COMPOSITION OF COMET 67P/CHURYUMOV-GERASIMENKO REFRACTORY CRUST AS INFERRED FROM VIRTIS-M/ROSETTA SPECTRO-IMAGER. E. Quirico¹, L. V. Moroz², P. Beck¹, B. Schmitt¹, G. Arnold², L. Bonal¹, G. Filacchione³, F. Capaccioni³, C. Leyrat⁴, D. Bockelée-Morvan⁴, S. Erard⁴, F. Tosi³, M. Ciarniello³, A. Raponi³, M. T. Capria³, M. C. De Sanctis³, G. Piccioni³, A. Barucci⁴, P. Drossart⁴, K. Marcus², and Rosetta VIRTIS team, ¹IPAG UGA/CNRS Grenoble France, ²German Aerospace Center DLR Berlin, Germany, ³IAPS-INAF, via del fosso del cavaliere, 100, 00133, Rome, Italy, ⁴LESIA Observatoire de Paris, Meudon, France

Introduction: The Visible InfraRed Thermal Imaging Spectrometer, VIRTIS [1] onboard ESA's Rosetta orbiter has completed two extensive mapping campaigns of the 67P/Churyumov-Gerasimenko comet nucleus in August-September 2014 [1,2]. Reflectance spectra were collected within the 0.4-5 μ m range and reveal a dark surface (normal albedo ~6 %), positive (red) near-infrared spectral slop, steeper red visible slope, and a broad feature that peaks at 3.2 μ m [1]. Here we address interpretation of these spectra through comparison with experimental data.

VIRTIS spectra: A full spectro-image cube, with thermal contribution removed [3] from the MTP06 observing campaign (August 2014) has been analyzed in order to retrieve the general behavior of the surface spectra.



1: representative nucleus surface vis+IR spectra ("neck" and "body") normalized at 2.72 μ m with thermal emission removed. High frequency spectral variations are due to noise and calibration artifacts.

The main spectral features of this data set are a single normalized infrared slope, two classes of normalized visible slopes ("neck" and "body") and a 3.2 μ m relative band depth that appears to vary independently of the slopes for the body.

Organics and opaque minerals: Dark surfaces of small solar system bodies are often interpreted as the presence of dark refractory organics. Primitive chondrites contain a polyaromatic black solid (1-5 wt%), which is insoluble in common organic solvents and extracted with chemical HF/HCl protocols (IOM, Insoluble Organic Matter). IOM shares similarities with terrestrial type III kerogens and coals, and coals samples have been used as fair analogs in earlier studies [4]. Raman spectroscopic analyses clearly evidenced that polyaromatics compounds are present in grains of plausible cometary origin (stratospheric IDPs, Antarc-

tic micrometeorites), but likely with a broader range of chemical compositions than chondritic IOM [5]. Therefore, we selected a series of coal samples from the Penn State University Coal Bank and Data Base covering a wide range of maturities, i.e. a wide range of chemical compositions and degrees of structural order of the polyaromatic structures. The reflectance spectra of these coal samples were collected with the Spectro- Gonio Radiometer at IPAG at normal incidence and 30° emergence.

The reflectance spectra strongly depend on maturity and grain size (Fig. 2a,b). All samples display very low reflectance in the visible range. In contrast, low maturity samples display a rather high reflectance level in the near-infrared range, while mature coals (e.g., anthracite) are spectrally flat and dark over the visible and near-infrared ranges. Mature coals cannot be considered as fair analogs of cometary refractory organics. Mature IOM is recovered in thermally metamorphosed chondrites that experienced high temperatures (> 600 °C) conditions over millions of years. The nearinfrared range appears then as a critical range for constraining the nature of the dark components of 67P/CG. Indeed, the reflectance spectra of primitive carbonaceous chondrites (Fig. 2b) and of IOM extracted from Orgueil CI chondrite are basically flat and dark in the visible and near-infrared [6].

A strong effect of grain size is observed. The reflectance level in the near infrared is found to increase upon decreasing grain size, in particular in the case of the DECS21 lignite whose composition is very close to that of the IOM of the CI Orgueil chondrite. As submicrometric particles are expected in the 67P/CG refractory crust, we infer that grain size cannot account for the high near infrared reflectance. Similar observations have been made on a wide range of terrestrial organics like solid oil bitumens, and that our general conclusions obtained from a series of coals would apply to polyaromatic solids that sample broader range of compositions and polyaromatic structures [7].

Furthermore, dark polyaromatic hydrocarbons that are ubiquitous in cometary and asteroid grains cannot account for the low reflectance of primitive chondrites, and of comet 67P/CG. In fact, the very low reflectance and spectrally flat reflectance spectra of primitive carbonaceous chondrites (Fig. 2a) and of their IOM strongly suggests spectral contribution from opaque minerals as sulfides and oxides, which cannot be dissolved using HF/HCl protocols. Sulfides (troilite, pyrrhotite, pentlandhite) and Fe-Ni alloys (kamacite, taenite) are ubiquitous in chondrites and cometary grains. They play a key role in the control of the low albedo of carbon-rich cosmomaterials [8,9], and likely for comet 67P/CG. Finally, sulfides can also exhibit red slopes in the visible and might account for this spectral characteristics of the spectra of comet 67P/CG [1].



Fig 2: *a)* Reflectance spectra of coal samples and bulk Orgueil chondrite. *b)* Reflectance of a lignite for various grain sizes.

The 3.2 μm band: The broad 3.2 μm band can be ssigned to OH, CH, H₂O, NH/NH₂ and NH⁴⁺ chemical groups, molecules or ions. The nucleus temperature of 220 K renders negligible a significant contribution from water ice, which is marginally detected in area of the nucleus just emerging from shadow [10]. The ubiquitous presence of NH/NH₂ chemical groups appears unlikely, as N-rich cometary grains are extremely scarce in collections [11]. The OH chemical groups trapped in minerals or inserted within the network of refractory polyaromatic solids is highly plausible. OH in proto-serpentines and glasses, which are stable up to 300 °C, are reported in primitive chondrites [12, 13]. However, the peak position of their band lies around $3.1 \,\mu\text{m}$, and the width is smaller than that of the 3.2µm band. In a carbonaceous structure, OH can be present as either alcohol (terminating -OH) or carboxylic

groups (-COOH). The carboxylic band is larger than the alcoholic, due to efficient proton exchange through hydrogen bond. The contribution of carboxylic groups appears thus highly plausible, but contribution of alcoholic OH cannot be rejected. Ions like NH⁴⁺ could also contribute to the 3.2 μ m band. OCN⁻ has been detected a few decades ago in interstellar ices, and laboratory experiments report that organic salty mixtures are recovered from photolysis of simple ices [14]. Minor amount of salts may be enough to contribute to the 3.2 μ m band, due to the high absorption cross section of ions.

Conclusion: VIRTIS reflectance spectra of comet 67P/CG point to the presence of a crust composed of refractory compounds as 1) polyaromatic organic solids mixed with 2) sulfides and Fe-Ni alloys. The presence of sulfides may also account for the red visible slope. The presence of OH chemical groups is inferred from the broad 3.2 µm band. Contributions from aliphatic or aromatic C-H groups is possible, as well as a contribution from salts (NH4⁺, possibly structural H₂O). Salts are expected as minor constituents due to the very low reflectance of the comet surface, but the large absorption coefficient of ions may make their spectral contribution significant. Analysis from other instruments aboard ROSETTA orbiter and PHILAE lander will help constrain further the contribution of minor species.

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