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# Hydroxylated Mg-rich amorphous silicates: a new component of the 3.2 $\mu\text{m}$ absorption band of comet 67P/Churyumov-Gerasimenko

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## ABSTRACT

The VIRTIS imaging spectrometer aboard Rosetta has shown that the nucleus surface of comet 67P/Churyumov-Gerasimenko (67P/CG) is characterized by a broad absorption band at around 3.2  $\mu\text{m}$ . The feature is ubiquitous across the surface and its attribution to (a) specific material(s) has been challenging. In the present paper, we report an experimental investigation showing that the interaction of hydrogen atoms with Mg-rich amorphous silicates determines the formation of hydroxyl groups. The resulting IR spectrum exhibits a broad feature around 3.2  $\mu\text{m}$  similar to that of comet 67P/CG. Hapke's radiative transfer model was employed to estimate an upper limit contribution of 65% of hydroxylated silicates to the observed cometary band intensity. The presence of a hydroxylated fraction in silicates on the cometary surface would represent an evolutionary link between primitive objects of the solar system and dust in the interstellar medium (ISM), where silicate grains can be hydroxylated after having interacted with hydrogen atoms. This link is consistent with the detection of the aliphatic organics in 67P/CG that also originate in the ISM.

**Keywords:** astrochemistry — comets:general — methods:laboratory:atomic processes — techniques:spectroscopic

## 1. INTRODUCTION

The payload instruments on-board ESA's Rosetta mission have observed the evolution of the Jupiter-family comet 67P/Churyumov-Gerasimenko (67P/CG) in a period from August 2014 to September 2016 and encompassing the perihelion passage occurring in August 2015 at a heliocentric distance of 1.24 AU. The data

collected have provided unprecedented spatial, spectral and temporal coverage of the changes occurring on a cometary surface and surrounding inner coma before, during and after perihelion passage (Taylor et al. 2017). Determining the nucleus surface composition was one of the primary scientific objectives of the Visible, Infrared and Thermal Imaging Spectrometer (VIRTIS) (Coradini et al. 2007).

When observed at global scale, the 67P/CG surface appears dominated by a dust layer, remarkably uniform in composition. The overall spectral reflectance is characterized by a low albedo (0.06) and red slope at visible

wavelengths while a wide absorption band centered at  $3.2\ \mu\text{m}$  is a distinctive feature in the infrared range (Cappacconi et al. 2015; Ciarniello et al. 2015). Temporal and spatial spectral variability at global scale has been observed on the 67P/CG surface (Ciarniello et al. 2016) in addition to spatial variations on meter-sized scales where color changes have been correlated with surface composition inhomogeneities and active sources (Filacchione et al. 2019). In particular, local water ice enrichments show higher albedo and flat-to-blue spectral response in contrast to the more dark and red reflectance typical of the other areas. The lack of the  $1.5$  and  $2.0\ \mu\text{m}$  ice absorption bands in the typical dark areas indicates a very dehydrated surface with the water ice abundance  $<1\%$  on average (Raponi et al. 2016). Although the surface appears dehydrated at global scales, crystalline water ice has been spectroscopically identified at infrared wavelengths on specific areas of the nucleus during the pre-perihelion phase (De Sanctis et al. 2015; Filacchione et al. 2016a; Barucci et al. 2016). Also  $\text{CO}_2$  ice has been detected for the first time on a cometary nucleus surface by VIRTIS in a small area located in the meridional Anhur region (Filacchione et al. 2016b).

The most striking spectral feature is the broad band between  $2.8$  and  $3.6\ \mu\text{m}$  centered at  $3.2\ \mu\text{m}$ , whose attribution is challenging. The band falls in a spectral region where the contribution to the absorption of X-H stretching vibrations in different functional groups is expected. C-H vibrations in aliphatic and aromatic C bonding have recently been established as sub-structures of the observed absorption band in newly calibrated VIRTIS spectra (Raponi et al. 2020). O-H vibrational modes in water ice, structural water or chemisorbed hydroxyl groups absorb from  $2.7$  to  $3.1\ \mu\text{m}$  but cannot explain the entire feature. Quirico et al. (2016) suggested several possibilities, OH groups in carboxylic acids inserted in a macromolecular organic solid and  $\text{NH}_4^+$  (ammonium) ions were proposed as plausible candidates to encompass the broad width of the cometary feature. More recently on the basis of laboratory experiments, the  $3.2\ \mu\text{m}$  band and some of its sub-features have been interpreted to be ammonium ( $\text{NH}_4^+$ ) salts (such as ammonium formate, sulfate, citrate) mixed with dark cometary surface material (Poch et al. 2020).

Silicates, together with powders of coal and iron sulfides, have been used to model the red visible and near infrared slope and low albedo of 67P/CG (Rousseau et al. 2018). Detection in the coma of a mineral phase, predominantly composed of silicates and carbonaceous components, was carried out by the COSIMA experiment aboard Rosetta (Bardyn et al. 2017). The presence of silicates in comets was first reported by Bregman

et al. (1987) and later confirmed by Campins & Ryan (1989) in comet 1/Halley and by Crovisier et al. (1997) in Hale-Bopp (C/1995 O1). During their journey from the birth sites around evolved stars through interstellar medium to comets, silicates interact with ions (mainly protons), which induce many effects such as amorphization, sputtering and implantation with the formation of OH groups (Demyk et al. 2001, 2004; Carrez et al. 2002; Jäger et al. 2003a; Brucato et al. 2004; Djouadi et al. 2005). The abundance of amorphous silicates in ISM is 98 % with respect to the crystalline counterpart, whereas the abundance varies between 70-98 % for Jupiter family comets (Sugita et al. 2005). Furthermore, the silicates are primarily Mg-rich e.g. Kelley et al. (2017). Direct evidence of silicate processing by ions has come from analysis of Interplanetary Dust Particles (IDPs) (Bradley 1994; Bradley et al. 1999, 2005). During their journey, silicates can also interact with hydrogen atoms both in diffuse and dense regions of the ISM.

In this paper, we experimentally investigate the consequence of the interaction of H atoms with analogues of interstellar silicate grains. Hydrogen atoms, with an energy of a few tens of meV, form hydroxyl groups in Mg-rich amorphous silicates with different Mg/Si ratios. The resulting IR spectrum is characterized by a broad absorption band centered at  $3.2\ \mu\text{m}$  similar to the one observed in 67P/CG spectrum.

## 2. EXPERIMENTS AND RESULTS

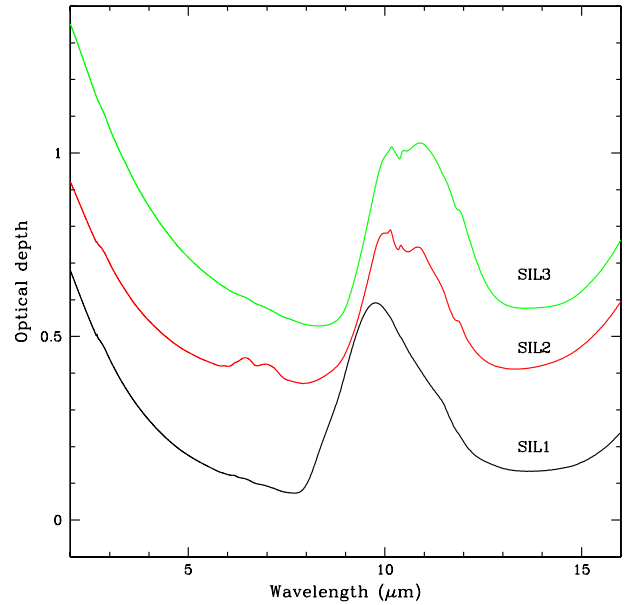
Hydroxylation of silicates has been reproduced in controlled laboratory conditions. The amorphous silicates were produced using a Nd-YAG solid state pulsed laser at  $1024\ \text{nm}$  equipped with II and IV harmonics at  $532$  and  $266\ \text{nm}$ , respectively. By using a focusing lens, the power density on the target was measured by LaserMate-P power meter (Coherent) to be  $1 \times 10^8\ \text{W cm}^{-2}$ . The target to be ablated was mounted inside a chamber, filled with a  $10\ \text{mbar}$  Ar atmosphere, on a rotating sample holder placed in front of the laser beam. Silicate grains were collected at a distance of  $5\ \text{cm}$  from the target on ZnSe windows and carbon stubs, respectively, for IR spectroscopy and electron microscopy. We have used pellets made out of oxide mixtures in two different proportions ( $\text{MgO}:\text{SiO}_2$  in a 1:1 and 2:1 mixture) and a natural forsterite olivine (dunite, Webster-Addie, N. Carolina, acquired from Wards Science) as targets. The oxide mixtures were prepared by weighing the exact amounts of MgO and  $\text{SiO}_2$  in order to have the starting stoichiometric composition of enstatite ( $\text{MgSiO}_3$ ) for the first sample (SIL1) and forsterite ( $\text{Mg}_2\text{SiO}_4$ ) for the second sample (SIL2). The mixtures were produced in the

**Table 1.** Atomic ratios of silicates produced by laser ablation period

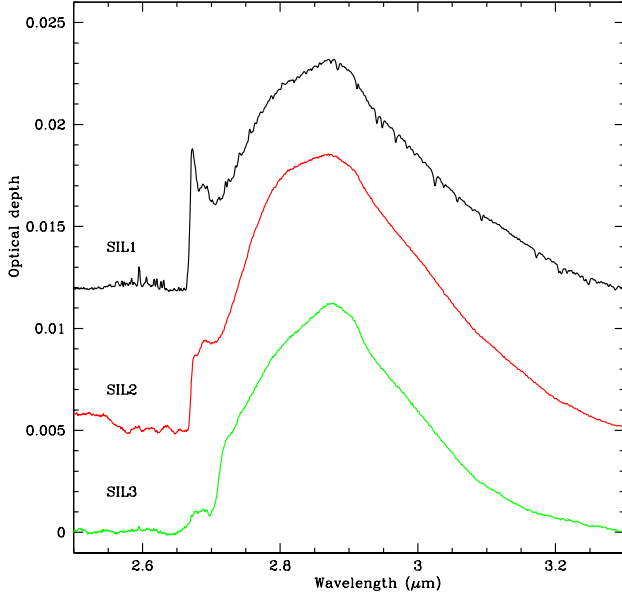
Sample name	Starting material	Measured ratios	
		Mg/Si	Fe/Si
SIL1	MgO:SiO <sub>2</sub> (1:1)	1.1	–
SIL2	MgO:SiO <sub>2</sub> (2:1)	1.7	–
SIL3	Natural Olivine	1.7	0.2

form of pellets (13 mm in diameter and a few millimeters in thickness) by pressing finely ground oxides at 10 tons. The third sample (SIL3) was prepared from natural olivine target. The three silicates (SIL1, SIL2 and SIL3) prepared in the present work are listed in Table 1. The chemical composition resulting from the process of vaporization and condensation was analysed with an Electron Dispersive X-ray (EDX) system (Oxford Inca Energy 350) linked to a Field Emission Scanning Electron Microscope (FESEM) (ZEISS SUPRA 25). The FESEM images show that mainly a fluffy structure of amorphous grain aggregates characterizes the morphology of the silicate samples. For a detailed characterization of texture, grain dimension and size distribution of the samples see Rotundi et al. (2000). The atomic ratio of the samples obtained by EDX is also reported in Table 1. Taking into account the variations due to non-homogeneity of the samples, the Mg/Si ratio is in agreement with the corresponding value of the starting oxide mixtures for SIL1, while it is slightly lower in the case of SIL2. The values,  $\text{Fe/Mg} = 0.11$  and  $(\text{Mg}+\text{Fe})/\text{Si} = 1.9$ , indicate that the composition of the sample obtained from natural olivine (SIL3) is Mg-rich.

Figure 1 shows the optical depth spectra of the silicates acquired with a Fourier Transform Infrared (FTIR) spectrometer (Bruker Equinox 55). Spectra acquisition was performed in air at room temperature, in the range 2–16  $\mu\text{m}$  at a spectral resolution of 2  $\text{cm}^{-1}$ . The spectra are characterized by a strong band around 10  $\mu\text{m}$  due to the Si-O stretching mode, whose profile slightly varies with the sample composition. The band is centered at 9.8  $\mu\text{m}$  for SIL1 and it shifts to 10.2  $\mu\text{m}$  as the Mg/Si ratio increases (for SIL2 and SIL3 samples). In the latter cases, an additional band at around 10.8  $\mu\text{m}$  is also evident. Jäger et al. (2003b) also reported a similar redshift in the band position with increasing MgO/SiO<sub>2</sub> ratio in their amorphous magnesium silicate samples, prepared by the sol-gel method. The absorption increase for wavelengths longer than 13  $\mu\text{m}$  is due

**Figure 1.** Infrared spectra of the silicates reported in Table 1. The spectra of SIL2 and SIL3 are offset in ordinate by 0.3 and 0.5, respectively.

to the low energy wing of the Si-O bending feature at around 20  $\mu\text{m}$ . The small double band at 6.5 and 7  $\mu\text{m}$ , more intense in the case of SIL2, is caused by traces of magnesium carbonate, formed during sample preparation (Jäger et al. 2003b). Figure 2 shows the silicate infrared spectra in the 3  $\mu\text{m}$  spectral range after continuum removal. A broad band centered at 2.88  $\mu\text{m}$ , produced by adsorbed water and chemisorbed hydroxyl groups, due to ambient contamination during the sample handling at the time of pellet preparation and also at the time of laser ablation, characterizes this region. Two narrow bands at 2.67  $\mu\text{m}$  and 2.69  $\mu\text{m}$  are respectively attributed to isolated Si-OH and Mg-OH groups (Iler 1979; Shinoda et al. 2002). Their relative intensity varies according to the Mg/Si ratio. In the case of SIL3, produced from natural olivine, only a weak band, resulting from the blend of the two features, is observed. Similar bands have been detected in silicates produced by the sol-gel method (Jäger et al. 2003b), suggesting that laser ablation and sol-gel techniques provide materials with chemical properties expected for cosmic silicates. In fact, the formation of silicates in space with a small content of isolated Si-OH and Mg-OH bonds can be considered highly probable, since H<sub>2</sub>O, the most abundant oxygen-bearing molecule, participates in the formation of olivine and pyroxene-type silicates around evolved stars (Gail & Sedlmayr 1998; Jäger et al. 2003b).



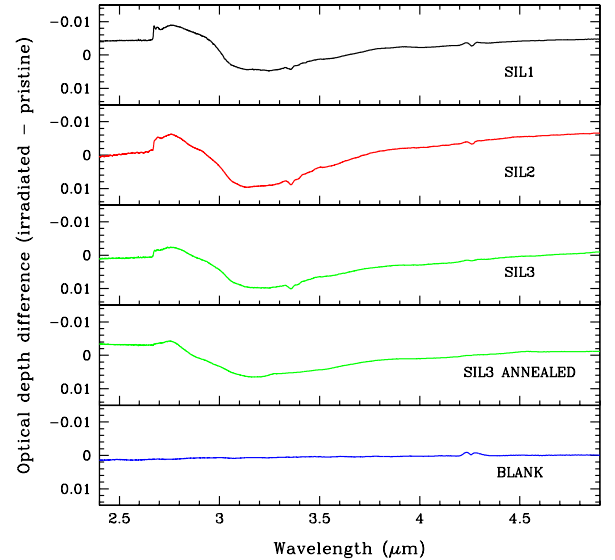
**Figure 2.** Infrared spectra, after continuum removal, of the silicates reported in Table 1 in the 2.5 - 3.3  $\mu\text{m}$  range. The spectra of SIL2 and SIL1 are offset in ordinate by 0.006 and 0.012, respectively.

To study the interaction of hydrogen with silicates, our samples were placed inside a vacuum chamber, with a base pressure of  $2 \times 10^{-8}$  mbar, on a rotating sample holder at the right angle intersection between an atomic hydrogen beam and the IR beam of an FTIR spectrophotometer (Bruker Vertex 80). H atoms were produced by microwave dissociation of molecular hydrogen; they have a Maxwellian velocity distribution at 300 K (Mennella 2006). After H atom exposure, the sample was rotated by  $90^\circ$  to face the IR beam, and we measured the IR spectrum with a resolution of  $2 \text{ cm}^{-1}$  in the range 2-5  $\mu\text{m}$  ( $5000\text{--}2000 \text{ cm}^{-1}$ ). For any spectral measurement of the silicate before and after irradiation, a background was acquired. Figure 3 shows the spectral changes, obtained by subtracting the pre-irradiated spectrum from the irradiated one, induced by H atom irradiation in amorphous silicates. The activation of a broad band centered at about 3.2  $\mu\text{m}$  takes place in all the silicates. At shorter wavelengths, an absorbance decrease in the irradiated sample (resulting in a negative optical depth difference in Figure 3) centered at 2.76  $\mu\text{m}$  (broad band) and bands at 2.67 and 2.69  $\mu\text{m}$  (sharp doublet) are observed. This behavior indicates that the H atoms induced a depletion of the O-H bonds already present in the starting silicate samples.

In addition, a weak feature at 3.36  $\mu\text{m}$  with a shoulder at 3.39  $\mu\text{m}$  is possibly due to asymmetric C-H stretching

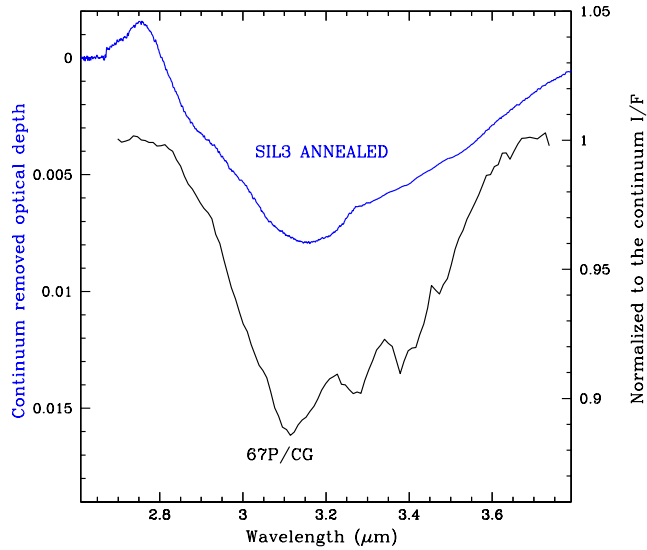
modes of aliphatic  $\text{CH}_3$  and  $\text{CH}_2$  groups. They originated from processing of carbonate, also present as substructure of the broad 3.2  $\mu\text{m}$  band. The faint feature at around 4.25  $\mu\text{m}$  is associated to uncompensated ambient  $\text{CO}_2$ . Irradiation of a blank ZnSe substrate with hydrogen (see Figure 3) does not induce any variation in the spectrum, demonstrating that the observed spectral changes are due to the interaction of hydrogen with silicate grains.

To investigate whether the presence of OH groups in the pristine silicates affects their interaction with hydrogen, we tried to eliminate/reduce them by annealing one of the samples (SIL3) at  $300^\circ\text{C}$  for 1 hour before exposure to H atoms. In the case of the annealed SIL3, only a small absorbance decrease centered at 2.76  $\mu\text{m}$  is present after hydrogen irradiation (see Figure 3), testifying that the starting sample was almost fully depleted of the chemisorbed hydroxyl groups. Despite that, the activation of the 3.2  $\mu\text{m}$  band does not vary. Hydroxylation of Mg-rich amorphous silicates by H atoms is therefore independent of the OH groups already present in silicates and of the specific composition of the samples.

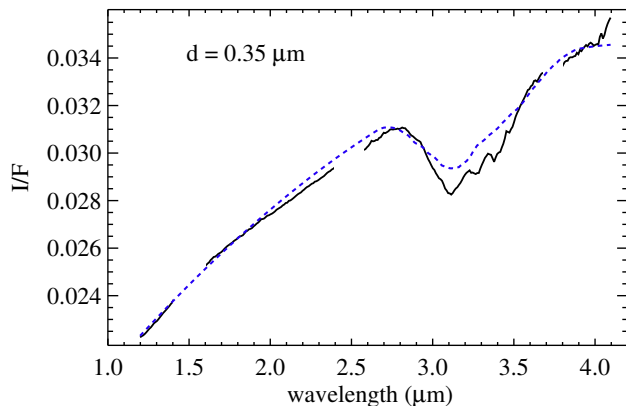


**Figure 3.** Spectral changes of silicates upon irradiation (shown after subtraction of the initial spectrum) of  $1 \times 10^{18}$  H atoms  $\text{cm}^{-2}$ . The spectrum of an irradiated ZnSe window (blank) after an irradiation is also reported for comparison. The feature at around 4.25  $\mu\text{m}$  is associated to uncompensated ambient  $\text{CO}_2$ . Note that vertical is inverted and therefore absorbance increases downwards.





**Figure 4.** Qualitative comparison of 3.2  $\mu\text{m}$  absorption band in SIL3 (blue line) first annealed at 300°C and then irradiated with  $1 \times 10^{18}$  H atoms  $\text{cm}^{-2}$  to the observed absorption band in the 67P/CG reflectance spectrum (black line). The left vertical axis is for the SIL3 spectrum whereas the right vertical axis refers to that of the cometary band.



**Figure 5.** Fit to the average 67P/CG reflectance spectrum (black line, [Raponi et al. \(2020\)](#)) by the modeled hydroxylated amorphous silicate mixed with the dark-red end-member (blue dashed line) using Hapke’s model for 5  $\mu\text{m}$  grain size and 15% of hydroxylated amorphous silicate abundance. See the Appendix for the meaning of  $d$  and other parameters.

### 3. DISCUSSION AND CONCLUSIONS

The spectral variations induced in Mg-rich silicates by atomic hydrogen are clear evidence for chemical reac-

tions producing hydroxyl groups on silicates. According to density functional quantum mechanical calculations, the formation of OH groups in Mg-rich silicate nanoclusters by impinging H atoms takes place without any significant energy barrier ([Kerkeni et al. 2017](#)). Moreover, the observed spectral evolution with H atom irradiation suggests that exchange reactions (abstraction and addition of H atoms in OH) are active. The equilibrium value for the number of OH groups depends on the cross section of the abstraction and addition processes. Consequently, an absorbance decrease as in the region of the bands at 2.76  $\mu\text{m}$  (broad band) and 2.67 and 2.69  $\mu\text{m}$  (sharp doublet) indicates a net reduction in the number of available OH bonds due to abstraction of H atoms already bonded to these groups. At longer wavelengths the exchange reactions induced by H atoms determines, as a net result, the formation of an absorption band; this is the case for the observed broad 3.2  $\mu\text{m}$  band.

Formation of OH bonds with a peak at around 2.8  $\mu\text{m}$  has been reported after implantation of keV to MeV energy range protons in silicates with different composition and structure (e.g. [Zeller et al. \(1966\)](#); [Djouadi et al. \(2011\)](#); [Schaible & Baragiola \(2014\)](#)). Exchange of H/D in hydroxyl groups has also been observed after 1.1 keV  $\text{D}^+$  implantation of Apollo lunar soils ([Ichimura et al. 2012](#)). Hydroxylated silicates produced by proton implantation have also been considered as a potential reservoir of water during the formation of terrestrial planets ([Djouadi et al. 2011](#)).

There are two substantial differences between the present work and previous implantation experiments. The first one concerns the interaction energy. Unlike proton implantation in silicates, where ions with high energy have been considered, the present experiments show the possibility to hydroxylize amorphous silicates via reactions with thermal (a few tens of meV) hydrogen atoms. This result extends the possibility to hydroxylate silicates in different environments: from the interstellar medium (ISM), where atomic hydrogen (10–100 K) is abundant, to the surface of airless planetary bodies (solar protons) such as the Moon.

The second difference is in the width of the band around 3.2  $\mu\text{m}$ . In the present experiments, it is much wider than that obtained by proton implantation due to multiple and independent overlapping absorption of hydroxyl groups. These groups are formed by hydrogen atom interaction on amorphous silicate defects, which determine a wider range of binding sites enhancing both physisorption and chemisorption of hydrogen.

The profile of the band formed by H atoms in the considered silicates (see Figure 3) is reminiscent of the 3.2  $\mu\text{m}$  absorption band in the reflectance spectrum of

67P/CG observed by VIRTIS onboard Rosetta (Raponi et al. 2020). Figure 4 shows the comparison of the cometary profile with that of annealed SIL3. The similarity in profile suggests that OH groups of hydroxylated amorphous silicates can be a constituent of the 67P/CG nucleus surface, together with aliphatic carbons, ammonium salts, water ice and possibly PAHs, Polyphenols (Quirico et al. 2016; Carlson et al. 2020; Poch et al. 2020; Raponi et al. 2020).

To quantitatively evaluate the spectral contribution of hydroxylated amorphous silicate to the  $3.2\ \mu\text{m}$  band, we have modeled the average reflectance (I/F) spectrum of the comet 67P/CG surface with a similar approach already used to estimate the spectral contribution of water ice (Raponi et al. 2020). The Hapke radiative transfer model (Hapke 2012) was adopted to calculate the reflectance of an intimate mixture of hydroxylated amorphous silicate with a synthetic continuum representing a dark-red terrain. Model fits to the average 67P/CG reflectance spectrum indicate that hydroxylated silicate can reproduce on average 65% of the  $3.2\ \mu\text{m}$  cometary band intensity with an abundance of hydroxylated amorphous silicate of 15%. An example of the resulting modeling is shown in Figure 5. For more detail see Table 2 and Figure 9 in the Appendix. The estimated contribution should be considered as an upper limit due to the involved assumptions (see Appendix). It is worth stressing that for an accurate quantitative estimation, one should also consider the contributions of the other proposed carriers of the  $3.2\ \mu\text{m}$  band as mentioned above.

The presence of a hydroxylated fraction in silicates on the surface of a comet can represent an evolutionary link between a primitive object of the solar system and dust in the ISM. The spectral homogeneity of the nucleus surface observed by VIRTIS indicates that the composition of the refractory surface materials does not change despite the rejuvenating processes active during the perihelion passages of 67P/CG (Ciarniello et al. 2016). The refractory material seen at the surface must be then representative of the bulk pristine material of the nucleus.

As for all cosmic dust, silicates participate in the life cycle of matter that brings dust from their circumstellar birth sites to the diffuse interstellar medium and dense clouds where stars form. The formation of planetary systems, like our solar system, can also take place during this cycle. Since silicates are involved in the global evolution of the interstellar matter, from diffuse medium to comets, they interact with hydrogen atoms in the ISM. The laboratory H atom fluence of  $1 \times 10^{18}\ \text{atoms cm}^{-2}$  used in the present experiments as reported in Figure 3 corresponds to an H atom exposure time of  $4 \times 10^3$  and  $4 \times 10^5$  years, respectively, in interstellar diffuse and dense regions (considering the respective H atom flux of  $8 \times 10^6$  and  $9 \times 10^4\ \text{atoms s}^{-1}\ \text{cm}^{-2}$  for these regions, Mennella (2010)). In addition, we observed the formation of the  $3.2\ \mu\text{m}$  band already at a lower fluence of ca.  $10^{16}\ \text{atoms cm}^{-2}$ . Therefore, hydroxylation can take place on a much shorter time scale compared to the residence time of  $3 \times 10^7$  years of dust grains in both dense and diffuse regions of the ISM. However, for a complete understanding of the degree of hydroxylation of the silicates in different regions of the ISM, we also need to know the effects of the dehydrogenation processes induced by energetic processing such as by UV photons and cosmic rays.

The evolutionary link suggested by the present results is consistent with the detection of the aliphatic matter in 67P/CG (Raponi et al. 2020). We thus can trace for both aliphatic carbon and hydroxylated amorphous silicates a common origin in the ISM during the journey of the dust from its birth-sites around evolved stars to our solar system.

## ACKNOWLEDGMENTS

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## APPENDIX

### A. MODELING OF THE SPECTRAL CONTRIBUTION OF HYDROXYLATED SILICATES TO THE $3.2\ \mu\text{m}$ FEATURE OF 67P/CG

We apply the Hapke model (Hapke 2012) to derive an upper limit of the amount of hydroxylated Mg-rich amorphous silicates contributing to the  $3.2\ \mu\text{m}$  band in-

tensity of 67P/CG (Raponi et al. 2020). To this aim, 67P/CG’s surface is modeled as an intimate mixture of a featureless dark-red synthetic component, representing predominantly the optically opaque phases in the comet regolith, and a hydroxylated Mg-rich amorphous silicate. The spectral output of the featureless end-member is modeled as a continuum by means of a 2nd degree polynomial, while for the hydroxylated Mg-rich amor-

phous silicate material, synthetic optical constants have been computed. Upon H atom irradiation, the optical properties of the amorphous silicates are modified by formation of the absorption feature centered at  $3.2 \mu\text{m}$ . This effect can be interpreted as an increase of the value of the imaginary part of the refractive index  $k$ ,  $\Delta k$ , in correspondence to the  $3.2 \mu\text{m}$  absorption feature. To estimate  $\Delta k$ , we represent the contribution of OH groups formed on the fluffy and amorphous grain aggregates in consideration by assuming a homogenous film of hydroxylated amorphous silicate of equivalent thickness  $d$ . Then the measured optical depth difference (irradiated - pristine) can be expressed as:

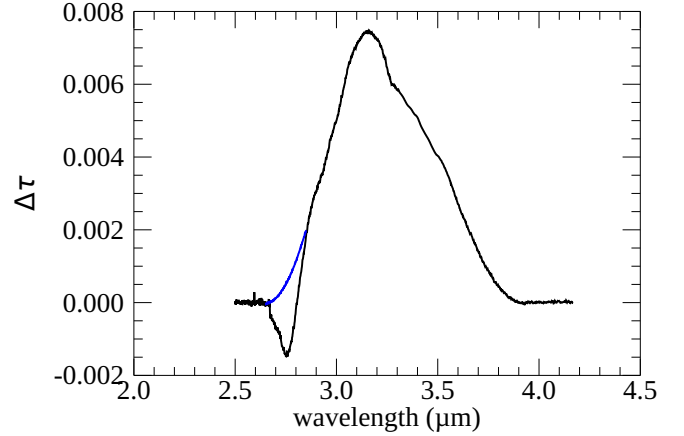
$$\Delta\tau(\lambda) = \frac{4\pi}{\lambda} d \Delta k. \quad (\text{A1})$$

The equivalent thickness  $d$  can be derived from the integrated optical depth through the following relation:

$$\int_{\text{band}} \Delta\tau(\nu) d\nu = NA = \frac{\rho d N_A}{m} A, \quad (\text{A2})$$

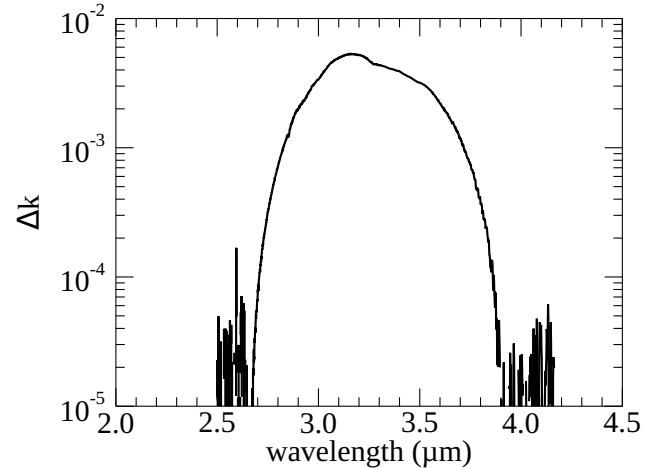
where  $N$  is the column density,  $A$  is the integrated band strength and  $N_A$  is Avogadro's number.  $\rho$  and  $m$  are the density and the molecular weight of the film, respectively. We evaluated the integral in the left hand term of Eq. A2 from the annealed SIL3 reported in Figure 6 and adopt  $A = 2 \times 10^{-17} \text{ cm molecule}^{-1}$ , as in the case of the OH groups in natural olivine (Schaible & Baragiola 2014). Moreover, we assumed  $\rho = 1 \text{ g cm}^{-3}$  and  $m = 101 \text{ g mol}^{-1}$  for hydroxylated silicate film with a starting silicate stoichiometry as  $[\text{MgO.SiO}_2]$ . We obtain a starting value of  $d = 0.35 \mu\text{m}$ . It is then possible to derive the corresponding increase of the imaginary part of the refractive index from Eq. A1 as seen in Figure 7. To see how the final results are affected by our assumptions, we also varied  $d$  by a factor of 10 higher and lower, reflecting possible uncertainties in the assumptions on  $A$ ,  $\rho$  and  $m$ .

Since the H atom processing of Mg-rich amorphous silicates does not lead to variations of the absorption spectrum outside the  $3.2 \mu\text{m}$  band, it is reasonable to assume the imaginary part of the refractive index  $k_b$  of the unprocessed silicate as a baseline. However, optical constant values of the unprocessed silicates analyzed in the present work are missing. Therefore, we adopted the optical constants of similar silicates. The choice is further justified by the fact that H atom irradiation modifies different Mg-rich amorphous silicates in a similar way, as also evidenced by the reported measurements. We considered real and imaginary parts of optical constants of Mg-rich glass from Dorschner et al. (1995). Further, to incorporate the effects of H atom processing on the



**Figure 6.** Optical depth difference (after continuum removal) for annealed SIL3. As mentioned in the text, the H atom irradiation process abstracts H atoms in OH groups already present in the sample, introducing a spurious negative signature in the  $\Delta\tau$  spectrum between  $2.65$  and  $2.85 \mu\text{m}$ . To eliminate this spurious signature, we discard the measurement in this range and replace it by a polynomial (blue segment) that connects the part of the optical depth difference spectrum shortward of  $2.65 \mu\text{m}$  with the region longward of  $2.85 \mu\text{m}$ .

optical constants, a synthetic imaginary part of the refractive index  $k_s = k_b + \Delta k$  is derived as shown in Figure 8, for the Mg-rich glass for different values of  $d$ .



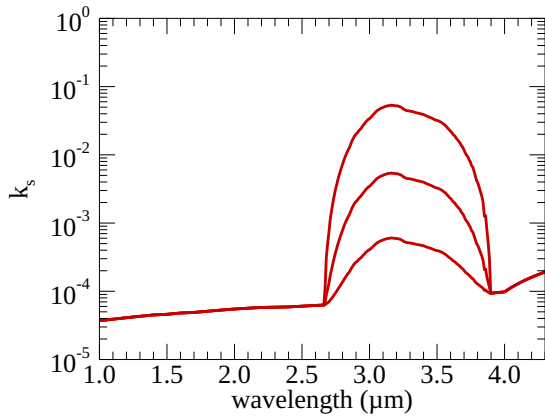
**Figure 7.**  $\Delta k$  as a function of wavelength for  $d = 0.35 \mu\text{m}$ .

For each synthetic refractive index values, a fit to the 67P/CG spectrum is performed in a similar way as Raponi et al. (2020) did for water ice. We forced the



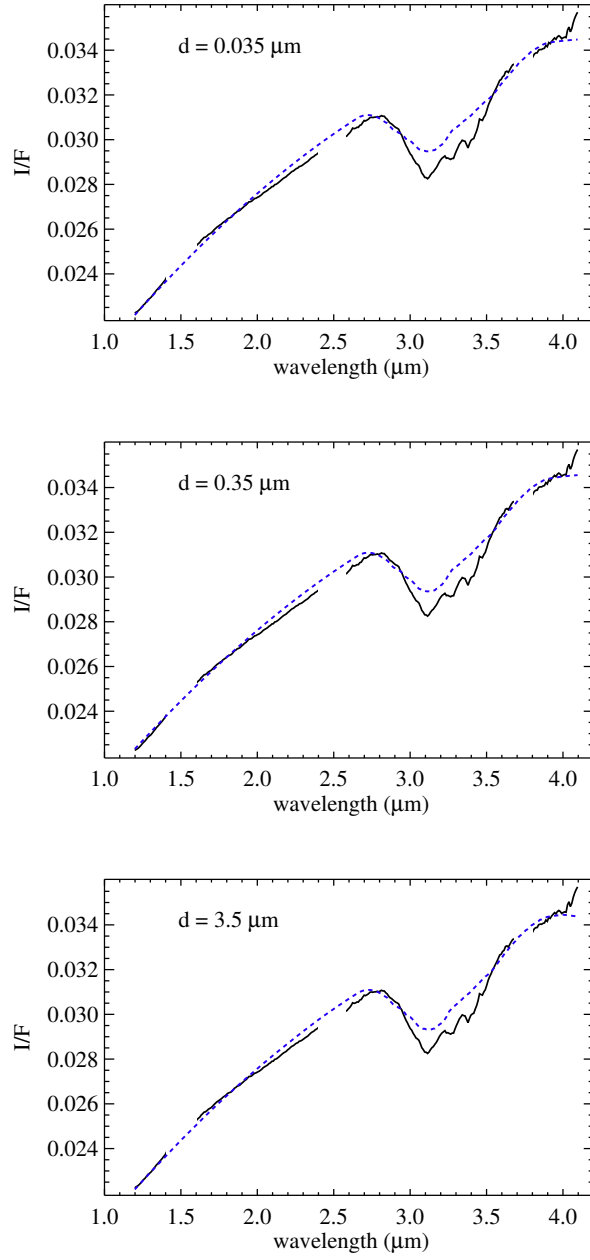
**Table 2.** Best fit parameters ( $R$ ,  $S$ ) of the model to the average reflectance spectrum of 67P/CG.

Equivalent film thickness $d$ $\mu\text{m}$	Hydroxylated silicate abundance $R$	Grain size $S$ $\mu\text{m}$	Fraction of the $3.2 \mu\text{m}$ band intensity due to hydroxylated silicates $F$
0.035	0.15	0.5	0.62
0.35	0.15	5	0.66
3.5	0.15	50	0.67

**Figure 8.** Imaginary part of the synthetic refractive index derived by using Mg-rich glass as baseline. The three curves represent the different values of  $k_s$  obtained for  $d$  values of 0.035, 0.35 and  $3.5 \mu\text{m}$  from top to bottom, respectively.

larger  $d$ , thus producing a smaller absorption for a given grain size. Given this, in order to reproduce the observed spectral contrast, a larger value of  $S$  is required in the modeling. One should note that a rigorous application of the Hapke’s model would limit its application to the geometric optics regime, where particles are larger than wavelength. This is the case for the derived value of  $S = 0.5 \mu\text{m}$  which implies that small particle sizes (likely sub- $\mu\text{m}$ ) are required to match the observed spectrum with the adopted set of optical constants.

fit to match the continuum level of the cometary spectrum in the range between  $2.7\text{--}2.9 \mu\text{m}$  and  $3.5\text{--}3.6 \mu\text{m}$  to ensure that the modeled absorption is not more intense than the one shown by 67P/CG. The best fits to the 67P/CG spectrum are reported in Figure 9 while the best fit parameters i.e. the amount of hydroxylated silicates with respect to dark-red terrain,  $R$ , and the corresponding grain size,  $S$ , are listed in Table 2. Note that  $R$  values reported in Table 2 represent the corresponding fractional cross section seen by the light propagating within the medium. These quantities can be interpreted as volumetric abundances under the assumption that the featureless dark-red terrain has the same grain size as the hydroxylated silicate. The derived  $R$  values are constant at 0.15, and  $F$  is very similar for the three cases with an average value of around 0.65. Conversely, the obtained  $S$  values increase with  $d$ . This can be explained by the fact that  $\Delta k$  as obtained from Eq. A1 is lower for



**Figure 9.** From top to bottom: best fits (blue dashed lines) to average 67P/CG reflectance spectrum (black lines) obtained with synthetic optical constants computed using Mg-rich glass (Dorschner et al. 1995) as baseline for different values of  $d$ .

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