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## Title: 67P/Churyumov-Gerasimenko: The Organic-rich surface of a Kuiper Belt comet as seen by VIRTIS/Rosetta

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Abstract: The Visible, InfraRed and Thermal Imaging Spectrometer (VIRTIS) on board Rosetta, now at comet 67P/Churyumov-Gerasimenko, has provided the first evidence of carbon-bearing species on a cometary nucleus as well as spatially resolving compositional variations across its surface. The very low reflectance of the nucleus (computed normal albedo of  $0.060 \pm 0.003$  at  $0.55~\mu m$ ) as observed by VIRTIS coupled with distinct spectral slopes in VIS and IR ranges (respectively 5-25% kÅ<sup>-1</sup> and 1.5-5% kÅ<sup>-1</sup>) suggests the presence of macromolecular carbon-bearing compounds in association with some opaque minerals. A very broad absorption is seen in the 2.9-3.6  $\mu m$  range across the entire illuminated surface. This is compatible with nonvolatile organic macromolecular materials, indicating a complex mixture of various types of C-H and/or O-H chemical groups, with no or minor contribution of N-H. Increases of the band depth and width of this broad absorption, correlated also to changes in the spectral slopes, occur in active areas, possibly associated with the presence of small amounts of water ice. There is no evidence even at the highest spatial resolution of 15-25m/pixel, of ice-rich patches, indicating a generally dehydrated nature for the entire surface layer currently illuminated by the Sun.

**One Sentence Summary:** Spectral data from the VIRTIS spectrometer on Rosetta shows that the surface of 67P/Churyumov-Gerasimenko is everywhere rich in organic materials with currently little or no water ice.

Main Text: Comets are probably the least-altered objects surviving from the origin of the Solar System, and from this point of view they carry the record of the physical processes that have led to their formation. The solid components we observe on the nuclei may have existed before the Solar System formed, as interstellar grains, or they could represent material that condensed in the early protosolar nebula (I). Previous information on the nucleus composition was mainly derived from measurements of the coma gaseous and dusty components either from ground based observations, from in-situ measurements (2,3) and from analysis of grains of cometary origin (4) or of presumed cometary origin, as stratospheric IDPs and Antarctic micrometeorites (5,6,7); unfortunately, only few direct observations of comet nuclei have been carried out, limiting the amount of information on their surface composition (8,9).

With the arrival at 67P/ Churyumov-Gerasimenko (hereafter referred to as 67P), of the Rosetta mission VIRTIS, the Visible, Infrared and Thermal Imaging Spectrometer, (10), is providing measurements of the surface composition of a comet and mapping its distribution across most of the surface of the nucleus.

The VIRTIS observations described in this paper were obtained in the period August-September 2014 (3.6-3.3AU from the Sun), with a ground spatial resolution varying between 15 and 30 m/pixel, and covering the spectral range  $0.5\text{-}5.0\mu\text{m}$ . Two VIRTIS images showing the three major building blocks of the nucleus, the "head", the "neck" and the "body", are presented in Figure 1, together with spectra representative of the composition of the three areas. The spectra show several common features: a very low albedo, a clear absorption in the range 2.9-3.6  $\mu$ m, a slightly reddish spectral slope with a slope change between at 1.0  $\mu$ m and a tentative absorption in the region of 0.9  $\mu$ m. The predominantly reflectance spectra also show definite evidence of a thermal emission in the range 3.5-5.0  $\mu$ m, corresponding to surface temperatures in the range 180-230K during daytime. A remarkable feature of all the spectra is the absence of water ice absorption bands (1.5, 2.0, 3.0  $\mu$ m), which indicates that no water ice-rich patches are

present, at a scale larger than several meters, across the nucleus surface, with an upper limit of about 1% on the water ice abundance at pixel level. This, along with the relatively high surface temperature, indicates that the top few millimeters of the surface layer are mainly composed of dark dehydrated refractory materials.

The derived normal albedo from VIRTIS data is  $0.060 \pm 0.003$  at  $0.55~\mu m$ , in excellent agreement with the value obtained by the Osiris team(11). The reflectance spectra in the VIS range display a positive slope in the range  $0.5~\mu m - 0.8~\mu m$  with a coefficient of 5-25% kÅ<sup>-1</sup>, which is also in good agreement with the Osiris results. The spectrum has a knee at around  $1.0~\mu m$  and displays a more neutral (1.5-5~% kÅ<sup>-1</sup>) spectral slope in the range  $1.0\text{-}2.0~\mu m$ . When compared to the reflectance of Trans Neptunian Objects this would associate 67P with the neutral BB or slightly red BR classes in the present taxonomy (12).

To take full advantage of the mapping capability of VIRTIS, the spectral slopes calculated in the ranges 0.5  $\mu$ m – 0.8  $\mu$ m and 1.0  $\mu$ m -2.0  $\mu$ m, were mapped onto the shape model, Fig. 2. The region located in the "neck", which is also the one associated with the first sign of activity in the period August-September 2014 (11), displays a more neutral slope than the average in both VIS and IR range.

Moving into the IR region, the most prominent feature observed is a wide absorption band extending from 2.9 to 3.6  $\mu$ m. The spectra shown in Fig1c extend to 5.0  $\mu$ m, but their analysis is limited to 4.0  $\mu$ m where the spectral interpretation is unaffected by the emissivity of the surface. The band is fairly asymmetric with a steeper slope towards the shorter wavelength region, a band depth (relative to the local continuum) of the order of 20% and a band center located at 3.2-3.3  $\mu$ m. The band is observed in both VIRTIS-M and VIRTIS-H spectra, independently calibrated, with similar band depth and band shape.

When this band is mapped across the surface of 67P the data accumulated so far indicate a very limited variability, localized in the "neck" region. Here, the absorption is deeper, broader and shifted towards shorter wavelengths (2.8 -3.6 µm) with respect to the other regions. The short wavelength shoulder of the "neck" band is most likely due to the addition, in this region, of a small percentage of water ice mixed with the dark material responsible for the overall appearance of the spectrum. This is in agreement with a slight increase in the reflectance (of the order of 10%) and the previously mentioned decrease of the VIS spectral slope for this same region and, is consistent with localized activity driven by volatiles, including water, in the uppermost few millimeters of the nucleus. This process is quite distinct from the diffuse activity observed by Osiris (11) in regions where VIRTIS observations indicate a dehydrated crust.

In contrast to the "neck" region the spectral features observed on the "head" and "body", examples of which are given in Figure 1a, are remarkably similar indicating a compositionally homogeneous surface, at the present spatial resolution. Some slight local variations are observed, but the general dry, organic-rich nature of the surface is confirmed

Comparison with laboratory spectra of carbonaceous chondrites of the CI, CM and CR types reveals that none of them fit the spectra of 67P (13,14,15). Spectra of bulk carbonaceous chondrites are basically flat in the near infrared range and cannot account for the red slope seen on 67P. Furthermore, their broad 3  $\mu$ m band due to structural hydroxyl or water is significantly shifted towards shorter wavelengths. This comparison confidently proves that the material that composes the surface of 67P is not identical to the main groups of primitive carbonaceous

chondrites. However, the reflectance spectra of Insoluble Organic Matter (IOM) extracted from the Murchison chondrite is dark and flat in both the visible and IR ranges (13).

The very low reflectance of 67P surface material throughout VIRTIS spectral range requires the presence of a darkening agent in the refractory component. Fe-bearing opaque minerals are known to absorb visible and near infrared light, and their presence in cometary grains is established from the analysis of grains from the comet 81P/Wild2 collected by the STARDUST mission, stratospheric dust particles and Antarctic micro-meteorites (5,6,7). IOM also contains some insoluble opaque minerals (e.g. sulfides, iron oxides) that are not dissolved by the chemical procedure of extraction from the bulk chondrites. Sulfides (troilite, pyrrhotite, pentlandite), Fe-Ni alloys, Fe-bearing crystalline and amorphous silicates have been identified in those dusts. In particular, analysis of the cometary dust samples indicate presence of amorphous silicates associated to Fe-Ni inclusions and of crystalline silicates, mainly Mg-rich olivines and low-Ca pyroxenes (Fo<sub>51-100</sub> and En<sub>58-100</sub>). Similar compositions (Fo<sub>48-100</sub> and En<sub>65-99</sub>) have been measured on Antarctic micrometeorites of presumable cometary origin (6,7). Iron sulfides (e.g., troilite, pyrrhotite) are common in meteorites, interplanetary dust particles and cometary dust; they are highly absorbing opaque phases and may play an important role in darkening and reducing spectral contrasts of diagnostic absorption bands if these minerals are fine-grained (16 and references therein). In addition to darkening over the infrared range, sulfides display a slope between 500 and 1000 nm in their reflectance spectra that may contribute to that in VIRTIS spectra. See Fig.3 for reference.

In many previous studies reddish surfaces of the outer solar system, e.g. Kuiper Belt Objects, have been modeled using tholins produced from N<sub>2</sub>:CH<sub>4</sub> gas mixtures (17). Although the reflectance spectra of those tholins may qualitatively account for the reddish slope of VIRTIS data, they are definitely too bright in the infrared to be considered as viable materials present at the surface of 67P. Also nitrogen-rich carbonaceous materials devoid of oxygen are not representative of the bulk macromolecular fraction of comets (18).

The broad band observed at  $\sim 3.3~\mu m$  in all VIRTIS spectra is a congested spectral region that results from the contribution of X-H vibrations in different chemical groups. CH and OH groups can be reasonably suspected, while a significant contribution of NH or NH2 is less likely. The absorption bands of water ice, structural water and hydroxyl in silicates and iron oxides or oxy-hydroxides are shifted towards shorter wavelength compared to VIRTIS spectra, and their contribution should be low if any, except in the "neck" active area where slightly wider and stronger bands are observed. The substructure in the band points to a complex mixture of both aromatic and aliphatic C-H bonds (but their presence cannot yet be firmly established); in addition, the broad feature may also be consistent with the presence of OH groups, either as carboxylic groups or alcoholic groups, inserted in a macromolecular organic solid. These chemical groups are known to account for the faint and broad feature in the IR spectra of IOM extracted from primitive meteorites (20,21). The position and shape of the band may depend on the alcohol/carboxylic groups ratio and on the groups onto which they are branched. They may account for some of the observed variability of the band shape (Fig.4).

VIRTIS clearly observed a different comet from the other Jupiter family comets (JFC) encountered so far. Previous spectroscopic observations of the surfaces of JFCs indicated the presence of water ice (9 and tentative identification of a weak band near 2.9 µm possibly compatible with hydrocarbons (8). Indeed, mass spectrometry of solid grains ejected from comet nuclei did show various species of organic materials ranging from aliphatic and aromatic

compounds to carboxylic acids and alcohols (22), but these compounds were never seen as absorption on comet nuclei. From this point of view 67P represents a different species in the cometary zoo.

The large scale homogeneity of the surface despite the rejuvenating processes acting on the nucleus (at least on the active portion of it) at every passage close to the Sun, are indicating that space weathering plays a minor role in determining the observed composition. The refractory compounds present on the surface must then be representative of the bulk pristine material. Organics compounds are formed upon irradiation of ices, by UV or energetic particles, or by polymerization of mixtures of ices kept at low temperatures (16). The VIRTIS observations indicate that high volatility ices (CH<sub>4</sub>, CO, CO<sub>2</sub>, CH<sub>3</sub>OH, etc.), along with water, must have been readily available at the time of the nucleus formation in the early phases of the Proto Solar Nebula. This suggest that the larger abundance of organics on the surface of 67P with respect to other JFC comets could be correlated to a formation scenario in which most of the material which constitute the nucleus of 67P is produced in a low temperatures environment consistent with large distances from the Sun, such as the Kuiper Belt region.

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The VIRTIS Team wishes to dedicate this paper to the memory of Angioletta Coradini, conceiver of the instrument, our leader and friend.

- **Fig. 1**. Left column: Visible true-color images of the nucleus acquired on the Neck (top panel, acquisition V1\_00366693519 taken on 15th Aug 2014 from 03:20 to 03:54, spatial resolution 25 m/px) and on the Head and Body regions (bottom panel, acquisition V1\_00368219081 taken on 1st Sep 2014 from 19:05 to 20:30, spatial resolution 12.5 m/px). Right panel: representative reflectance spectra (thermal emission removed) of the three regions in the 0.5-4  $\mu$ m range by VIRTIS-M (red, black and blue curves) and in the 2-4  $\mu$ m range by VIRTIS-H (light blue curve). Instrumental bridging zones and order sorting filters gaps are indicated by light gray bars.
- **Fig. 2** Variability of the VIS (0.5-0.8 μm, left column) and IR (1-2.5 μm, right column) spectral slopes across the nucleus in percentage for K-Angstroms. VIRTIS-M data are averages calculated on illuminated points having incidence and emission angles below 80 deg taken from 160 observations acquired from 7th Aug 2014 to 2nd Sep 2014. Slopes maps, sampled at 1 by 1 degrees spatial resolution, are shown projected on a nucleus shape model (courtesy OSIRIS team) for different viewing orientations.
- **Fig. 3.** The spectrum of the "head" shown in Figure 1 is compared to those of several other compounds described in the text. Some of the spectra are scaled but no attempt to fit the VIRTIS data has been made. Enstatite, Pyrrothite and Troilite spectra are scaled down by 100%, 75% and 50% respectively. The Murchison IOM is from (13). Enstatite spectrum from (23). Troilite and Carbon Black spectra from (24), Pyrrothite spectrum from (25).
- Fig. 4. The spectrum of the "head" in the spectral range 2.5- $4.5\mu m$  is compared to several other organic compounds described in the text. The VIRTIS spectrum is rescaled in arbitrary units to compare the X-H stretch region with Ethanol and Acetic acid spectra (26), a cometary tholins (obtained after ion irradiation of a mixture of 80%  $H_2O$ , 16%,  $CH_3OH$ , 3.2%  $CO_2$ , and 0.8%

C<sub>2</sub>H<sub>6</sub>) (27) and a refractory residue obtained after UV irradiation of a mixture of H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub>:CO:CO<sub>2</sub> in the ratio 2:1:1:1:1 (28)

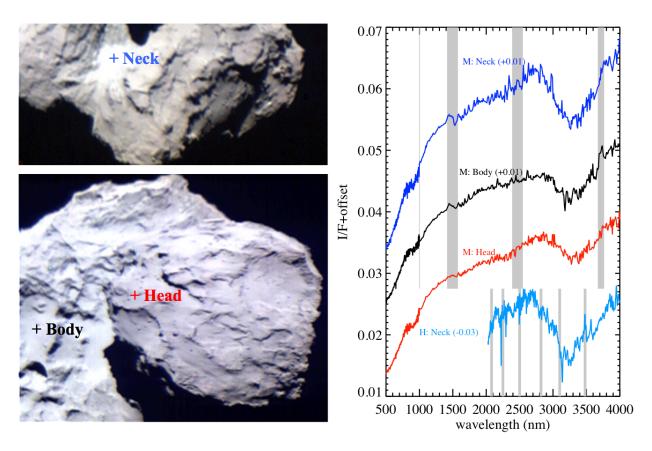


Figure 1

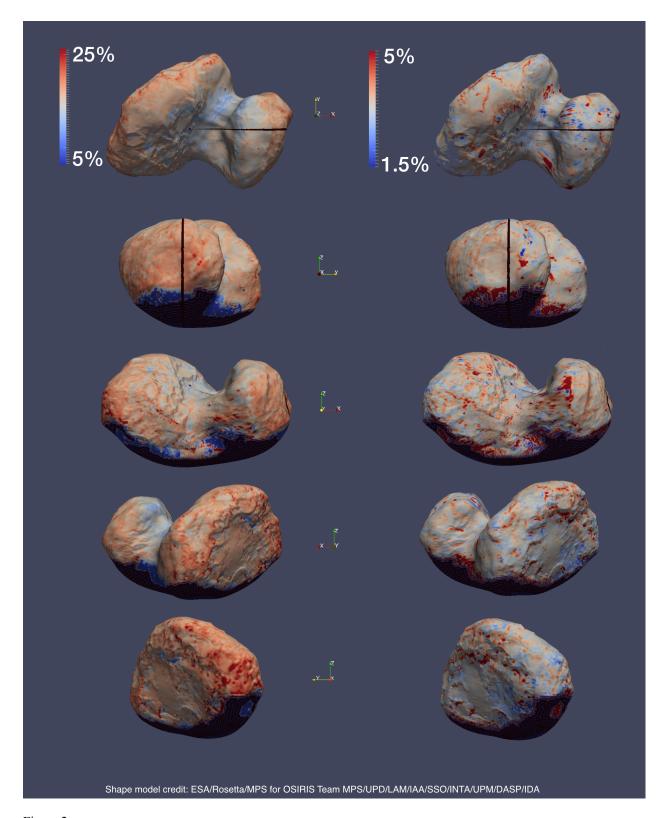


Figure 2

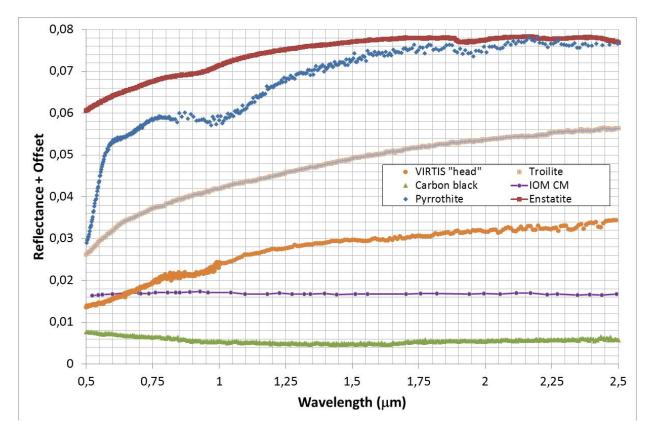


Figure 3

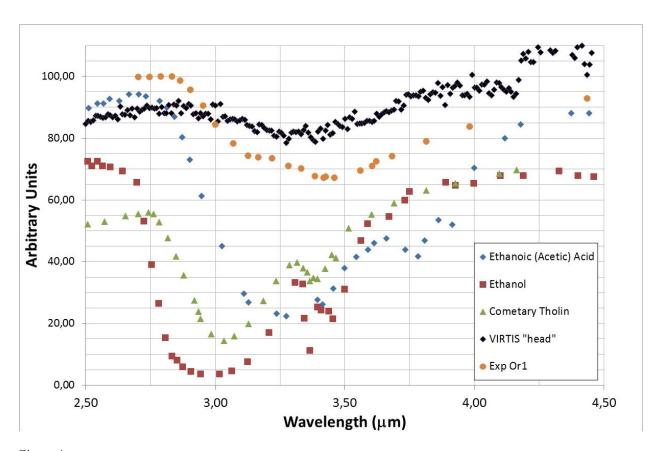


Figure 4