH}_4^+$ , in good agreement with absorption characteristics of  
528 the  $\text{NH}_4\text{Cl}$  mineral (De Sanctis et al., 2016). As reported in the present work, the  $2.21 \mu\text{m}$  spectral  
529 feature has a great variability in terms of depth and area under different viewing configurations,  
530 thus implying that the band parameters variations in the Ceres's spectra may be due to different  
531 observation geometries during the mapping of the surface by the *Dawn* mission (Russell and  
532 Raymond, 2012) and not only in relation to the abundance of the  $\text{NH}_4\text{Cl}$  mineral. In analogy to the  
533 previous spectral features, the band at  $\sim 3.05 \mu\text{m}$  for the salammoniac sample is also relevant,  
534 relatively to its variations, for the detection of  $\text{NH}_4^+$ . In fact, the shape of the  $3.05 \mu\text{m}$  band varies  
535 under different viewing configurations, becoming more defined at high incidence angles compared  
536 to other studies on ammonium minerals that describe the  $3.05 \mu\text{m}$  feature as a broad water-  
537 saturated band (e.g. Ehlmann et al., 2018; Ferrari et al., 2019).

538 Ammonium sulphate exhibits absorption characteristics located in the  $3.0 - 3.3 \mu\text{m}$  spectral range,  
539 consistent with the spectra of comet 67P as mapped by the Visible and InfraRed Thermal Imaging  
540 Spectrometer, Mapping Channel (VIRTIS-M) instrument (Coradini et al., 2007). Poch et al. (2020)  
541 propose the presence of ammonium salts (possibly including ammonium sulfate), mixed with  
542 opaques, based on the well defined absorption bands at  $3.1$  and  $3.3 \mu\text{m}$ . From the data we report in  
543 the mascagnite sample, this specific spectral feature, has a great variability especially for high  
544 incidence and emergence angles which may affect its correct identification and quantification from  
545 remote observations.

546 In the *Virgil Fossae* area, on Pluto, two possible ammonia bands at  $\sim 1.65$  and  $2.21 \mu\text{m}$  were  
547 identified (Dalle Ore et al., 2019) by the Linear Etalon Imaging Spectral Array (LEISA) onboard the  
548 *New Horizons* mission (Schmitt et al., 2017). The  $1.65$  and  $2.21 \mu\text{m}$  bands have been unambiguously  
549 attributed, similarly to the findings for Ceres, to the possible presence of ammonium minerals such  
550 as  $\text{NH}_4\text{Cl}$  related to recent cryovolcanism activity (Cruikshank et al., 2019). Furthermore, the surface  
551 of Charon, the largest Pluto's moon, shows the same absorption characteristics at  $2.21 \mu\text{m}$ ,  
552 attributed to hypothetical different ammonium minerals, in a non-univocal way given the similarity  
553 of the  $2.21 \mu\text{m}$  band with that of ice. (Cook et al., 2018, 2007). The spectra here reported shown a  
554 great variability of the  $2.21 \mu\text{m}$  features, related to the different viewing geometries especially at  
555 high emergence angle. The data collected in this work can help to understand if the  $\text{NH}_3$  spectral  
556 feature on these bodies is either related to ammoniated salts, in this case salammoniac or  
557 mascagnite, or to other possible forms such as ice or other compounds. Recently, some features in  
558 the Charon's spectrum at  $1.60$  and  $1.63 \mu\text{m}$  were discovered for the first time, consistent with  $\text{NH}_4\text{Cl}$   
559 absorption bands. Our data might provide information on its abundance on this moon (Cook et al.,  
560 2023). Finally, the data presented in this paper can be usefull to interpret the spectra from the Near-  
561 Infrared Spectrograph (NIRSpec) (Rauscher et al., 2007) on board the James Webb Space Telescope  
562 (JWST) of Trans Neptunian Object (TNO).

## 563 5. Conclusions

564 This study reported a systematic investigation of reflectance spectra in the near and visible infrared  
565 ( $1\text{-}4.2 \mu\text{m}$ ) varying the observation geometries of two natural analogues ammonium bearing  
566 minerals, mascagnite [ $(\text{NH}_4)_2\text{SO}_4$ ] and salammoniac ( $\text{NH}_4\text{Cl}$ ), with  $32\text{-}80 \mu\text{m}$  powder granulometry  
567 and at room temperature. These data are of potentially great interest for the detection of nitrogen  
568 and ammonium compounds on the surface of icy objects. We analysed the effects of incidence and  
569 emergence angles, with a series of three different angles of incidence ( $i = 0^\circ, 30^\circ$  and  $60^\circ$ ) and nine  
570 emergence angles in the range  $e = \pm 70^\circ$ , on the spectral characteristics of  $\text{NH}_4^+$  absorption features  
571 in order to provide laboratory data in relevant conditions to identify and quantify these minerals by  
572 remote sensing analysis.

573 We have shown that the collected reflectance spectra are affected by the change in observation  
574 geometries. We notice that divergence from nadir-like measurements becomes significant for  $e \geq 40^\circ$ .  
575 Characteristic  $\text{NH}_4^+$  features are located at  $\sim 1.06, 1.3, 1.56, 2.02, 2.2$  and  $3.0 \mu\text{m}$ . Depth and  
576 area parameters of these features display a dual behaviour: (i) for absorption bands located below  
577  $2 \mu\text{m}$  and for incidence angles close to the azimuth and low emergence angles, the parameter values  
578 tend to increase, conversely, for high emergence angles, the values tend to decrease; (ii) spectral  
579 features above  $2 \mu\text{m}$  generally increase with different trends depending on the angle of incidence.  
580 The greatest increase occurs for  $i = 60^\circ$ . Reflectance values generally increase with increasing angle  
581 of incidence and angle of emission with maximum values for  $i = 60^\circ$  and  $e = \pm 70^\circ$  i.e. high phase  
582 angles and very low phase angles (opposition effect). However, bands below two microns reduce  
583 reflectance values increasing phase angles (g) especially for incidence angles equal to  $0^\circ$  and  $30^\circ$ .

584 The spectral features at  $\sim 3.0 \mu\text{m}$  show the clearest variation in shape resulting in its desaturation  
585 and corresponding better definition as geometry changes, important for remote sensing  
586 identification of  $\text{NH}_4^+$  features.

587 Our results can have a direct application for different objects inside the Solar System, especially  
588 small icy bodies. On these bodies, large surface slopes and surfaces characterised by rough  
589 topography are observed. The high emergence and incidence angles encountered during a probe  
590 fly-by can produce a misinterpretation when using laboratory spectra measured with nadir viewing  
591 geometries.

592 The use of laboratory data are needed to correctly deconvolve remote sensing hyperspectral data  
593 of planetary surfaces. The analysis of the surfaces of icy bodies for traces of  $\text{NH}_4^+$  by current and  
594 future missions will provide important knowledge about the abundance of nitrogen on these bodies,  
595 their environment and their potential for the evolution of life. The laboratory spectra reported here  
596 add information on the band dependance on viewing geometries of two selected ammonium  
597 bearing minerals and should aid the remote data interpretation from *New Horizons*/LEISA and  
598 *Dawn*/VIR spectrometers.

### 599 **Acknowledgments**

600 This work has been done in the frame of the Trans-National Access program, project number 20-  
601 EPN2-081, of Europlanet 2024 RI which has received funding from the European Union's Horizon  
602 2020 research and innovation program under grant agreement No 871149. We would like to thank  
603 the two anonymous reviewers for their suggestions and comments that greatly improved the  
604 manuscript.

### 605 **On-line data**

606 The complete sets of data (Fastelli et al. 2021b) presented in this paper are available online in the  
607 CSS database of the SSHADE database infrastructure (<https://vwww.sshade.eu>) [doi:  
608 10.26302/SSHADE/EXPERIMENT\_BS\_20231304\_001]

609

610 **References**

- 611 Beck, P., Barrat, J.-A., Grisolles, F., Quirico, E., Schmitt, B., Moynier, F., Gillet, P., Beck, C., 2011. NIR spectral  
612 trends of HED meteorites: Can we discriminate between the magmatic evolution, mechanical  
613 mixing and observation geometry effects? *Icarus* 216, 560–571.  
614 <https://doi.org/10.1016/j.icarus.2011.09.015>
- 615 Beck, P., Pommerol, A., Thomas, N., Schmitt, B., Moynier, F., Barrat, J.-A., 2012. Photometry of meteorites.  
616 *Icarus* 218, 364–377. <https://doi.org/10.1016/j.icarus.2011.12.005>
- 617 Berg, B.L., Cloutis, E.A., Beck, P., Vernazza, P., Bishop, J.L., Takir, D., Reddy, V., Applin, D., Mann, P., 2016.  
618 Reflectance spectroscopy (0.35–8 $\mu$ m) of ammonium-bearing minerals and qualitative comparison  
619 to Ceres-like asteroids. *Icarus* 265, 218–237. <https://doi.org/10.1016/j.icarus.2015.10.028>
- 620 Binzel, R.P., DeMeo, F.E., Burt, B.J., Cloutis, E.A., Rozitis, B., Burbine, T.H., Campins, H., Clark, B.E., Emery,  
621 J.P., Hergenrother, C.W., Howell, E.S., Lauretta, D.S., Nolan, M.C., Mansfield, M., Pietrasz, V.,  
622 Polishook, D., Scheeres, D.J., 2015. Spectral slope variations for OSIRIS-REx target Asteroid (101955)  
623 Bennu: Possible evidence for a fine-grained regolith equatorial ridge. *Icarus* 256, 22–29.  
624 <https://doi.org/10.1016/j.icarus.2015.04.011>
- 625 Bishop, J.L., Bell III, J.F., Bell, J., Moersch, J.E., 2019. Remote Compositional Analysis: Techniques for  
626 Understanding Spectroscopy, Mineralogy, and Geochemistry of Planetary Surfaces. Cambridge  
627 University Press.
- 628 Bonnefoy, N., 2001. Développement d'un spectrophoto-goniomètre pour l'étude de la réflectance  
629 bidirectionnelle de surfaces géophysiques: application au soufre et perspectives pour le satellite Io.  
630 Grenoble 1.
- 631 Brissaud, O., Schmitt, B., Bonnefoy, N., Doute, S., Rabou, P., Grundy, W., Fily, M., 2004. Spectrogonio  
632 radiometer for the study of the bidirectional reflectance and polarization functions of planetary  
633 surfaces. 1. Design and tests. *Applied optics* 43, 1926–1937.
- 634 Ciarniello, M., De Angelis, S., Carli, C., De Sanctis, M.C., 2017. Photometric properties of Occator's bright  
635 spots analogue materials, in: European Planetary Science Congress. pp. EPSC2017-766.
- 636 Clark, B.E., Helfenstein, P., Bell, J.F., Peterson, C., Veverka, J., Izenberg, N.I., Domingue, D., Wellnitz, D.,  
637 McFadden, L., 2002. NEAR Infrared Spectrometer Photometry of Asteroid 433 Eros. *Icarus* 155,  
638 189–204. <https://doi.org/10.1006/icar.2001.6748>
- 639 Clark, R.N., Roush, T.L., 1984. Reflectance spectroscopy: Quantitative analysis techniques for remote  
640 sensing applications. *Journal of Geophysical Research: Solid Earth* 89, 6329–6340.
- 641 Comodi, P., Fastelli, M., Maturilli, A., Balic-Zunic, T., Zucchini, A., 2021. Emissivity and reflectance spectra at  
642 different temperatures of hydrated and anhydrous sulphates: A contribution to investigate the  
643 composition and dynamic of icy planetary bodies. *Icarus* 355, 114132.
- 644 Comodi, P., Mellini, M., Zanazzi, P.F., 1990. Scapolites; variation of structure with pressure and possible role  
645 in the storage of fluids. *European Journal of Mineralogy* 2, 195–202.
- 646 Comodi, P., Stagno, V., Zucchini, A., Fei, Y., Prakapenka, V., 2017. The compression behavior of blödite at  
647 low and high temperature up to ~ 10 GPa: Implications for the stability of hydrous sulfates on icy  
648 planetary bodies. *Icarus* 285, 137–144.
- 649 Cook, J.C., Dalle Ore, C.M., Protopapa, S., Binzel, R.P., Cartwright, R., Cruikshank, D.P., Earle, A., Grundy,  
650 W.M., Ennico, K., Howett, C., 2018. Composition of Pluto's small satellites: Analysis of New  
651 Horizons spectral images. *Icarus* 315, 30–45.
- 652 Cook, J.C., Desch, S.J., Roush, T.L., Trujillo, C.A., Geballe, T.R., 2007. Near-Infrared Spectroscopy of Charon:  
653 Possible Evidence for Cryovolcanism on Kuiper Belt Objects. *ApJ* 663, 1406–1419.  
654 <https://doi.org/10.1086/518222>
- 655 Cook, J.C., Protopapa, S., Dalle Ore, C.M., Cruikshank, D.P., Grundy, W.M., Lisse, C.M., Schmitt, B.,  
656 Verbiscer, A., Singer, K.N., Spencer, J., Stern, S.A., Weaver, H.A., 2023. Analysis of Charon's  
657 spectrum at 2.21- $\mu$ m from New Horizons/LEISA and Earth-based observations. *Icarus* 389, 115242.  
658 <https://doi.org/10.1016/j.icarus.2022.115242>
- 659 Coradini, A., Capaccioni, F., Drossart, P., Arnold, G., Ammannito, E., Angrilli, F., Barucci, A., Bellucci, G.,  
660 Benkhoff, J., Bianchini, G., Bibring, J.P., Blecka, M., Bockelee-Morvan, D., Capria, M.T., Carlson, R.,  
661 Carsenty, U., Cerroni, P., Colangeli, L., Combes, M., Combi, M., Crovisier, J., Desanctis, M.C.,

662 Encrenaz, E.T., Erard, S., Federico, C., Filacchione, G., Fink, U., Fonti, S., Formisano, V., Ip, W.H.,  
663 Jaumann, R., Kuehrt, E., Langevin, Y., Magni, G., Mccord, T., Mennella, V., Mottola, S., Neukum, G.,  
664 Palumbo, P., Piccioni, G., Rauer, H., Saggin, B., Schmitt, B., Tiphene, D., Tozzi, G., 2007. Virtis: An  
665 Imaging Spectrometer for the Rosetta Mission. *Space Sci Rev* 128, 529–559.  
666 <https://doi.org/10.1007/s11214-006-9127-5>

667 Cord, A.M., Pinet, P.C., Daydou, Y., Chevrel, S.D., 2003. Planetary regolith surface analogs:: optimized  
668 determination of Hapke parameters using multi-angular spectro-imaging laboratory data. *Icarus*  
669 165, 414–427.

670 Cruikshank, D.P., Grundy, W.M., DeMeo, F.E., Buie, M.W., Binzel, R.P., Jennings, D.E., Olkin, C.B., Parker,  
671 J.W., Reuter, D.C., Spencer, J.R., Stern, S.A., Young, L.A., Weaver, H.A., 2015. The surface  
672 compositions of Pluto and Charon. *Icarus, Special Issue: The Pluto System* 246, 82–92.  
673 <https://doi.org/10.1016/j.icarus.2014.05.023>

674 Cruikshank, D.P., Umurhan, O.M., Beyer, R.A., Schmitt, B., Keane, J.T., Runyon, K.D., Atri, D., White, O.L.,  
675 Matsuyama, I., Moore, J.M., McKinnon, W.B., Sandford, S.A., Singer, K.N., Grundy, W.M., Dalle Ore,  
676 C.M., Cook, J.C., Bertrand, T., Stern, S.A., Olkin, C.B., Weaver, H.A., Young, L.A., Spencer, J.R., Lisse,  
677 C.M., Binzel, R.P., Earle, A.M., Robbins, S.J., Gladstone, G.R., Cartwright, R.J., Ennico, K., 2019.  
678 Recent cryovolcanism in Virgil Fossae on Pluto. *Icarus* 330, 155–168.  
679 <https://doi.org/10.1016/j.icarus.2019.04.023>

680 Dalle Ore, C.M., Cruikshank, D.P., Protopapa, S., Scipioni, F., McKinnon, W.B., Cook, J.C., Grundy, W.M.,  
681 Schmitt, B., Stern, S.A., Moore, J.M., 2019. Detection of ammonia on Pluto’s surface in a region of  
682 geologically recent tectonism. *Science advances* 5, eaav5731.

683 De Angelis, S., Carli, C., Tosi, F., Beck, P., Brissaud, O., Schmitt, B., Potin, S., De Sanctis, M.C., Capaccioni, F.,  
684 Piccioni, G., 2019. NIR reflectance spectroscopy of hydrated and anhydrous sodium carbonates at  
685 different temperatures. *Icarus* 317, 388–411. <https://doi.org/10.1016/j.icarus.2018.08.012>

686 De Angelis, S., De Sanctis, M.C., Ammannito, E., Carli, C., Di Iorio, T., Altieri, F., 2014. The Ma\_Miss  
687 instrument performance, I: Analysis of rocks powders by Martian VNIR spectrometer. *Planetary and*  
688 *Space Science* 101, 89–107. <https://doi.org/10.1016/j.pss.2014.06.010>

689 De Angelis, S., Ferrari, M., De Sanctis, M.C., Ammannito, E., Raponi, A., Ciarniello, M., 2021a. High-  
690 Temperature VIS-IR Spectroscopy of NH<sub>4</sub>-Phyllosilicates. *Journal of Geophysical Research: Planets*  
691 126, e2020JE006696.

692 De Angelis, S., Tosi, F., Carli, C., Potin, S., Beck, P., Brissaud, O., Schmitt, B., Piccioni, G., De Sanctis, M.C.,  
693 Capaccioni, F., 2021b. Temperature-dependent, VIS-NIR reflectance spectroscopy of sodium  
694 sulfates. *Icarus* 357, 114165.

695 De Sanctis, M.C., Raponi, A., Ammannito, E., Ciarniello, M., Toplis, M.J., McSween, H.Y., Castillo-Rogez, J.C.,  
696 Ehlmann, B.L., Carrozzo, F.G., Marchi, S., Tosi, F., Zambon, F., Capaccioni, F., Capria, M.T., Fonte, S.,  
697 Formisano, M., Frigeri, A., Giardino, M., Longobardo, A., Magni, G., Palomba, E., McFadden, L.A.,  
698 Pieters, C.M., Jaumann, R., Schenk, P., Mugnuolo, R., Raymond, C.A., Russell, C.T., 2016. Bright  
699 carbonate deposits as evidence of aqueous alteration on (1) Ceres. *Nature* 536, 54–57.  
700 <https://doi.org/10.1038/nature18290>

701 De Sanctis, M.C., Mitri, G., Castillo-Rogez, J., House, C.H., Marchi, S., Raymond, C.A., Sekine, Y., 2020. Relict  
702 Ocean Worlds: Ceres. *Space Sci Rev* 216, 60. <https://doi.org/10.1007/s11214-020-00683-w>

703 Ehlmann, B.L., Hodyss, R., Bristow, T.F., Rossman, G.R., Ammannito, E., De Sanctis, M.C., Raymond, C.A.,  
704 2018. Ambient and cold-temperature infrared spectra and XRD patterns of ammoniated  
705 phyllosilicates and carbonaceous chondrite meteorites relevant to Ceres and other solar system  
706 bodies. *Meteoritics & Planetary Science* 53, 1884–1901. <https://doi.org/10.1111/maps.13103>

707 Fastelli, M., Comodi, P., Maturilli, A., Zucchini, A., 2020. Reflectance Spectroscopy of Ammonium Salts:  
708 Implications for Planetary Surface Composition. *Minerals* 10, 902.  
709 <https://doi.org/10.3390/min10100902>

710 Fastelli, M., Comodi, P., Schmitt, B., Beck, P., Poch, O., Sassi, P., Zucchini, A., 2022. Reflectance spectra (1–5  
711  $\mu\text{m}$ ) at low temperatures and different grain sizes of ammonium-bearing minerals relevant for icy  
712 bodies. *Icarus* 115055.



713 Fastelli, M., Zucchini, A., Comodi, P., Maturilli, A., Alemanno, G., Palomba, E., Piergallini, R., 2021. NIR-MID  
714 Reflectance and Emissivity Study at Different Temperatures of Sodium Carbonate Minerals: Spectra  
715 Characterization and Implication for Remote Sensing Identification. *Minerals* 11, 845.

716 Fastelli, M., Schmitt, B., Beck, P., Poch, O., Comodi, P., 2021b. Near-infrared BRDF spectra in the principal  
717 plane of Salammoniac and Mascagnite 32–80µm grain size powders at 300K. SSHADE/CSS (OSUG  
718 Data Center). Dataset/Spectral Data. [doi: 10.26302/SSHADE/EXPERIMENT\\_BS\\_20231304\\_001](https://doi.org/10.26302/SSHADE/EXPERIMENT_BS_20231304_001)

719 Ferrari, M., De Angelis, S., De Sanctis, M.C., Ammannito, E., Stefani, S., Piccioni, G., 2019. Reflectance  
720 spectroscopy of ammonium-bearing phyllosilicates. *Icarus* 321, 522–530.  
721 <https://doi.org/10.1016/j.icarus.2018.11.031>

722 Fornasier, S., Hasselmann, P.H., Barucci, M.A., Feller, C., Besse, S., Leyrat, C., Lara, L., Gutierrez, P.J., O'Klay,  
723 N., Tubiana, C., Scholten, F., Sierks, H., Barbieri, C., Lamy, P.L., Rodrigo, R., Koschny, D., Rickman, H.,  
724 Keller, H.U., Agarwal, J., A'Hearn, M.F., Bertaux, J.-L., Bertini, I., Cremonese, G., Deppo, V.D.,  
725 Davidsson, B., Debei, S., Cecco, M.D., Fulle, M., Groussin, O., Güttler, C., Hviid, S.F., Ip, W., Jorda, L.,  
726 Knollenberg, J., Kovacs, G., Kramm, R., Kührt, E., Küppers, M., Forgia, F.L., Lazzarin, M., Moreno,  
727 J.J.L., Marzari, F., Matz, K.-D., Michalik, H., Moreno, F., Mottola, S., Naletto, G., Pajola, M.,  
728 Pommerol, A., Preusker, F., Shi, X., Snodgrass, C., Thomas, N., Vincent, J.-B., 2015.  
729 Spectrophotometric properties of the nucleus of comet 67P/Churyumov-Gerasimenko from the  
730 OSIRIS instrument onboard the ROSETTA spacecraft. *A&A* 583, A30. [https://doi.org/10.1051/0004-  
731 6361/201525901](https://doi.org/10.1051/0004-6361/201525901)

732 Fortes, A.D., Choukroun, M., 2010. Phase Behaviour of Ices and Hydrates. *Space Sci Rev* 153, 185–218.  
733 <https://doi.org/10.1007/s11214-010-9633-3>

734 Fortes, A.D., Grindrod, P.M., Trickett, S.K., Vočadlo, L., 2007. Ammonium sulfate on Titan: Possible origin  
735 and role in cryovolcanism. *Icarus* 188, 139–153. <https://doi.org/10.1016/j.icarus.2006.11.002>

736 Füre, E., Marty, B., 2015. Nitrogen isotope variations in the Solar System. *Nature Geoscience* 8, 515–522.

737 Gatta, G.D., Comodi, P., Zanazzi, P.F., Ballaran, T.B., 2005. Anomalous elastic behavior and high-pressure  
738 structural evolution of zeolite levynite. *American Mineralogist* 90, 645–652.

739 Guidobaldi, G., Cambi, C., Cecconi, M., Comodi, P., Deneele, D., Paris, M., Russo, G., Vitale, E., Zucchini, A.,  
740 2018. Chemo-mineralogical evolution and microstructural modifications of a lime treated  
741 pyroclastic soil. *Engineering Geology* 245, 333–343. <https://doi.org/10.1016/j.enggeo.2018.09.012>

742 Hapke, B., 2012. Theory of reflectance and emittance spectroscopy. Cambridge university press.

743 Hapke, B., 1986. Bidirectional reflectance spectroscopy: 4. The extinction coefficient and the opposition  
744 effect. *Icarus* 67, 264–280. [https://doi.org/10.1016/0019-1035\(86\)90108-9](https://doi.org/10.1016/0019-1035(86)90108-9)

745 Hapke, B., 1981. Bidirectional reflectance spectroscopy: 1. Theory. *Journal of Geophysical Research: Solid  
746 Earth* 86, 3039–3054.

747 Hasebe, K., 1981. Studies of the crystal structure of ammonium sulfate in connection with its ferroelectric  
748 phase transition. *Journal of the Physical Society of Japan* 50, 1266–1274.

749 Kargel, J.S., 1992. Ammonia-water volcanism on icy satellites: Phase relations at 1 atmosphere. *Icarus* 100,  
750 556–574. [https://doi.org/10.1016/0019-1035\(92\)90118-Q](https://doi.org/10.1016/0019-1035(92)90118-Q)

751 King, T.V., Clark, R.N., Calvin, W.M., Sherman, D.M., Brown, R.H., 1992. Evidence for ammonium-bearing  
752 minerals on Ceres. *Science* 255, 1551–1553.

753 Krohn, M.D., Altaner, S.P., 1987. Near-infrared detection of ammonium minerals. *GEOPHYSICS* 52, 924–930.  
754 <https://doi.org/10.1190/1.1442362>

755 Larson, A.C., Von Dreele, R.B., 1987. Generalized structure analysis system (GSAS). Los Alamos National  
756 Laboratory LA-UR-86-748.

757 Levy, H.A., Peterson, S.W., 1952. Neutron diffraction study of the crystal structure of ammonium chloride.  
758 *Physical Review* 86, 766.

759 Magrin, S., La Forgia, F., Pajola, M., Lazzarin, M., Massironi, M., Ferri, F., Da Deppo, V., Barbieri, C., Sierks,  
760 H., 2012. (21) Lutetia spectrophotometry from Rosetta-OSIRIS images and comparison to ground-  
761 based observations. *Planetary and Space Science, Rosetta Fly-by at Asteroid (21) Lutetia* 66, 43–53.  
762 <https://doi.org/10.1016/j.pss.2011.10.001>

763 Mustard, J.F., Glotch, T.D., 2019. Theory of Reflectance and Emittance Spectroscopy of Geologic Materials  
764 in the Visible and Infrared Regions. *Remote Compositional Analysis: Techniques for Understanding*  
765 *Spectroscopy, Mineralogy, and Geochemistry of Planetary Surfaces* 21–41.

766 Neish, C.D., Prockter, L.M., Patterson, G.W., 2012. Observational constraints on the identification and  
767 distribution of chaotic terrain on icy satellites. *Icarus* 221, 72–79.  
768 <https://doi.org/10.1016/j.icarus.2012.07.009>

769 Nelson, R.M., Buratti, B.J., Wallis, B.D., Lane, A.L., West, R.A., Simmons, K.E., Hord, C.W., Esposito, L.W.,  
770 1987. Voyager 2 Photopolarimeter observations of the Uranian satellites. *Journal of Geophysical*  
771 *Research: Space Physics* 92, 14905–14910. <https://doi.org/10.1029/JA092iA13p14905>

772 Pelkey, S.M., Mustard, J.F., Murchie, S., Clancy, R.T., Wolff, M., Smith, M., Milliken, R., Bibring, J.-P.,  
773 Gendrin, A., Poulet, F., Langevin, Y., Gondet, B., 2007. CRISM multispectral summary products:  
774 Parameterizing mineral diversity on Mars from reflectance. *Journal of Geophysical Research:*  
775 *Planets* 112. <https://doi.org/10.1029/2006JE002831>

776 Pilorget, C., Okada, T., Hamm, V., Brunetto, R., Yada, T., Loizeau, D., Riu, L., Usui, T., Moussi-Soffys, A.,  
777 Hatakeda, K., Nakato, A., Yogata, K., Abe, M., Aléon-Toppani, A., Carter, J., Chaigneau, M., Crane, B.,  
778 Gondet, B., Kumagai, K., Langevin, Y., Lantz, C., Le Pivert-Jolivet, T., Lequertier, G., Lourit, L.,  
779 Miyazaki, A., Nishimura, M., Poulet, F., Arakawa, M., Hirata, N., Kitazato, K., Nakazawa, S., Namiki,  
780 N., Saiki, T., Sugita, S., Tachibana, S., Tanaka, S., Yoshikawa, M., Tsuda, Y., Watanabe, S., Bibring, J.-  
781 P., 2022. First compositional analysis of Ryugu samples by the MicrOmega hyperspectral  
782 microscope. *Nat Astron* 6, 221–225. <https://doi.org/10.1038/s41550-021-01549-z>

783 Pisello, A., De Angelis, S., Ferrari, M., Porreca, M., Vetere, F.P., Behrens, H., De Sanctis, M.C., Perugini, D.,  
784 2022a. Visible and near-InfraRed (VNIR) reflectance of silicate glasses: Characterization of a  
785 featureless spectrum and implications for planetary geology. *Icarus* 374, 114801.  
786 <https://doi.org/10.1016/j.icarus.2021.114801>

787 Pisello, A., Ferrari, M., De Angelis, S., Vetere, F.P., Porreca, M., Stefani, S., Perugini, D., 2022b. Reflectance  
788 of silicate glasses in the mid-infrared region (MIR): Implications for planetary research. *Icarus* 388,  
789 115222.

790 Poch, O., Istiqomah, I., Quirico, E., Beck, P., Schmitt, B., Theulé, P., Faure, A., Hily-Blant, P., Bonal, L., Raponi,  
791 A., Ciarniello, M., Rousseau, B., Potin, S., Brissaud, O., Flandinet, L., Filacchione, G., Pommerol, A.,  
792 Thomas, N., Kappel, D., Mennella, V., Moroz, L., Vinogradoff, V., Arnold, G., Erard, S., Bockelée-  
793 Morvan, D., Leyrat, C., Capaccioni, F., De Sanctis, M.C., Longobardo, A., Mancarella, F., Palomba, E.,  
794 Tosi, F., 2020. Ammonium salts are a reservoir of nitrogen on a cometary nucleus and possibly on  
795 some asteroids. *Science* 367, eaaw7462. <https://doi.org/10.1126/science.aaw7462>

796 Pommerol, A., Schmitt, B., 2008a. Strength of the H<sub>2</sub>O near-infrared absorption bands in hydrated  
797 minerals: Effects of measurement geometry. *Journal of Geophysical Research: Planets* 113.  
798 <https://doi.org/10.1029/2008JE003197>

799 Pommerol, A., Schmitt, B., 2008b. Strength of the H<sub>2</sub>O near-infrared absorption bands in hydrated  
800 minerals: Effects of particle size and correlation with albedo. *Journal of Geophysical Research:*  
801 *Planets* 113.

802 Potin, S., Beck, P., Schmitt, B., Moynier, F., 2019. Some things special about NEAs: Geometric and  
803 environmental effects on the optical signatures of hydration. *Icarus* 333, 415–428.

804 Quinn, R.C., Chittenden, J.D., Kounaves, S.P., Hecht, M.H., 2011. The oxidation-reduction potential of  
805 aqueous soil solutions at the Mars Phoenix landing site. *Geophysical Research Letters* 38.  
806 <https://doi.org/10.1029/2011GL047671>

807 Rauscher, B.J., Fox, O., Ferruit, P., Hill, R.J., Waczynski, A., Wen, Y., Xia-Serafino, W., Mott, B., Alexander, D.,  
808 Brambora, C.K., 2007. Detectors for the James Webb Space Telescope Near-Infrared Spectrograph.  
809 I. Readout Mode, Noise Model, and Calibration Considerations. *Publications of the Astronomical*  
810 *Society of the Pacific* 119, 768.

811 Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *Journal of applied*  
812 *Crystallography* 2, 65–71.

- 813 Russell, C.T., Raymond, C.A., 2012. The Dawn Mission to Vesta and Ceres, in: Russell, C., Raymond, C. (Eds.),  
814 The Dawn Mission to Minor Planets 4 Vesta and 1 Ceres. Springer, New York, NY, pp. 3–23.  
815 [https://doi.org/10.1007/978-1-4614-4903-4\\_2](https://doi.org/10.1007/978-1-4614-4903-4_2)
- 816 Schmitt, B., Philippe, S., Grundy, W.M., Reuter, D.C., Côte, R., Quirico, E., Protopapa, S., Young, L.A., Binzel,  
817 R.P., Cook, J.C., Cruikshank, D.P., Dalle Ore, C.M., Earle, A.M., Ennico, K., Howett, C.J.A., Jennings,  
818 D.E., Linscott, I.R., Lunsford, A.W., Olkin, C.B., Parker, A.H., Parker, J.Wm., Singer, K.N., Spencer,  
819 J.R., Stansberry, J.A., Stern, S.A., Tsang, C.C.C., Verbiscer, A.J., Weaver, H.A., 2017. Physical state  
820 and distribution of materials at the surface of Pluto from New Horizons LEISA imaging  
821 spectrometer. *Icarus*, Special Issue: The Pluto System 287, 229–260.  
822 <https://doi.org/10.1016/j.icarus.2016.12.025>
- 823 Schröder, S.E., Grynko, Ye., Pommerol, A., Keller, H.U., Thomas, N., Roush, T.L., 2014. Laboratory  
824 observations and simulations of phase reddening. *Icarus* 239, 201–216.  
825 <https://doi.org/10.1016/j.icarus.2014.06.010>
- 826 Sefton-Nash, E., Catling, D.C., Wood, S.E., Grindrod, P.M., Teanby, N.A., 2012. Topographic, spectral and  
827 thermal inertia analysis of interior layered deposits in Iani Chaos, Mars. *Icarus* 221, 20–42.
- 828 Singer, R.B., McCord, T.B., Clark, R.N., Adams, J.B., Huguenin, R.L., 1979. Mars surface composition from  
829 reflectance spectroscopy: A summary. *Journal of Geophysical Research: Solid Earth* 84, 8415–8426.  
830 <https://doi.org/10.1029/JB084iB14p08415>
- 831 Stephan, K., Jaumann, R., Krohn, K., Schmedemann, N., Zambon, F., Tosi, F., Carrozzo, F.G., McFadden, L.A.,  
832 Otto, K., De Sanctis, M.C., Ammannito, E., Matz, K.-D., Roatsch, T., Preusker, F., Raymond, C.A.,  
833 Russell, C.T., 2017. An investigation of the bluish material on Ceres. *Geophysical Research Letters*  
834 44, 1660–1668. <https://doi.org/10.1002/2016GL071652>
- 835 Toby, B.H., 2001. EXPGUI, a graphical user interface for GSAS. *Journal of applied crystallography* 34, 210–  
836 213.
- 837 Wang, C.H., Wright, R.B., 1974. Raman scattering study of the effect of pressure and temperature on the  
838 order-disorder phase transition in ammonium chloride. *The Journal of Chemical Physics* 60, 849–  
839 854.
- 840 Warell, J., Bergfors, C., 2008. Mercury's integral phase curve: Phase reddening and wavelength dependence  
841 of photometric quantities. *Planetary and Space Science* 56, 1939–1948.  
842 <https://doi.org/10.1016/j.pss.2008.09.002>
- 843