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Some things special about NEAs: Geometric and environmental effects on the optical signatures of hydration

3

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5

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11

12 ABSTRACT

Here were report on a laboratory study aiming to reproduce specificities of 13 near-Earth Asteroid. We study how the elevated surface temperature, their 14 15 surface roughness (rock or regolith), as well as observation geometry can affect 16 the absorption features detected on asteroids. For that purpose, we selected a recent carbonaceous chondrite fall, the Mukundpura CM2 chondrite which fell in 17 18 India in June 2017. Bidirectional reflectance spectroscopy was performed to 19 analyze the effect of the geometrical configuration (incidence, emergence and 20 azimuth angle) on the measurement. Our results show that reflectance spectra 21 obtained under warm environment (NEA-like) tends to show shallower absorption 22 bands compared to **low-temperature** conditions (MBA-like), but still detectable in our 23 experiments under laboratory timescales. Irreversible alteration of the sample because 24 of the warm environment (from room temperature to 250°C) has been detected as an

25 increase of the spectral slope and a decrease of the band depths (at 0.7µm, 0.9µm and 26 2.7µm). Comparing the **meteoritic chip** and the **powdered sample**, we found that 27 surface texture strongly affects the shape of the reflectance spectra of meteorites and 28 thus of asteroids, where a dust-covered surface presents deeper absorption 29 features. We found that all spectral parameters, such as the reflectance value, 30 spectral slope and possible absorption bands are affected by the geometry of 31 **measurement.** We observed the disappearance of the 0.7 µm absorption feature at 32 phase angle larger than 120°, but the 3µm band remains detectable on all measured 33 spectra.

- 34
- 35
- 36 1. INTRODUCTION
- 37

38 Many meteorite groups record the action of water at some point of their geological history (Brearley 2006). Fingerprints of aqueous alteration have been identified in the 39 40 form of secondary minerals such as carbonates, phyllosilicates or iron oxides. Asteroids, 41 which are the astronomical counterpart of meteorites, also display evidence of aqueous 42 alteration. A first evidence, derived from visible ground-based optical observations, is 43 the presence of absorption bands at 0.7 and 0.9 µm, which can be attributed to Fe 44 bearing phyllosilicates (Vilas 2008). A more direct evidence of the presence of hydrated or hydoxylated minerals at the surface of asteroids is the presence of an absorption 45 46 band around 3-µm. For main-belt asteroids (MBAs), observations in this spectral region are only possible for the **brightest** objects (Vilas 1994; Takir and Emery 2012). Spectral 47 48 surveys have shown that objects with an absorption band at 0.7 µm always show the 49 presence of a 3-µm feature, but that the reciprocal is not true (Usui et al. 2019; Vilas 50 **1994)**.

51

52 Two space missions are presently orbiting possibly volatile-rich near-Earth 53 asteroids (NEAs): Hayabusa-2 (Kitazato et al. 2019) and OSIRIS-Rex (Hamilton et al. 54 2019). While hydration seems to be a general process among the MBAs population 55 (Fornasier et al. 2014), evidence of hydrated near-Earth asteroid is scarce (Rivkin et al. 56 2002). Rivkin and DeMeo (2018) calculated the theoretical amount of hydrated NEAs 57 according to their spectral group and found $17 \pm 3\%$ for the Ch-group and $43 \pm 6\%$ 58 corresponding to C-complex bodies. However, observations from Stuart and Binzel 59 (2004) and Carry et al. (2016) resulted in the statistics of 6 ± 3% of NEAs showing 60 signs of Ch asteroids, and 16 ± 7% showing signatures of C-complex asteroids. While 61 NEAs are certainly more accessible for sample-return purposes, it is not known today 62 whether they experienced specific, or more intense, geological processes when 63 compared to main-belt asteroids. First, it has been shown that the orbital evolution of 64 the NEA (101955) Bennu, the target of the OSIRIS-REx mission, could have led to a 65 significant heating of the surface (over 500 K (Delbo and Michel 2011)) by absorption of 66 solar radiation, which is much higher than the surface temperature experienced in the 67 main-belt (Schorghofer 2008). Second, many NEAs seem to exhibit a rubble pile 68 structure. These rubble-pile asteroids are interpreted as re-agglomerated fragments of a 69 prior object that was catastrophically destroyed following a hypervelocity collision 70 (Michel, Benz, and Richardson 2003, 2004). Last, small NEAs visited by space missions 71 appear devoid of a significant amount of **dust-like** regolith (Fujiwara et al. 2006), which is at odd with larger objects visited by space missions (Veverka et al. 1997). 72

73

74

In this article, we investigate how the environment of NEAs and the observations

themselves can influence the signatures of aqueous alteration. For that purpose, we selected a freshly fallen aqueously altered meteorite, the Mukundpura CM2 chondrite. The impact of thermal processing on the infrared signature has been studied in situ using a high-temperature, high-vacuum reflectance cell. The effect of observation geometry and the impact of surface texture (comparison **between** rock and **dust no larger than a few hundreds of microns**) have been investigated using a custom-made reflectance-goniometer (Potin et al. 2018).

- 82
- 83 **2.** Sample and methods

2.1 Meteorite sample

- 84
- 85

The Mukundpura meteorite fell in India on June 6, 2017 (Tripathi, Dixit, and Bhandari 2018) and was immediately collected by the authorities, reducing the risk of post-fall alteration. The first petrographic observations of the newly fallen meteorite were performed using a Zeiss polarizing microscope and electron microprobe (Ray and Shukla 2018)and characterized the meteorite as belonging to the CM group.

91

Mukundpura presents a dark matrix and several millimeter-size bright inclusions
(see Figure 1). The sample used in this study was taken from the exterior of the whole
meteorite and thus showed a smooth fusion crust **on one of its side.** Only the interior of
the **sample, the side opposite to the crust**, was studied in reflectance spectroscopy.



- 97 Figure 1: Picture of the Mukundpura meteorite sample used in this study (interior
 98 side showing).
- 99

100	This sample was first studied as a chip of the meteorite , then powdered to
101	investigate the effect of texture on the reflectance spectra.
102	
103	2.2 Bidirectional reflectance spectroscopy
104	2.2.1 Definition and methods for bidirectional reflectance spectroscopy
105	under fixed geometry, room temperature and atmospheric pressure.
106	
107	Reflectance spectroscopy studies are conducted using the custom-made
108	bidirectional reflectance goniometers SHINE (SpectropHotometer with variable
109	INcidence and Emergence) (Brissaud et al. 2004) and SHADOWS
110	(Spectrophotometer with cHanging Angles for the Detection Of Weak Signals)
111	(Potin et al. 2018), whose methods of measurement are quite similar. The goniometer
112	illuminates the sample with a monochromatic light between 340 nm and 5000 nm and
113	under a specific direction (incidence angle). Table 1 summarizes the different spectral
114	resolutions over the whole spectral range.

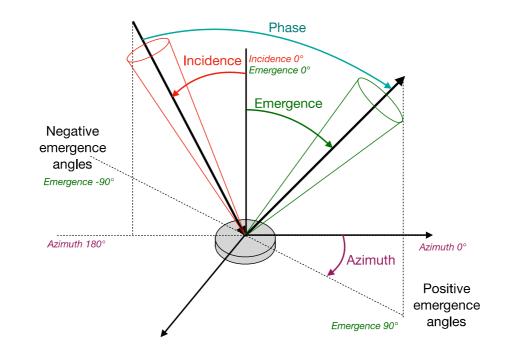
116 **Table 1: Spectral resolution of the reflectance spectrum**

Spectral range	Spectral resolution
400 nm – 679 nm	4.85 nm – 4.75 nm
680 nm – 1499 nm	9.71 nm – 9.38 nm
1500 nm – 2999 nm	19.42 nm – 18.73 nm
3000 nm – 5000 nm	38.84 nm – 38.44 nm

117

118

The reflected light is measured under fixed values of emergence and azimuth angles. All three parameters, incidence, emergence and azimuth angles, constitute the geometrical configuration under which the spectra will be recorded. Figure 2 presents a schematic view of the reflectance measurement and the different angles involved.



123

Figure 2: Schematic definition of the geometrical configuration, incidence,
emergence and azimuth angles, for the reflectance spectroscopy. Picture from
Potin et al. (2018).

Nominal configuration for a "single spectrum" reflectance spectroscopy study consists of a nadir illumination (incidence angle of 0°) and an emergence angle of 30° in the principal plane (azimuth 0°). The angular resolutions are $\pm 2.9^{\circ}$ for the incidence angle and $\pm 2.05^{\circ}$ for the emergence and azimuth angles.

132

133 2.2.2 Reflectance spectroscopy under asteroidal conditions.

134

Low-temperature reflectance spectra are acquired using SHINE coupled with
the double environmental chamber CarboN-IR (Beck et al. 2015; Grisolle et al. 2014).
The outer cell is put under vacuum while gaseous nitrogen is injected inside the inner
cell to increase the thermal exchanges and ensure thermalization of the sample. This

139 technique reduces the thermal gradient inside the meteorite but needs two sapphire 140 windows to close the outer and inner cells. The light passing through these two 141 windows creates reflections between the sample and the inner cell window, but also 142 between the windows themselves. The small absorption of the sapphire added to the 143 multiples reflections reduce the contrast of reflectance measured on a sample. To 144 evaluate the effect of the two windows on the measurement, reflectance spectra of a 145 calibration target were acquired, with and without the sapphire windows. Using these 146 spectra, the effects of the windows have been removed from the meteorite data. The 147 spectra were acquired, with a nadir illumination and emergence angle of 30°, from 80K 148 to room temperature 290K every 10K, and from 400 nm to 1000 nm with a 10 nm 149 spectral sampling.

150

Reflectance spectroscopy at high temperature can be conducted with SHADOWS
using a heating vacuum cell, nicknamed MIRAGE (Mesures en InfraRouge sous
Atmosphère Gazeuse et Etuvée) (see Figure 3).

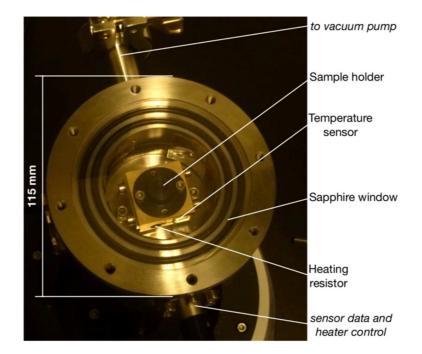


Figure 3: Annotated picture of the MIRAGE cell.

155

156

158 This cell only needs one sapphire window, and the presence of reflections 159 between the window and the sample has already been investigated and corrected 160 through the work on the SERAC cell (Spectroscopie En Réflexion sous Atmosphère **Contrôlée)** (Pommerol et al. 2009). Other sources of error need to be taken into account 161 162 with MIRAGE, but were previously unknown on SERAC, due to the difference between 163 the illumination methods of the two setups. To remove all these effects, reflectance 164 spectra of Mukundpura were acquired with and without the sapphire window, and used 165 to correct the instrumental biases due to the cell on all the acquisitions. The spectra 166 were acquired from 360 nm to 1200 nm every 10 nm in order to analyze the shape of 167 the 700 nm and 900 nm bands. Acquisitions are set from room temperature (294 K) to 168 510K every 20K during the increase of temperature, and from 490K to room 169 temperature every 40K when the cell is cooling down. The illumination is fixed at nadir, 170 and the observation at 30°.

172

2.2.3 Bidirectional Reflectance Distribution Function (BRDF)

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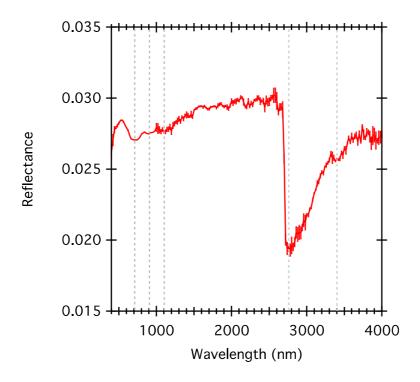
174 To simulate observations from a spacecraft orbiting its target or from a ground-175 based observatory, one has to take into account the scattering geometry of the system: 176 the angle of the light illuminating the surface, as well as the angle from which the spectra 177 are acquired. In the laboratory, bidirectional reflectance spectra were acquired with 178 SHADOWS for 70 different geometrical configurations: incidence, emergence and 179 azimuth angles. The incidence angle was set from nadir to grazing illumination (0° to 180 60° with a 20° step), and for each incidence, spectra were acquired at several 181 measurement angles from -70° to 70°, corresponding to grazing emergence respectively 182 in the backscattering and forward scattering directions in the principal plane, with a 10° 183 step. To analyze the lateral scattering of the sample, spectra at incidence 20° with the same list of emergence angles were taken with a 30° azimuth angle outside the principal 184 185 plane. The SHADOWS goniometer cannot measure light reflected at a phase angle lower than 5° so opposition spectra are absent from the dataset. The spectral resolution is 186 187 identical to the resolutions displayed in Table 1. The angular resolutions are $\pm 2.9^{\circ}$ for the incidence angle and $\pm 2.05^{\circ}$ for the emergence and azimuth angles. 188

189

The series of spectra has been first acquired on the **chip**. The studied surface originated from a broken piece of a larger sample and therefore was not **horizontal when placed on the goniometer (tilt of about 5°)**. This was taken into account during the analysis and photometric corrections were applied to the data. The same set of reflectance spectra have been acquired after manual grinding of the meteorite, to compare the photometric and spectral variations due to surface texture.

- **3. Reflectance spectroscopy**
- 198 3.1 Spectral features of the Mukundpura CM chondrite

The reflectance spectrum of the powdered meteorite is displayed on Figure 4. A
first series of spectra was acquired under vacuum, starting at room temperature then at
60°C. There was no evidence of degassing of the sample.



202

Figure 4: Reflectance spectrum of the Mukundpura meteorite (powder) with a nadir illumination and an emergence angle of 30°. The grey doted lines mark the position of the typical CM absorption bands at 700 nm, 900 nm, 1100 nm, 2760 nm and 3400 nm.

207

The reflectance spectrum shows all characteristics of CM chondrites (Cloutis, Hudon, et al. 2011): (1) a low reflectance value, less than 3% over the whole spectral range, (2) the Fe³⁺-Fe²⁺ charge-transfer band at 700 nm (Tomeoka, Mcsween, and Buseck 1989),

211	(3) the Fe^{2+} crystal field transition bands at 900 and 1100 nm, (4) organics features at
212	3400 nm and (5) the –OH stretching band at 2750 nm related to the presence of Mg-OH
213	bearing phyllosilicates.
214	
215	The beginning of a strong UV absorption feature is visible shortwards of 500 nm,
216	though it is not possible to analyze this band with the current data starting at 400 nm.
217	This absorption feature is likely due to metal-O charge transfer (Cloutis et al. 2008).
218	
219	The detection of both the iron features (700 nm and 900 nm) and the Mg-rich
220	phyllosilicates band at 2750 nm indicates an extensive aqueous alteration of the
221	meteorite on the parent body (Takir et al. 2013; Beck et al. 2010).
222	
223	3.2 Assessing the impact of regolithisation: comparison between the chip and
224	the powdered sample
225	
226	Reflectance spectroscopy of the meteoritic chip was conducted under the same
227	geometrical configuration as the powder. The sample was placed on its fusion crust on
228	the sample holder so that the studied surface was revealing the interior of the meteorite.
229	Both spectra are presented in Figure 5.
230	

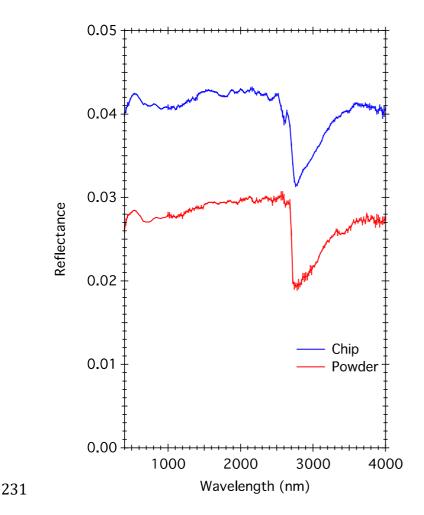


Figure 5: Reflectance spectra of the raw meteorite (blue) and after manualpowdering (red).

235 The major difference between the two sets of spectra is the reflectance value of 236 the continuum, around 4.2% in the case of the raw meteorite and around 2.8% for the 237 powder. This behavior is distinct from the "standard" behavior observed for pure 238 material when the grain size is decreased, which is to observe an increase in reflectance 239 with decreasing grain size (Pommerol and Schmitt 2008b). Several possible 240 explanations emerge. The first explanation is related to petrography: the surface of the 241 raw meteorite is heterogeneous due to the presence of mm-sized chondrules and bright 242 inclusions, while the powder has all the elements finely mixed into a rather

243 homogeneous volume. Opaques "hidden" beneath the surface will be more visible in the 244 powder spectra, lowering the global amount of reflected light. The model developed by 245 Hapke (1981) states that the reflectance of an intimate mixtures depends on the viewing 246 geometry and properties of the particles in the mixtures such as single scattering albedo, 247 diameters, porosity and mass fraction. The spectra of mixtures composed of materials 248 with contrasted absorption properties will depend on the style of the mixture. In the 249 case of a spatial mixture of two spectral endmembers, the resulting spectrum is a linear 250 mix of the endmember spectra, weighted by their surface area. The spectra of the raw 251 meteorite, where the size of the bright and dark patches are less than 1 mm² can be 252 interpreted by a linear mixture of the bright and dark endmembers. When powdering 253 the meteorite, the style of mixture between the dark and bright materials will change, 254 since it will become an intimate mixture. In that case, mixtures are expected to be linear 255 in single scattering albedo space, and therefore the mixture of the spectra becomes 256 highly non-linear. For the same amount of bright and dark material, the intimate 257 mixture (powder) will be darker than in the case of a geographic mixture (**chip**) 258 (Pommerol and Schmitt 2008b).

259

The second explanation could be the difference of porosity between the two samples. Theory and laboratory measurements agree that increasing the porosity of a sample lowers the general reflectance (Hapke 2008; Cloutis et al. 2018; Shepard and Helfenstein 2011; Cloutis, Hiroi, et al. 2011) The presence of bright inclusions coupled with the differences in both grain size and porosity between the samples can explain the higher reflectance of the raw meteorite.

266

267

Both samples present the same absorption features, but with different band

depth and broadness. Relative band depths are calculated considering a linear
continuum between the two inflexion points of the bands and using the following
formula:

271

$$BD = 1 - \frac{R_{band}^c}{R_{continuum}^c}$$

273

where c is the central wavelength of the absorption band, R_{band}^c and $R_{continuum}^c$ are respectively the measured reflectance of the sample and the interpolated reflectance of the continuum at wavelength c. The depth of the UV absorption band is calculated as the ratio between the reflectance measured at 540 nm and 400 nm:

278

279
$$UV \ ratio = \frac{R^{540nm}}{R^{400\,m}}$$

280

Table 2 presents the calculated band depths of the UV absorption, the Fe²⁺ 700
 nm band, the phyllosilicates 3 μm feature and the organics band around 3400 nm.

283

Table 2: Band depths of the Vis-NIR absorption features and UV ratio calculated

285 for the chip and powdered samples.

	UV ratio	700 nm band	3 μm band	Organics
Chip	1.0618 ± 0.0074	0.0139 ± 0.0037	0.1992 ± 0.0090	0.0080 ± 0.0061
Powdered meteorite	1.089 ± 0.018	0.0306 ± 0.0017	0.3252 ± 0.0009	0.0281 ± 0.0088

286

We found that grinding of the sample affects the absorption features, resulting in a deeppening of the bands. Again, the size of the grains will affect the depth of the absorption features, following the general trend where band depth increases with increasing grain size. It should be noted that all absorption bands are detectable in both reflectance spectra. This implies that even in the absence of a well developped **finegrained** regolith, as seems to be the case for some near-earth objects (Benner et al. 2008; Hasegawa et al. 2008), the water-related features should be detectable. In order words, the lack of **dust-size** regolith does not explain the scarcity of water-related absorption signatures among the NEAs population.

296

297 **4** Effects of temperature on the optical absorptions

298

299 Several processes may warm the surface of small bodies, NEAs included. First, the 300 initial decay of extinct radionuclide such as ²⁶Al, could have been strong enough to heat up and differentiate small bodies (Grimm and Mcsween 1993,1989; Mahan et al. 2018), 301 302 but this process was not efficient for km-size objects (Ghosh et al. 2006). Secondly, 303 impacts can generate enough heat to locally metamorphose or even melt the surface 304 (Bland et al. 2014), though the models cannot describe a global increase of the 305 temperature of the object. This is consistent with some of the heated meteorites 306 showing foliation or shock-induced deformations (Nakamura 2006). The initial 307 accretion process is based on low energy impacts and thus can be disregarded as a 308 source of heating for the small bodies (Nakamura 2005). Then, electromagnetic 309 induction due to solar winds during the early T Tauri phase can induce enough heat to 310 alter the mineralogy of asteroids. But as the solar winds usually occur on the poles of the 311 stars, they are unlikely to have produced enough heat in the mid-plane where the small 312 bodies are concentrated (Mahan et al. 2018). Last but not least, the relatively close 313 distance between the Sun and the NEAs over their lifetime induces an elevated sunlight

314 flux on the surface, and so warming up the small body. This process depends on albedo, 315 surface roughness and thermal inertia. An elevated thermal inertia will reduce the 316 difference of temperature between the direct sub-solar surface (strongly heated) and 317 the rest of the body (rather cool) and the rotation period, as well as the pole position, 318 of the asteroid will also have an impact on the temperature at the surface. In the case of 319 a slow-rotating body or an asteroid oriented so that its rotation axis is near the 320 orbital plane with a pole facing toward the Sun, the sub-solar point will accumulate a 321 lot of heat and will reach higher temperatures than the night-side, and the whole surface 322 of the body will present a wide range of temperatures that strongly vary with time. On 323 the contrary, fast-rotating asteroids, or with their rotation axis almost perpendicular 324 to the orbital plane, will present a rather homogeneous and moderate temperature on 325 their surface. For example, according to models, (101955) Bennu could have undergone 326 temperatures as high as 500K (Delbo and Michel 2011), while other NEAs could have 327 experienced temperatures over 1500K during a close approach to the Sun (Marchi et al. 328 2009). Note however that Dunn et al. (2013) calculated that the temperature of 72 NEAs 329 is distributed between 143 and 300K.

330

Reflectance spectra of asteroids can be affected by surface temperature, an effect which was studied for S-type asteroids and ordinary chondrites, but which is much less known for C-type asteroids. In this section, we present the spectral variations of the powdered Mukundpura meteorite under a wide range of environmental conditions, from cryogenic to high temperature. We focus on the iron features in the visible range.

336

To characterize the spectral variations across changes in temperature, thereflectance spectra are adjusted using a linear continuum and three modified Gaussian

339 profiles (Sunshine, Pieters, and Pratt 1990) representing the UV, 700 nm and 900 nm 340 absorption bands. The modified Gaussian model (MGM) includes a correction factor 341 acting on the symmetry of the left and right wings of the profile. Its value can be fixed 342 empirically. The least residual errors were achieved with a correction factor of 1.12. For 343 each MGM, so for each absorption feature, the amplitude, band position and full width at 344 half maximum (FWHM) are set as free parameters. The resulting model is as follow:

345

346
$$R(\lambda) = A\lambda + B + MGM(\lambda, a_{UV}, p_{UV}, \sigma_{UV}) + MGM(\lambda, a_{700nm}, p_{700nm}, \sigma_{700nm})$$

- + $MGM(\lambda, a_{900nm}, p_{900nm}, \sigma_{900nm})$
- 348

with $R(\lambda)$ the calculated reflectance at the wavelength λ , A and B respectively the slope and offset of the continuum, and a_X , p_X and σ_X the amplitude, position and FWHM (linked to σ) of the band X. The model parameters for the UV absorption may differ from reality, as the data cover less than half the band.

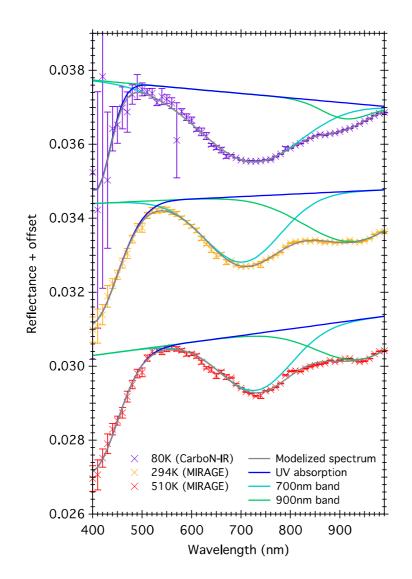
353

354 4.1 Variations from cryogenic to high temperatures.

355

In order to highlight the effect of temperature on the sample, Figure 6 presents a

- 357 comparison between the extreme spectra, obtained at 80 K and 510 K, and the
- 358 acquisition at room temperature.



359

Figure 6: Comparison between the reflectance spectra of the powdered Mukundpura meteorite acquired at 80K (purple), room temperature (orange) and 510K (red). The modeled spectra (grey) and the different modeled absorption bands, UV (navy blue), 700 nm (blue), and 900nm (green) are also presented. An offset of +0.003 and -0.003 has been added respectively to the 80K and 510K spectra.

367 In Figure 6, subtle variations of the spectra related to temperature can be368 observed. The fit parameters for each spectrum are compared in Table 3.

	80K	294K	510K
Continuum slope (nm ⁻¹)	-1.210.10-6	6.299.10 ⁻⁷	1.797.10 ⁻⁶
Continuum offset	0.0352	0.0341	0.0326
BD700nm (%)	0.183	0.177	0.153
P _{700nm} (nm)	710	702	730
FWHM _{700 nm} (nm)	330	252	239
BD900nm (%)	0.043	0.136	0.107
P _{900nm} (nm)	910	926	940
FWHM900 nm (nm)	167	327	298
BDuv (%)	0.298	0.327	0.314
Puv (nm)	404	394	396
FWHM _{UV} (nm)	105	176	171
Reflectance max	0.0344	0.0342	0.0334
Position of the max (nm)	491	539	560

Table 3: Parameters of the modeled spectra at each temperature.

371

372 The increase of temperature induces a modification of the continuum slope, as 373 seen by the spectrum at 80K having a negative (blue) slope, while the spectra acquired 374 at room temperature and 510K present a positive (red) slope. A decrease of reflectance 375 of the continuum is observed at 510K, representing 7.4% relative to the initial value at 376 80K. Variations of the absorption features as well as the continuum induce an apparent 377 displacement and decrease of the maximum of reflectance, from 0.0344 of reflectance at 378 491 nm in the spectrum acquired at 80K, to a reflectance of 0.0334 at 560 nm for the 379 spectrum at 510K. The reflectance maximum also decreases with increasing temperature, losing 0.001 of reflectance between the two extreme spectra.

381

382 In the case of the low temperature measurements, a blue shift of nearly 20 nm of 383 the position of the 700 nm band can be observed when compared to the high 384 temperature measurement. The band gets broader and deeper, as the FWHM gains 385 around 97 nm and the depth increases by a factor 1.2. It is interesting to note that 386 opposite effects occur in the case of the 900 nm band, except for the position: with 387 decreasing temperature, the band is shifted by 30 nm towards shorter wavelengths, the 388 band depth is reduced by a factor 2.5 and its FWHM is reduced by approximately 389 130nm.

390

391 Fe-related absorptions can be expected to be sensitive to temperature (Hinrichs and 392 Lucey 2002). The 700 nm feature in CM chondrites is interpreted by Fe²⁺-Fe³⁺ charge 393 transfer ($Fe^{2+}+Fe^{3+}->Fe^{3+}+Fe^{2+}$) within a phyllosilicate structure. Charge transfer bands 394 in -OH bearing silicates generally display an increase of their intensity under low-395 temperature, as observed by Smith (1977). As measured in transmission (absorbance), 396 the intensity of the Fe²⁺-Fe³⁺ charge transfer band of chlorite and biotite has been 397 measured to increase by a factor of 2 when cooling the sample to liquid helium 398 temperature (5.5 K), and by about 25 % when cooling the sample to 80K. This effect was 399 interpreted by a depopulation of one or more electronic levels close to the ground state of the $Fe^{2+}+Fe^{3}$ -> $Fe^{3+}+Fe^{2+}$ transition (Smith 1977). While our lowest temperature 400 401 measurements are not as low as liquid helium, they are cold enough to induce a 402 significant increase in the depth of the 0.7 µm feature. Note that a broadening of the 403 700nm band was also observed by Smith (1977) study, which could explain the change 404 in the position of the visible maxima from around 539 nm (room temperature) to 491 405 nm (80 K), when added to a possible displacement and broadening of the UV absorption.

406

407 4.2 Irreversible alteration at high temperatures

408 Reflectance spectra of Mukundpura were recorded during a high temperature
409 experiment. Spectra were acquired during a heating and cooling cycle of the sample and
410 are presented in Figure 7.

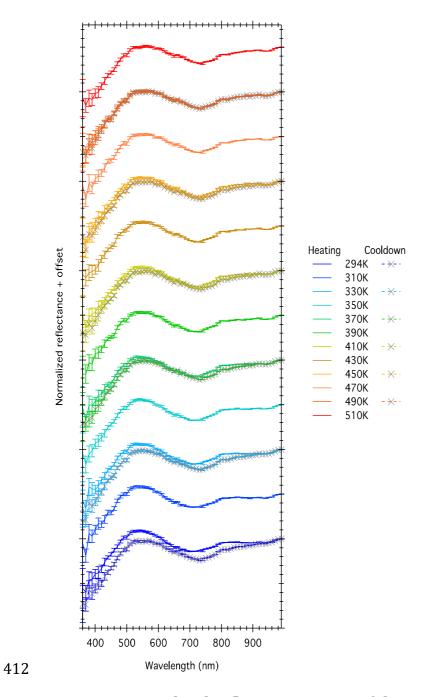


Figure 7: Normalized reflectance spectra of the powdered Mukundpura meteorite
acquired during the increase of temperature from 294K to 510K (solid lines) and
during cooling (dashed lined and grey markers). The different offsets have been
added for clarity but are identical for spectra acquired at the same temperature.

417 The high temperature experiments reveal irreversible alterations of the sample,418 as seen when comparing the two spectra taken at 294K, at the beginning and at the end

of the experiment. The oxidation of the sample by ambient air is not relevant in ourmeasurements as they were performed under secondary vacuum.

421

422 The difference between the two spectra is a combination of variations in the 423 continuum of the spectrum and in the 3 detectable absorptions bands. The differences 424 involve an apparent reddening of the sample as the spectrum acquired after heating 425 presents a stronger spectral slope compared to the initial measurement, an apparent displacement of the 700 nm band to longer wavelengths, and both a shift and decrease 426 427 of the reflectance maximum around 550nm. The whole series of spectra are adjusted using the model described above. Resulting modeled spectra of the first and last 428 429 measurements of the experiment are presented in Figure 8.

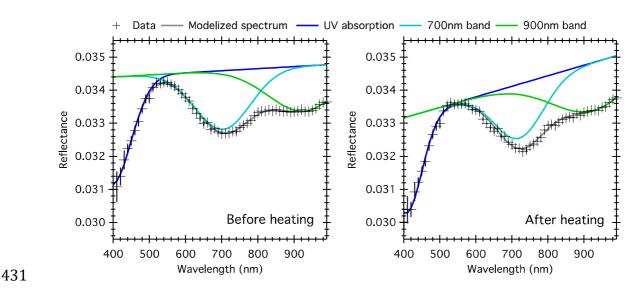
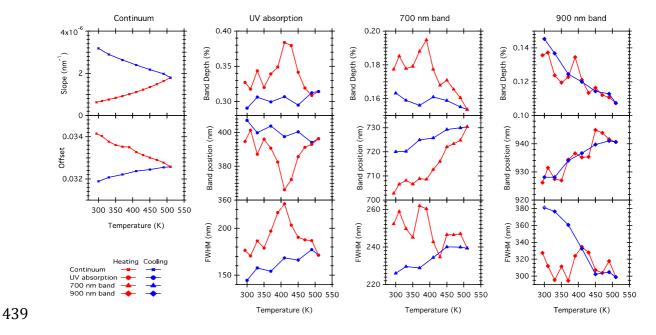


Figure 8: Reflectance spectra of powdered Mukundpura meteorite at room
temperature (294 K) before (left) and after (right) warming to 510 K, as well as
the MGM fit to the data (Navy blue: continuum and UV absorption. Blue:
continuum and 700nm band, Green: continuum and 900nm band)

437 The variation the model parameters calculated for the spectra measured during 438 the heating and cooling cycle, is presented in Figure 9.



440 Figure 9: Variations of the continuum and absorption bands during the heating 441 (red) and cooling (blue) cycle of the sample.

442

443 Based on this analysis, the continuum slope and all the three absorption features 444 show an irreversible alteration due to temperature. In the case of Mukundpura, the 445 temperature cycle up to 510 K and down leads to an increase of the continuum slope, 446 from 6.30 10⁻⁷ nm⁻¹ to 3.18 10⁻⁶ nm⁻¹ after the thermal ramp, coupled with a decrease of 447 the general reflectance level represented by the continuum offset, from 0.0341 to 448 0.0319.

449

450 With increasing temperature, the 700 nm band first increases and then decreases 451 in amplitude, while getting narrower and shifting towards longer wavelengths. During 452 cooling, the amplitude of this feature only marginally changes and returns to a value only slightly lower than prior heating (0.163% against 0.177%). Upon heating, the 453

position of the 700 nm band changes significantly. When heating to 520 K the maxima of
absorption shifts from 703 to 730 nm, and upon cooling it returns to a value of 720 nm.
The position of the 700 nm band is thus not reversible upon heating. This effect could be
interpreted by the occurrence of redox process (Fe³⁺ reduction of Fe²⁺ oxidation) within
the phylosilicates occurring upon heating, since the oxygen fugacity is sensitive to
temperature.

460

The 900 nm also reveals some variability with temperature but in a different way than the 700 nm band. The amplitude of the band decreases upon heating from 0.130% to 0.107% while the position shifts to higher wavelength by about 15 nm (from 926 to 941 nm). Unlike the 700 nm band, these changes are reversible when returning to ambient temperature (except the FWHM which significantly increases upon cooling). The 900 nm band is interpreted as a crystal field band, which are known to shift, broaden and change in intensity with temperature (Burns 1993), in a reversible manner.

The combined spectral variations due to temperature induce the apparent displacement of the maximum of reflectance from 530 nm to 558 nm at the end of the thermal cycle. The value of the maximum reflectance has been altered as well, slightly decreasing from 0.0342 to 0.0335 after the experiment.

473

Irreversible alterations also occurred outside the visible spectral range. To compare the different effects observed, the same thermal cycle was imposed on 2 other CM chondrites. Figure 10 presents the reflectance spectra over the whole spectral range of the 3 samples before and after the experiment. As the spectroscopy measurements on the whole spectral range was conducted after the temperature ramp, the samples were prepared into another sample holder, the surfaces have slightly changed between the
two experiments. To remove this photometry effect, the spectra are normalized at
560nm.

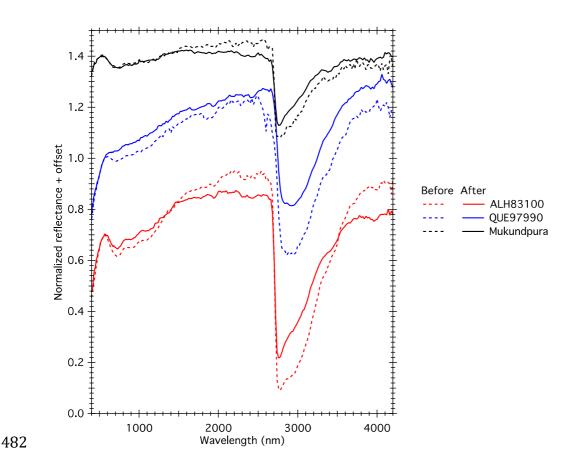


Figure 10: Normalized reflectance spectra of the CM chondrites ALH83100 (red), QUE97990 (blue) and Mukundpura (black) acquired before (doted line) and after (solid line) a thermal cycle at 520 K. The spectra are normalized at 560 nm and offseted for clarity, -0.3 and +0.4 respectively for ALH83100 and Mukundpura. All samples were manually powdered before the experiment.

488

The thermal experiment resulted in another alteration, this time of the 3μm
absorption band. Table 4 presents the band depth and width of the 3μm band before and
after the thermal cycle for the 3 chondrites.

Table 4: Band depth and FWHM of the 3µm band before and after the thermal

	Band depth (%)		FWHM (nm)	
	Before	After	Before	After
Mukundpura	32.52 ± 0.08	26.17 ± 0.30	410	370
ALH83100	66.86 ± 0.39	54.27 ± 0.17	560	490
QUE97990	49.43 ± 0.57	35.21 ± 0.15	650	530

493 cycle for the 3 CM chondrites.

494

For each sample, the thermal heating reduces both the depth and width of the band. A faint displacement of the band is also detected, which can be explained by the faster reduction of one of the component of the band compared to the others. The alteration of the 3µm band can be due to the release of the absorbed water molecules, and the water contained in (oxy)hydroxide minerals (Garenne et al. 2014).

500

501 The present analysis of the reflectance spectra obtained under NEA-like 502 temperatures for CM chondrites reveals that, at laboratory timescale, the presence and 503 so the detection of 700 nm, 900 nm and 3µm bands is not affected by temperature, 504 though the bands can be strongly weakened. Still, a shift of the 700 nm band and a 505 narrowing of the 3µm feature can be predicted for objects that experienced significant 506 thermal processing. Conversely, the shape and mostly the position of the 700nm ands 507 3µm features could potentially be used as a criterion of primitiveness of Ch and Cgh 508 asteroids.

509

510 **5** Bidirectional reflectance spectroscopy: effects of observation geometry

512 During a flyby or when orbiting around an asteroid, the observation geometry is very 513 variable (incidence, observation and azimuth angles), and differ from the observation 514 geometry under which laboratory data are typically obtained. This geometry depends on 515 the incidence angle of the sunlight on the surface, and the position of the spacecraft. 516 Figure 11 presents the resulting spectra of the powdered Mukundpura meteorite. The 517 same set of spectra was also acquired on the **meteoritic chip**.

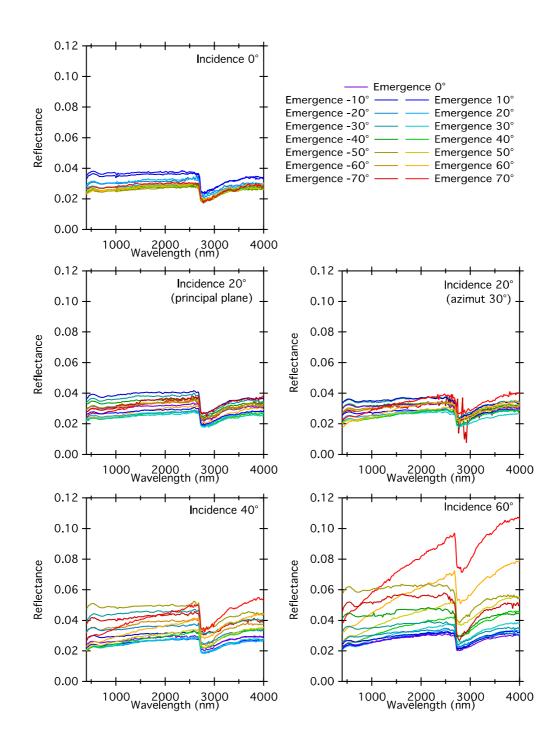


Figure 11: Complete set of spectra of the powdered Mukundpura meteorite acquired in bidirectional reflectance distribution function mode. Each panel corresponds to an incidence angle: 0° (top panel), 20° in the principal plane (middle left panel) and at 30° azimuth (middle right panel), 40° (bottom left panel) and 60° (bottom right panel).

The dependence of the reflectance spectra to the geometrical configuration is easily seen on Figure 11. Spectra acquired with an incidence angle of 0° present the same slope, and the photometric level stays between 2 and 4% of reflectance, whatever the emergence angle. But spectra acquired under an incidence angle of 60° show drastic variations according to emergence angle. The reflectance value at 4 µm spreads from 2 to 11%, and **an increase of the spectral slope is observed with increasing phase angle, an effect called phase reddening.**

531

In this section, we investigate the different variations of the reflectance spectra when the geometrical configuration is changed. As the two samples, **the chip** and powder have been analyzed under the same set of geometrical configurations, variations due to the texture of the sample can also be analyzed.

536

537 5.1 Photometric dependence with the geometry

538

The bidirectional reflectance distribution function (BRDF) presented on Figure displays the measured reflectance values at different emergence angles for several incidence angles. The polar representation of a BRDF enables a quick overview of the distribution of the reflected light (see Figure 12). In this representation, the BRDF of a perfectly lambertian surface would appear as a half circle.

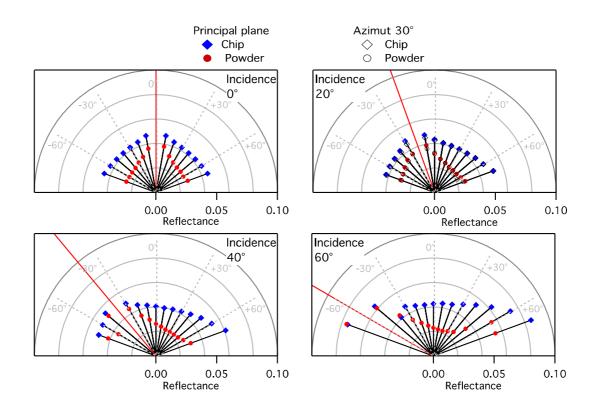


Figure 12: Bidirectional reflectance distribution function of Mukundpura at 547 560nm. The red line represents the incidence angle and the value of reflectance at 548 each emergence angle is displayed by the colored dots (Blue diamonds: meteoritic 549 chip in the principal plane. Red circles: powder in the principal plane. Open 550 squares: raw meteorite at 30° azimuth angle and 20° incidence angle. Open 551 circles: powder at 30° azimuth angle and 20° incidence angle).

For all geometrical configurations investigated, the chip presents a higher
reflectance than the powder. The causes of this effect have been already discussed in 3.2.
The BRDFs shows an increase in reflectivity around the incidence direction
(backscattering) and towards high phase angles (forward scattering). It is important to
note that both samples show these two behaviors, being more marked when the
incidence is close to grazing (60°) and more pronounced on the powder.

Irregularities in the shape, composition, and refractive index of the particle willbroaden the forward and backward scattering (Hapke 2002).

561 This increase of reflectance with decreasing phase angle (backscattering) is due 562 to a combination of two effects. First, the shadows hiding opposition effect (SHOE) where, at phase angle close to 0°, the shadow of one particle over the others around is 563 564 the smallest, resulting in a strong increase of reflectance in the incidence direction 565 (Hapke 1986). The second process is the coherent backscattering opposition effect 566 (CBOE) describing constructive interferences of the light scattered coherently backward 567 (Hapke 2002). However, this effect only occurs at very low phase angle, not observable 568 in our experiment.

569

To make the powder, the original sample was manually powdered but not sieved, leaving a large distribution of grain sizes. The surface texture of the powder can then be seen as rougher than the **chip**. The SHOE effect is weaker in case of the **meteoritic chip** as the sample is compact, with little porosity, limiting shadowing of one particle over another. The variation of the BRDF with grain size has already been investigated (Dozier, Schneider, and McGinnis 1981; Pommerol and Schmitt 2008a; Reddy et al. 2015).

577

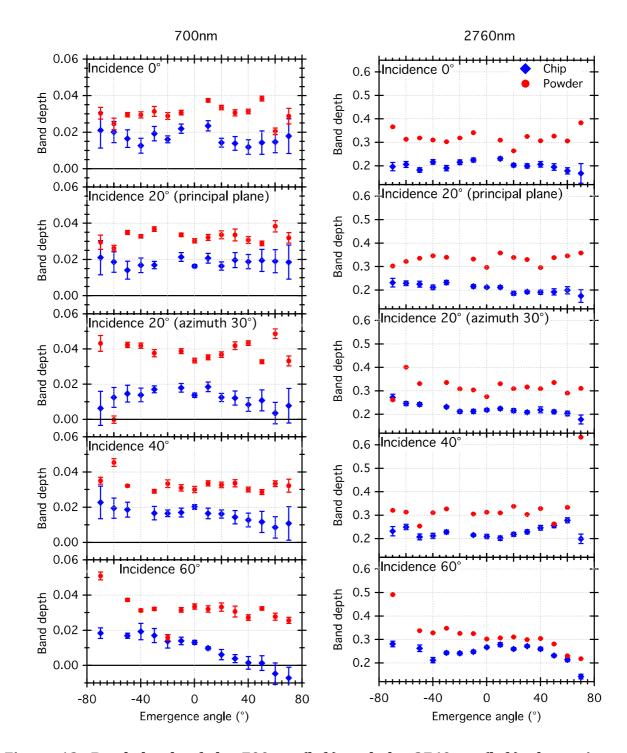
578 Backward scattering has been observed on several small bodies of the Solar 579 System and is often linked to the study of the surface regolith (Belskaya and Shevchenko 580 2000). Conversely, the study of the bidirectional scattering behavior of a small body, 581 more importantly the strength of the forward scattering and backscattering lobes, can 582 be used to determine the **texture, more importantly the presence of dust** on the 583 surface.

586

587	The presence of absorption bands in the reflectance spectra of asteroids is, with
588	the spectral slope, commonly used as a criterion to classify small bodies. For example, C-
589	types asteroids exhibits hydration related features around 0.7 μm and 3 μm (Takir and
590	Emery 2012). In this section, we present the influence of observation geometry on the
591	detection and depth of absorption features in the bidirectional reflectance spectra of
592	Mukundpura.

593

594 For both the **chip** and powdered samples, the band depths of the 700 nm and 2760 595 nm features are calculated according to the formula in section 3.2. The results are 596 presented in Figure 13.



597

Figure 13: Band depth of the 700nm (left) and the 2760nm (left) absorption
features of Mukundpura for the different geometries. Note the different vertical
scales.

602

First, it is important to note that the absorption features detected on the

603 meteoritic chip are generally fainter than for the powdered sample's spectra, in all 604 observation geometries studied. Previous laboratory measurements have shown variation in the band depth of absorption features as a function of geometrical 605 606 configurations, mostly the decrease of band depth at larger phase angles (Pommerol and 607 Schmitt 2008a; Beck et al. 2012, 2011). This effect is generally explained by an increase 608 of the relative number of photons scattered out of the sample before entering any of the 609 grains. Radiative transfer modeling confirms this hypothesis (Pommerol and Schmitt 610 2008a).

611

But several behaviors are observed with our measurements, **depending on** the incidence angle, not only the phase angle. **For illuminations near nadir**, the band depth decreases until phase angle around 40°, then increases with the phase angle. **In case of grazing illumination, the band depth only decreases with increasing phase angle.**

617

618 In case of the iron 700nm feature at grazing incidence (60°) , the band disappears 619 from the spectra at phase angles larger than 90°, but only on the raw sample. For the 620 powder, the iron band is detectable at all geometrical configurations and the general 621 trend leads us to think that the band will be detectable even at phase angle larger than 622 120°. The hydration feature at 2760nm is detectable through all our measurements, but 623 begins to fade at 110° phase angle until reaching a depth of 14% at 130°, the largest 624 phase angle studied. According to this trend, the band will also disappear from the 625 spectra, at phase angles greater than 140° or 150° but these are clearly extreme conditions of observation. 626

627

628	The geometry of illumination and observation has an important impact in the
629	depth of the absorption bands. Under all observation geometries, the band depths are
630	stronger for the powder than for the $\boldsymbol{chip}.$ The depth of the $3\mu m$ band is variable with
631	the observation geometry but it is always significant. The depth of the $0.7 \mu m$ band is
632	also variable with observation geometry but can disappear under extreme geometries.
633	Nevertheless, for ground-based observations, mostly obtained at low phase angle, the
634	observation geometry cannot explain the disappearance of the 0.7 μm band.
635	
636	
637	5.3 Geometry dependency of the spectral slope
638	5.3.1 Phase reddening
639	
640	Reflectance spectra of most carbonaceous chondrites present a faint red slope,
641	even if blue-sloped spectra can occur under specific conditions (Cloutis et al. 2013). The
642	phase reddening observed on the reflectance spectra of Mukundpura (Figure 11)
643	results from the wavelength dependence of the single-scattering albedo (Gradie and
644	Veverka 1986). This phenomenon was observed on asteroids such as (4) Vesta (Gehrels
645	et al. 1970; Blanco and Catalano 1979), on several Main Belt asteroids (Beth E. Clark et
646	al. 2002), NEAs (Sanchez et al. 2012) and on the Moon (Lane and Irvine 1973; Johnson et
647	
	al. 2013) and more recently on (101955) Bennu (Binzel et al. 2015). On our spectra, this
648	al. 2013) and more recently on (101955) Bennu (Binzel et al. 2015). On our spectra, this effect is more important at high incidence angle (at 60°), where observations have been
648 649	
	effect is more important at high incidence angle (at 60°), where observations have been

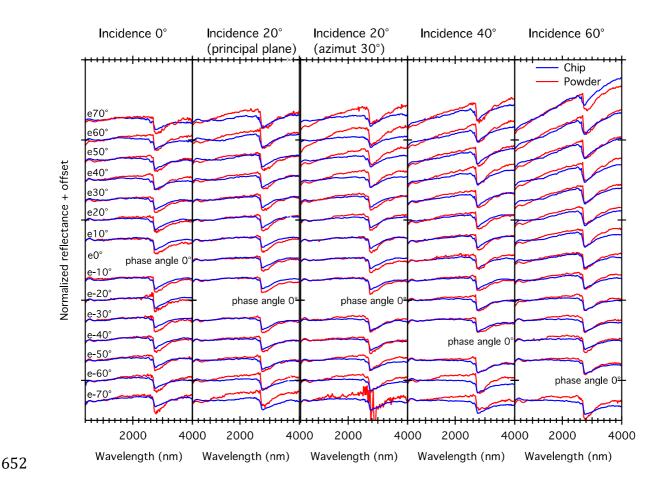


Figure 14: Reflectance spectra of the Mukundpura meteorite normalized at
1000nm (Blue: chip, Red: powder) taken under different geometrical
configurations. Offset for clarity.

656 Sanchez et al. (2012) determined the spectral slope as the fitted linear continuum between 0.7 and 1.55µm. This method is commonly used around absorption bands or 657 658 for measurements on a limited spectral range, but in case of wider spectral ranges, the 659 continuum should not be considered as linear (Parente et al. 2011). The spectral slope 660 can also be calculated as the ratio between the reflectance measured at two separated 661 wavelength, in the visible (Schröder et al. 2014), or between the maximum of reflectance 662 value and the absolute reflectance at 1.5µm (Cloutis et al. 2011) In our case, the spectral 663 range is too wide to adopt a linear approach to the continuum, thus we the spectral 664 slope as a color ratio.

666 The value of the spectral slope is calculated as the ratio between the reflectance 667 at 2000 nm and the reflectance at 500 nm:

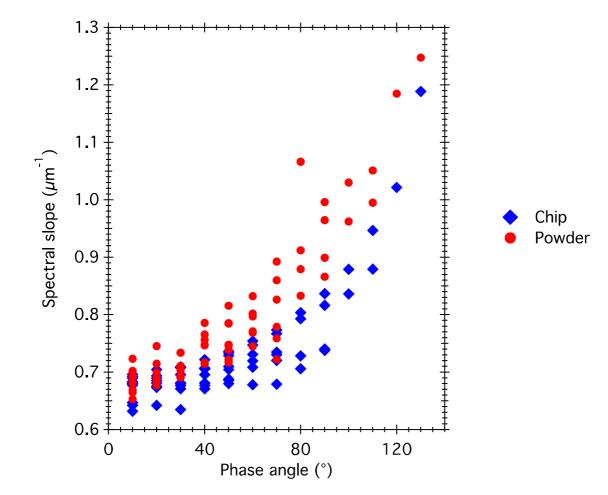
669
$$Spectral slope (\mu m^{-1}) = \frac{1}{1.5} \frac{\text{Reflec}_{2000 nm}}{\text{Reflec}_{500 nm}}$$

668

671

both sets of spectra.

670 The variation of the spectral slope with phase angle is displayed on Figure 15, for





673 **Figure 15: Effect of the phase angle on the spectral slope of the reflectance spectra**

674 **(spectral reddening) of the raw Mukundpura meteorite and its powder.**

675

The reflectance spectra of the powder are redder-sloped than the spectra of the

677 raw meteorite. At low phase angle, the raw meteorite spectra have a slope of 678 0.6721 ± 0.023 while the powder displays a slope of 0.6861 ± 0.021 . This value is averaged 679 over the 10 configurations with a phase angle of 10° and the error corresponds to the 680 standard deviation. At the largest phase angle studied, g = 130°, the slope of the **chip** 681 spectrum reaches 1.1885 ± 0.0064 compared to 1.2474 ± 0.0090 for the powder spectrum. 682

683 Previous investigations pointed out that the surface particle density and texture 684 can radically change the spectral slope from slightly blue to strongly red (Binzel et al. 685 2015; Britt and Pieters 1988). Cloutis, Hiroi, et al. (2011) showed that a change of 686 porosity applied to the same sample can induce a change in the spectral slope. But the 687 abundance of opaque minerals in the chondrite should not induce significant effects on 688 the spectral reddening (Cloutis, Hudon, et al. 2011). Several laboratory measurements 689 showed that larger grains also induce less red-sloped reflectance spectra (Binzel et al. 690 2015; Gillis-Davis et al. 2013; Johnson and Fanale 1973; Cloutis, Hudon, et al. 691 2011; Cloutis et al. 2013).

692

693 The variation of slope with the phase angle, i.e. the phase reddening, is 694 pronounced for both raw meteorite and powder. We found that the spectral slope does 695 not vary linearly with the phase angle and that the curve of spectral reddening is 696 different between the meteorite and the powder. In our case, the spectral reddening of 697 the powder is more pronounced at low phase angle but both samples reach roughly the 698 same value at high phase angles. The difference in porosity and granulometry between 699 the two samples induces changes in the spectral slopes. Recently, the analysis of phase 700 reddening has been used to highlight the presence of regolith at the surface of the 701 large boulders of Bennu (DellaGiustina et al. 2019).

5.3.2 Bidirectional dependency of the spectral slope The value of the spectral slope varies with increasing phase angle, as it has been measured for example by the Hayabusa spacecraft on the NEA Itokawa (Abe et al. 2006). Reflectance spectra of the asteroid acquired with a phase angle of 30° showed a spectral slope 6% redder than the spectra at 8° (Abe et al. 2006). This effect was also measured on the NEA (433) Eros, with an increase of the spectral slope reaching 11% between phase angles of 0° and 100° (Clark et al. 2002).

710

The spectral reddening is calculated for each sample as the ratio between the spectral slope at a given phase angle and the spectral slope at the lowest phase angle g available, so 10°.

714
$$Spectral Reddening = \frac{Spectral slope_{g}}{Spectral slope_{g=10^{\circ}}}$$

For the two types of surfaces and for each incidence angle, the spectral reddeningof the spectra is displayed in Figure 16.

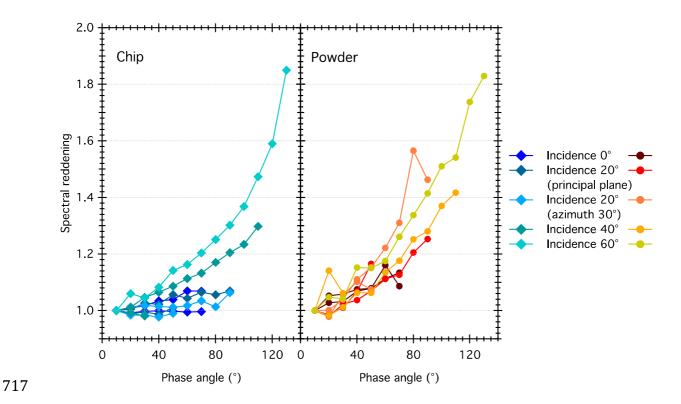


Figure 16: Spectral reddening of the reflectance spectra of the chip (left) and
ground (right) Mukundpura meteorite for each incidence angle.

721 Both samples show a dependence of the reddening, not only with phase angle but 722 also with incidence angle. For a phase angle of 70°, the reddening reaches 1.07±0.01 for 723 the **meteoritic chip** and 1.13±0.02 for the powder measured at nadir incidence, while it 724 reaches 1.20±0.01 for the **chip** and 1.26±0.01 for the powder for the same phase angle 725 but at incidence 60°. At low incidence angle ($\leq 20^\circ$) the spectral reddening of the **chip** 726 always remains weak (< 1.07) even at phase angle as high as 90°, while for the powder 727 the reddening increases steadily even at nadir illumination and is already larger than 1.2 728 at 80° phase angle. Conversely the spectral reddening seems to depend on the incidence 729 angle at all phase angles for the **chip**, while for the powder the effect is noticeable only 730 above 60°. Our observations reveal that spectral reddening could be used to detect the

presence, or absence of a **fine-grained** regolith on the surface of a small body by looking
at phase reddening at low incidence angle.

733

Neither the spectral slope nor the spectral reddening show a linear relation with
the phase angle, but rather an exponential dependence. MBAs can only be observed with
ground-based telescopes at phase angles smaller than 30°, where the reddening is
modest (between 1.01 and 1.06 for the powder sample and between 0.98 and 1.05 for
the raw meteorite). However, NEAs can be observed over a wider range of phase angles,
from opposition to 90° (Sanchez et al. 2012). In this configuration, the reddening of the
spectra can reach 1.46 for a dust-covered surface and 1.3 in case of a raw surface.

741

742 Particular attention to phase reddening should be given as the variation of spectral slope in asteroid observations is generally mainly attributed to space 743 weathering (irradiation by cosmic ions and micro-meteorites bombardment) (Hapke 744 2001; Chapman 2004; Clark et al. 2002). Several laboratory studies irradiated meteoritic 745 746 samples, either with ions or pulsed laser radiations, in order to reproduce the processes 747 occurring on airless bodies. Using the meteorite Epinal, (Strazzulla et al. 2005) showed 748 that ion irradiation increases the spectral slope by a factor of 6 and, comparing the 749 experimental results with spectra of several NEAs, evaluated the timescale for 750 weathering the near-earth asteroids between 10^4 and 10^6 years. (Sanchez et al. 2012) 751 measured reflectance spectra on three ordinary chondrites and found that an increase of 752 30° to 120° of phase angle can mimic the reddening of the reflectance spectrum induced by 0.1x10⁶ to 1.3x10⁶ years of irradiation at 1AU from the Sun. So in case of NEAs, the 753 754 geometry of observation can induce the same reddening of the spectra as space 755 weathering.

757 6 CONCLUSION

Laboratory reflectance spectroscopy can help understand the specificities of Ccomplex NEAs observations when compared to C-type MBAs. We have shown that temperature, surface texture, as well as observation geometry (incidence, emergence and azimuth angle) can all have an impact on reflectance spectra. When comparing **chips** and powdered samples, we found that:

-Both samples display spectral signatures of hydration and thus the absence, or
presence, of a **fine-grained** regolith at the surface cannot explain the lack of hydrated
NEAs.

Dust covered surfaces are expected to be darker than rock covered surfaces
because of the apparent homogeneity of the composition of the powder compared to the
heterogeneity of the surface of the raw meteorite clearly displaying clasts and inclusions
inside a dark matrix.

-BRDF analysis of the two samples shows that the **powdered sample** presents
stronger forward scattering and backscattering lobes compared to the raw meteorite.
This is due to the SHOE, increased by the rougher texture of the powder.

-Absorption features appear fainter in the case of the raw sample, due to the
higher amount of photons being scattered out of the surface before having entered the
sample. Following this result, absorption features should be more difficult to detect on
surfaces lacking **fine-grained** regolith, i.e. rubble pile NEAs.

At large phase angle, the reflectance spectra of the **powdered sample** present a
steeper spectral slope compared to the measurement on the **chip**.

-Spectral reddening of the powder appears relatively insensitive to the incident
angle while for the raw meteorite at a given phase angle, the reflectance spectra are
redder when the illumination approaches grazing incidence.

782

783 The surface temperature experienced by NEAs can have an effect on their 784 spectral signatures. The temperature affects the reflectance spectra of a meteorite, 785 mostly by modifying the depth, position and width of the iron features around 700nm 786 and 900nm. Our measurements show that at laboratory timescale, irreversible 787 alterations of the sample can be induced by only one heating-cooling cycle, simulating 788 successively the sunrise and sunset on the surface of the small body. The hydration 789 feature at 3µm becomes fainter but is still detectable on the reflectance spectra. 790 However, our series of measurements after a single thermal cycle at high temperature 791 do not allow us to make any assumption on the possible disappearance of the features 792 after numerous cycles of heating and cooling. Further investigations of these irreversible 793 alterations are currently conducted.

794 Several effects due to the geometrical configuration of observation have been 795 highlighted by our measurements. First, carbonaceous chondrites do not behave as a 796 lambertian surface in the VNIR. Second the spectral slope and the depths of the 797 absorption features are impacted by the direction of illumination and the emergence 798 angle. Most importantly, our results show that in the case of the raw meteorite the 799 hydration signatures in the visible range disappear from the reflectance spectra at large 800 phase angle. Keeping in mind that NEAs can be observed at larger phase angles 801 compared to MBAs, and that their surfaces seem depleted in **fine-grained** regolith, this 802 geometry effect could also contribute to the apparent dehydration of NEAs.

803

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