

# Ammonium salts observed by VIRTIS-M on the nucleus of comet 67P/Churyumov-Gerasimenko

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## 1. Introduction

The nucleus of comet 67P/Churyumov-Gerasimenko was mapped by the Visible, InfraRed and Thermal Imaging Spectrometer, Mapping Channel (VIRTIS-M) on-board the Rosetta spacecraft. The nucleus appeared almost spectrally uniform from 0.4 to 4  $\mu\text{m}$ , characterised by a very low reflectance of few percent, a positive (red) spectral slope, and a broad absorption feature from 2.9 to 3.6  $\mu\text{m}$ , centred at 3.2  $\mu\text{m}$  [1]. This absorption band is the most prominent feature and is widespread on the surface of comet 67P nucleus. Earlier analyses of these reflectance spectra suggested that the darkness and slope could be due to refractory poly-aromatic organics and opaque minerals (anhydrous sulphides and Fe-Ni alloys), but the attribution of the 3.2- $\mu\text{m}$  absorption feature has remained elusive [1,2,3]. It has been proposed to be mainly due to semi-volatile components of low molecular weight, most plausibly carboxylic ( $-\text{COOH}$ ) bearing molecules or ammonium ( $\text{NH}_4^+$ ) ions, with possible contribution from C–H stretches [2]. To test these hypotheses, we performed a series of laboratory measurements of the reflectance spectra of carboxylic acids or ammonium salts under simulated cometary-like conditions.

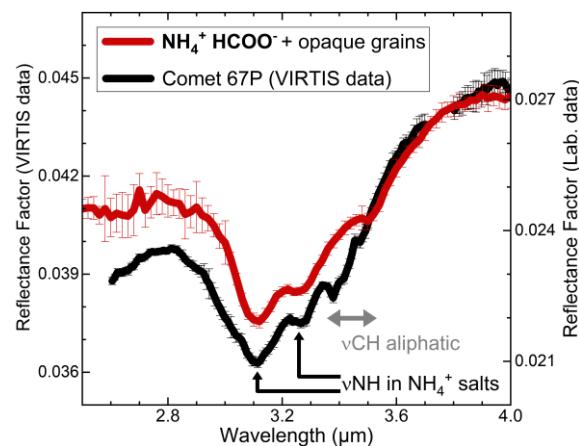
## 2. Laboratory measurements

Cometary dust appears to be made of aggregates of sub-micrometre-sized (sub- $\mu\text{m}$ ) grains [4]. Moreover, cometary nuclei are porous (70–85 %), and their surfaces partially covered by this dust are likely to have a high porosity [5]. We have developed an experimental protocol aiming at simulating these structural properties of cometary dust, following the same methodology as described in [6].

Sub- $\mu\text{m}$  grains of opaque iron sulphide (pyrrhotite,  $\text{Fe}_{1-x}\text{S}$ ,  $0 < x < 0.2$ ) were dispersed in a liquid water solution containing carboxylic acids or ammonium

salts. The liquid mixture was then nebulised to produce droplets that were frozen in liquid nitrogen to form icy dust particles. Finally, these particles were placed inside a thermal-vacuum chamber under cometary-like temperature (170–200 K) and high vacuum ( $< 10^{-5}$  mbar). Under these conditions, the water ice sublimated, and after several hours, a sublimate residue composed of a porous surface of opaque sub- $\mu\text{m}$  grains mixed with a carboxylic acid or ammonium salts was obtained.

The reflectance spectra of these sublimate residues were measured from 0.4 to 4  $\mu\text{m}$  using the spectro-radio-goniometer SHINE of the Cold Surfaces Spectroscopy facility of the Institut de Planétologie et d’Astrophysique de Grenoble (IPAG) [7].



**Figure 1:** Average reflectance spectrum of comet 67P nucleus observed by VIRTIS-M [8], compared to a sublimate residue composed of  $\leq 17$  wt%  $\text{NH}_4^+$   $\text{HCOO}^-$  and  $\geq 83$  wt% opaque pyrrhotite grains measured in the laboratory at 170–200 K.

### 3. Results

Figure 1 shows that the sublimate residue containing  $\leq 17$  wt% ammonium formate ( $\text{NH}_4^+ \text{HCOO}^-$ ) exhibits an absorption band matching very closely the spectral position, asymmetric shape and maxima of absorption at 3.1 and 3.3  $\mu\text{m}$  of the absorption feature observed on comet 67P. We found that several ammonium salts (such as ammonium sulphate or ammonium citrate) also provide a good match to the VIRTIS spectrum. However, carboxylic acids, such as lactic acid, have very different absorption features. Consequently, the 3.1- and 3.3- $\mu\text{m}$  absorption bands observed on comet 67P appear to be due to the N–H stretching vibrations of  $\text{NH}_4^+$  in ammonium salts (several counter-ions may be expected). Additional absorption features present between 3.35 and 3.50  $\mu\text{m}$  have been attributed to C–H stretching vibrations of aliphatic carbonaceous compounds [8]. The depth of the absorption feature on comet 67P suggests that the dust may contain several percent of ammonium salts, with a probable upper limit of about 40 wt%. The determination of a more precise concentration of the salts remains difficult because the band depth depends on many physical properties of the surface (grain sizes, mixing mode etc.) which may differ in our experiments compared to the comet.

### 4. Conclusions and perspectives

#### 4.1. A new cometary reservoir of nitrogen

The 3.2- $\mu\text{m}$  absorption feature observed on the entire surface of the comet 67P nucleus can be mainly attributed to ammonium salts and aliphatic organic matter [8]. The exact composition and concentration of the salts remain unknown. If they comprise more than about 5 wt% of the dust, these salts could be the major reservoir of nitrogen in the comet, dominating over the refractory organic matter and volatile species. Consequently, the abundance of nitrogen in comet 67P may be closer to the solar elemental composition than previously thought [9].

#### 4.2. $\text{NH}_4^+$ and the asteroid-comet continuum

As mentioned earlier [10], the absorption feature of comet 67P shares similarities with other features observed around 3.1  $\mu\text{m}$  on several asteroids. Could some of these absorption features be partly due to ammonium salts? Ammoniated phyllosilicates and

ammonium salts have also been detected on the dwarf planet Ceres [11]. Could Ceres have inherited its ammonium ions from outer Solar System objects similar to comet 67P? In addition, ammonium salts have been tentatively detected in the environment of proto-stars [12], so their detection on comet 67P suggests a possible compositional link between asteroids, comets and the proto-solar nebula.

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