INTERNATIONAL SPACE SCIENCE INSTITUTE

This work took advantage of the collaboration of the **ISSI team** « Comet 67P Surface Composition »

Ammonium salts detected on the surface of comet 67P/Churyumov-Gerasimenko, relics of interstellar ices?

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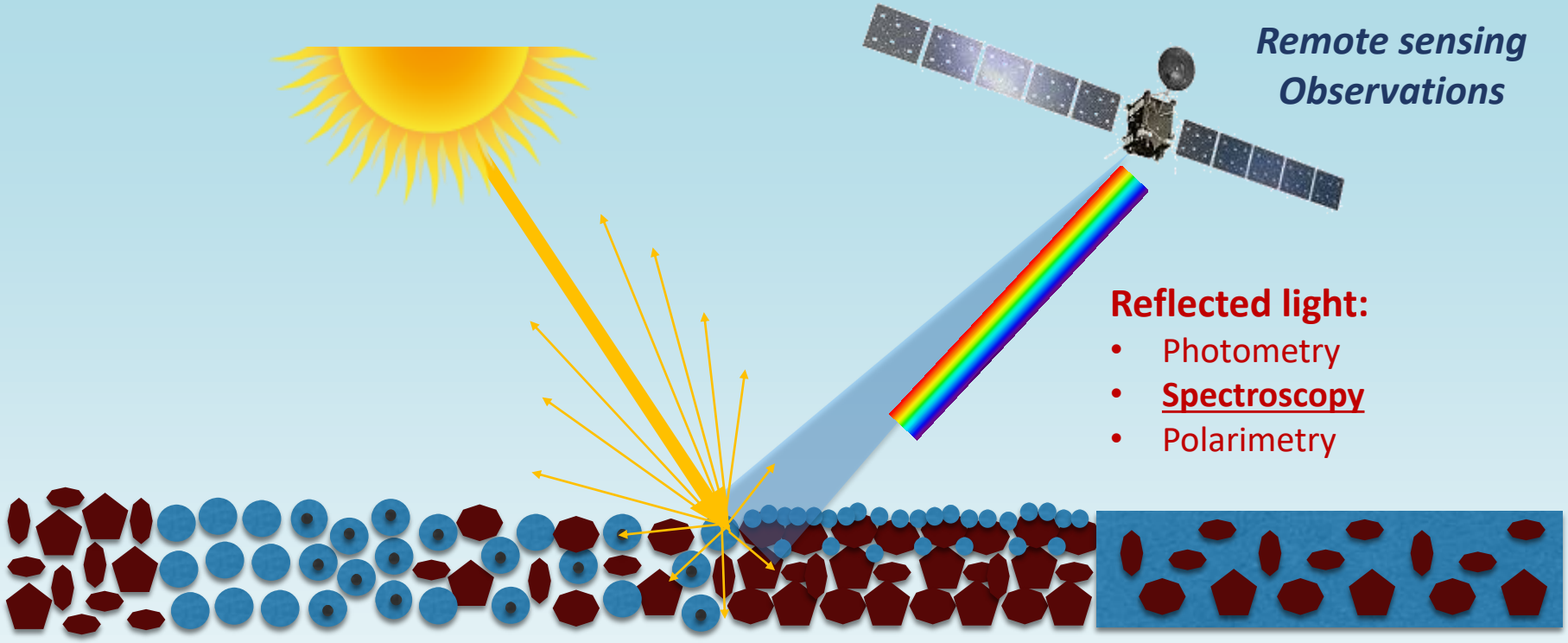
Atelier glaces astrophysiques – Paris, CNES – 4 Octobre 2019

General Context

Revealing the physical & chemical properties of planetary surfaces from their remote sensing observations



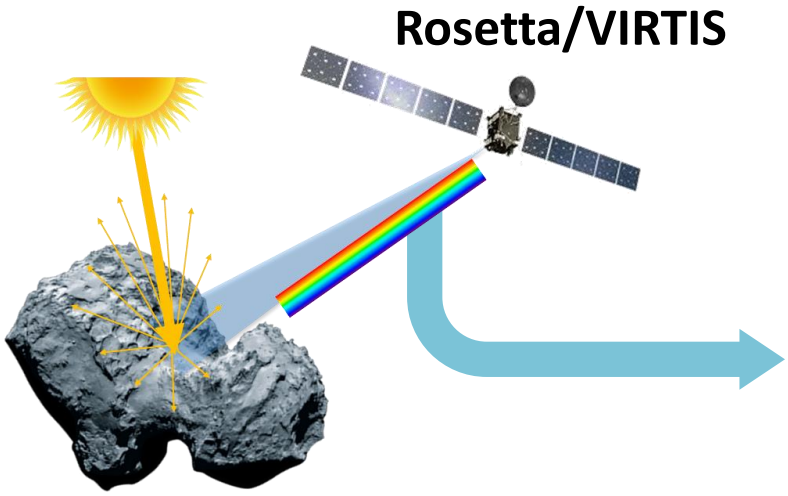
Planetary surfaces are complex

*Grains sizes, composition, **ice**/**dust** mixing modalities…*

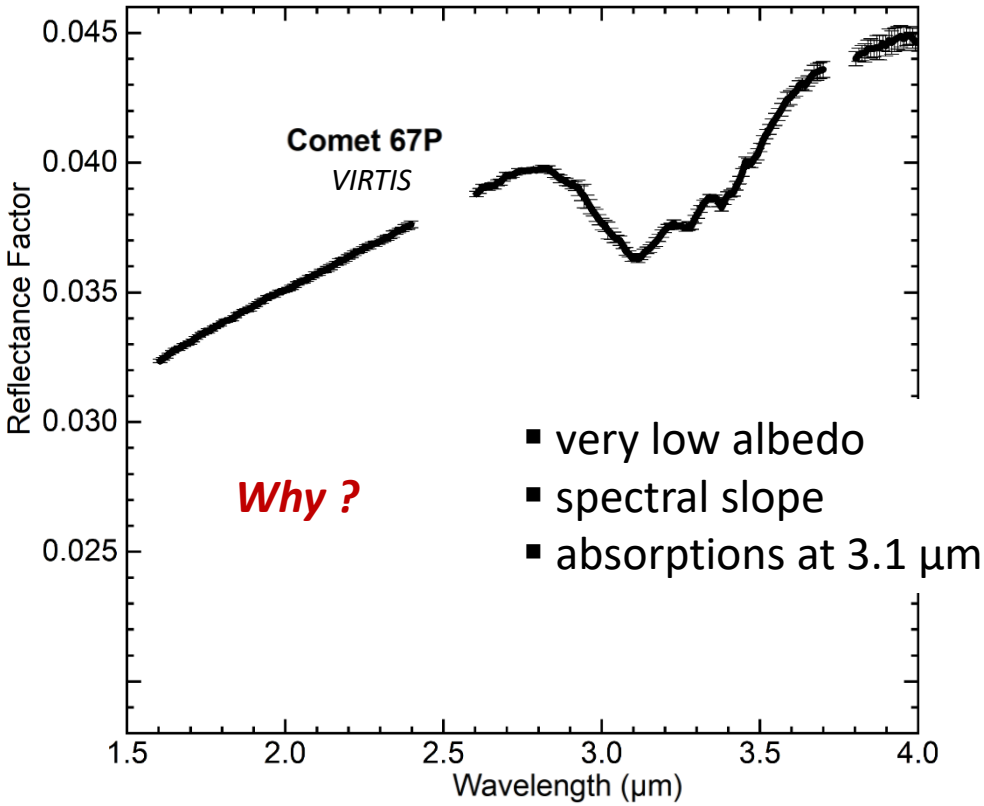
Processes: Sublimation, Photolysis…

Need of experimental and theoretical simulations to interpret the observations

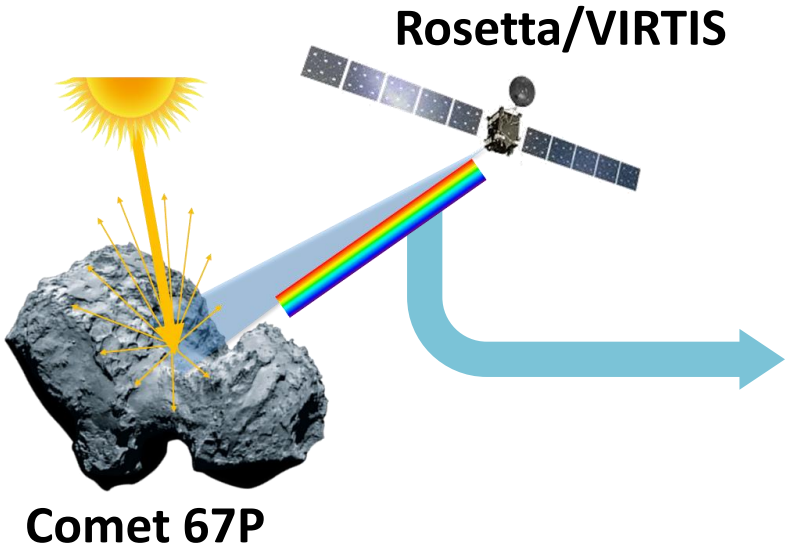
Observation of Comet 67P Nucleus



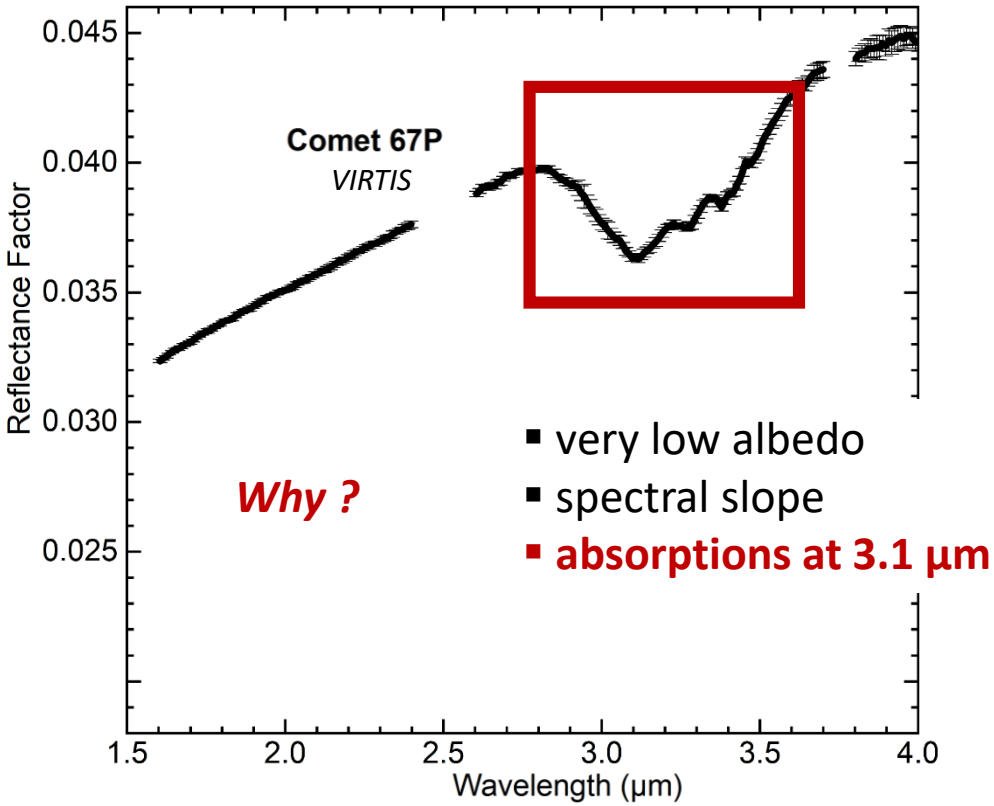
Reflectance spectrum of comet 67P whole surface average



Observation of Comet 67P Nucleus



Reflectance spectrum of comet 67P whole surface average



- very low albedo
- spectral slope
- **absorptions at 3.1 μm**

Why ?

Compounds responsible for **absorptions at 3.1 μm** ?

Carboxylic acids ***–COOH ?***
Alcohols ***–OH ?***
Ammonium ***NH_4^+ salts ?***

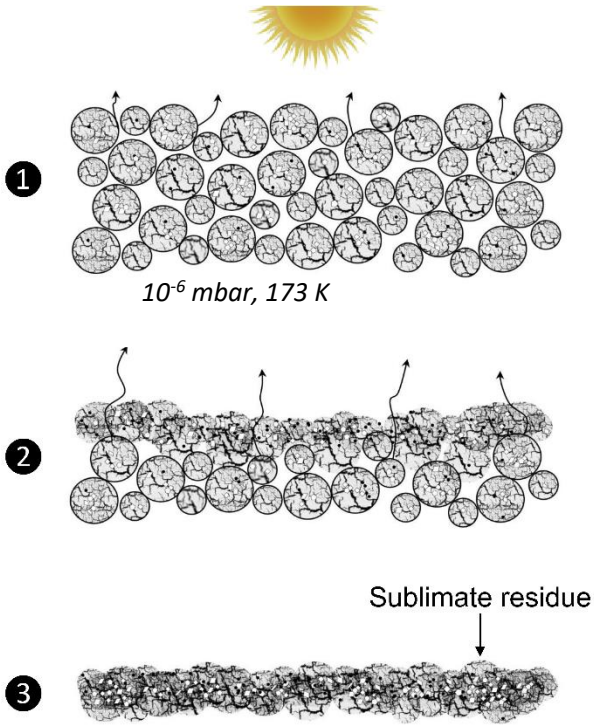
Capaccioni *et al.* (2015); Quirico *et al.* (2016)

Need of experimental reference spectra to interpret the observation

LABORATORY EXPERIMENTS

Preparation of an analogue of cometary surface

Sublimation of a mixture made of water ice + opaque grains + NH_4^+ $HCOO^-$



Porous surface of opaque grains + NH_4^+ $HCOO^-$

Measurements of reflectance spectra

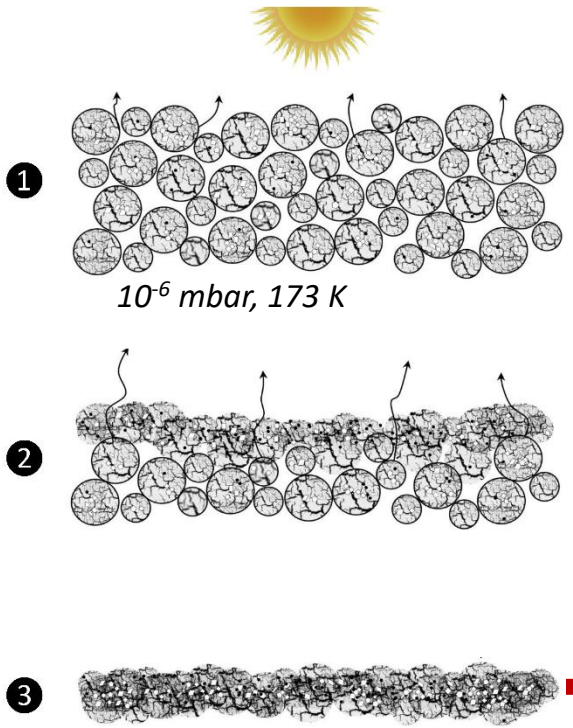
Spectro-goniometer at IPAG

Sample in simulation chamber 170-200 K, 10^{-6} mbar

THE SALTY DUST OF COMET 67P

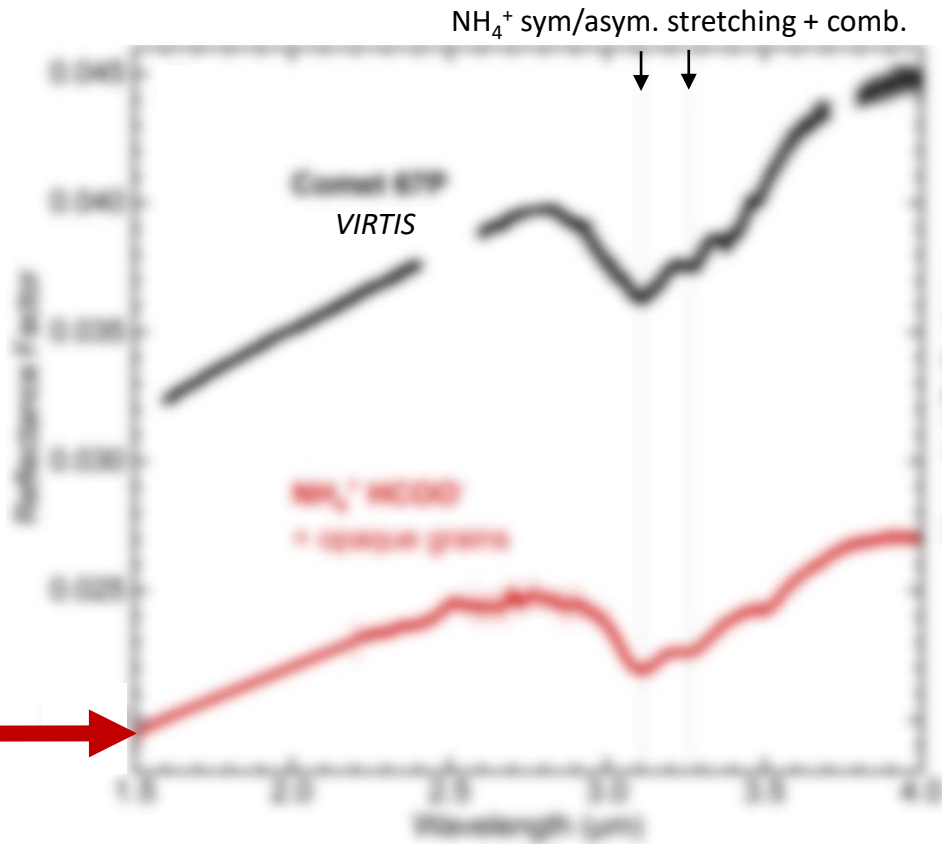
➢ **Identification of ammonium NH_4^+ salt on the nucleus**

Sublimation of a mixture made of water ice + opaque grains + NH_4^+ $HCOO^-$



Porous surface of opaque grains
+ 17 wt% of NH_4^+ $HCOO^-$

Reflectance spectra



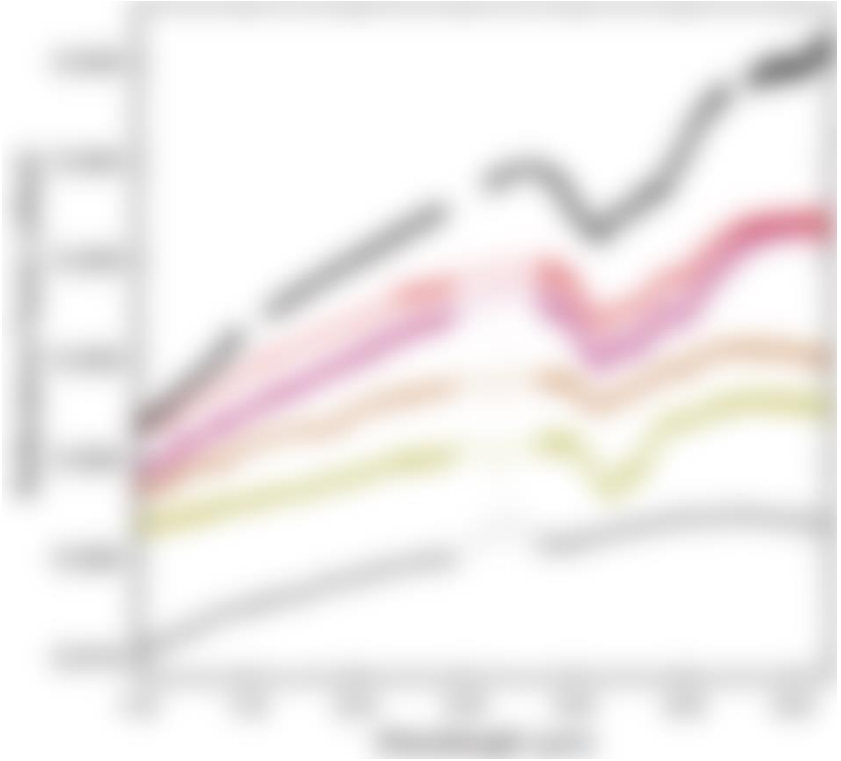
Poch *et al.*, in revision

➢ **Position + assymetric shape + 3.1 + 3.3 µm absorptions can all be attributed to NH_4^+ salts**
➢ **Ammonium salts are the main carriers of the 3.1-µm feature observed on comet 67P**

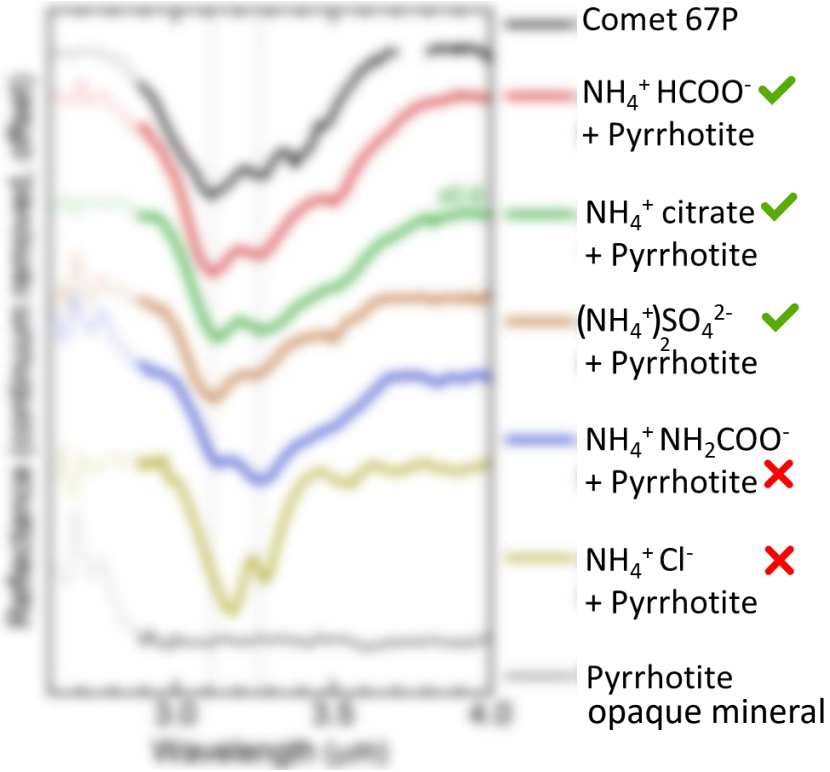
The Salty Dust of Comet 67P

➢ **Several anions may be associated to NH_4^+**

Reflectance spectra
of sublimate residues



Continuum removed reflectance spectra
of sublimate residues

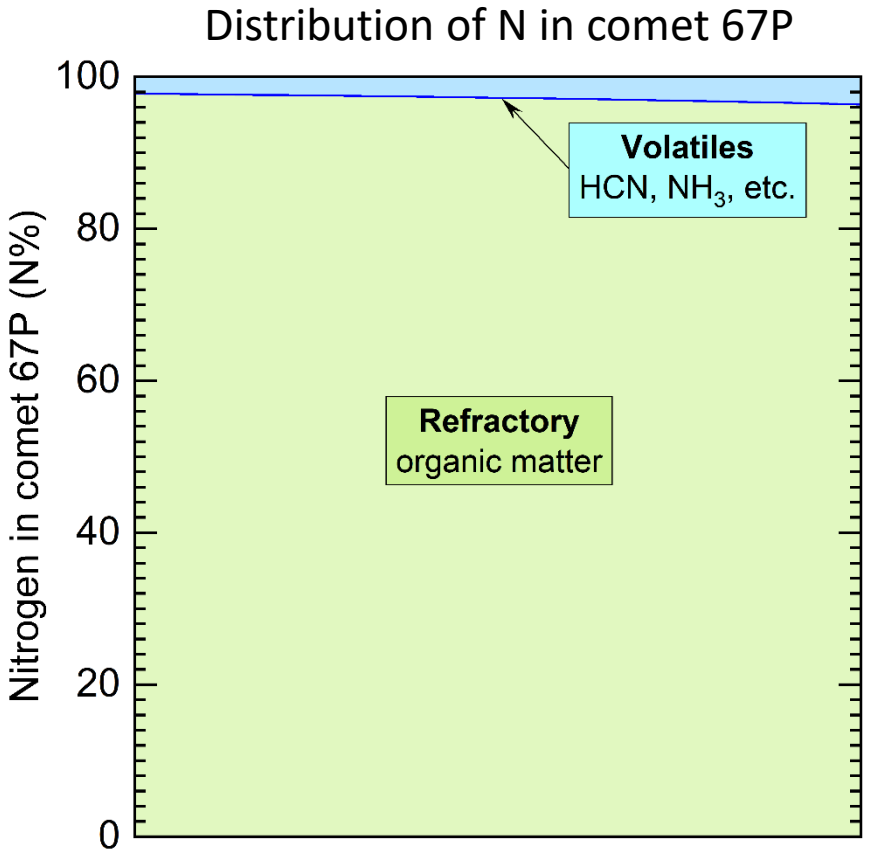


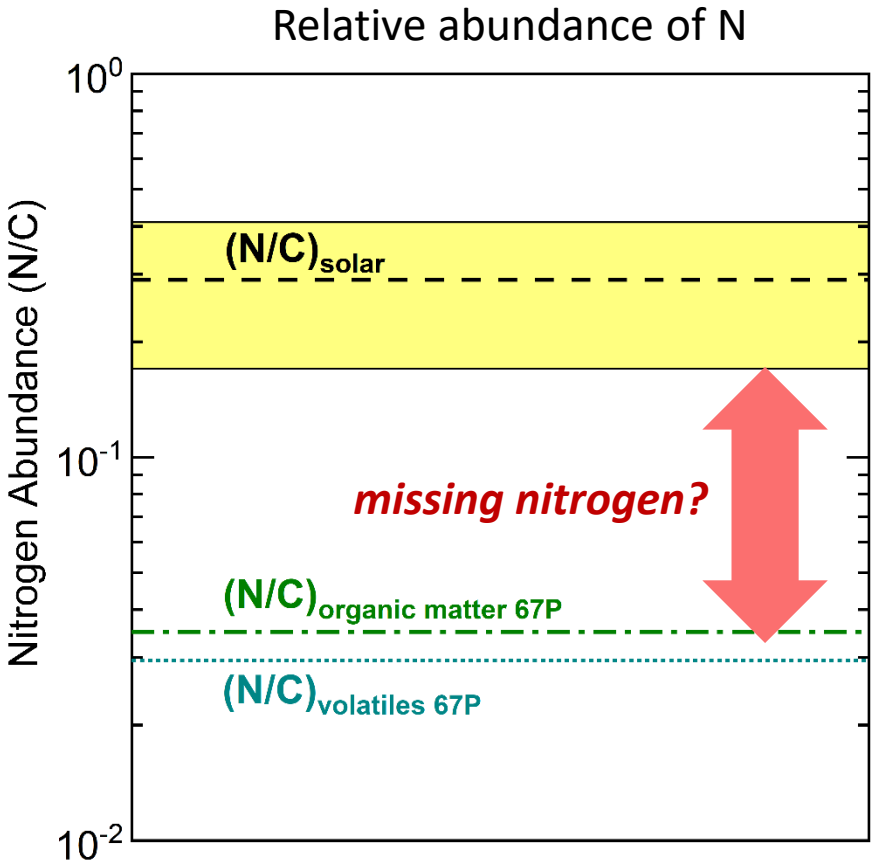
➢ **Several NH_4^+ salts match the observed spectrum**

➢ **A mixture of different salts may be present on comet 67P**

A New Cometary Reservoir of Nitrogen

➢ **Nitrogen in comet, before the detection of NH_4^+ salts**





Estimations from data obtained by Rosetta instruments (ROSINA, COSIMA, etc.)
Le Roy+ (2015); Rotundi+ (2015); Bardyn+ (2017); Fray+ (2017)

Solar N/C from Lodders (2010)

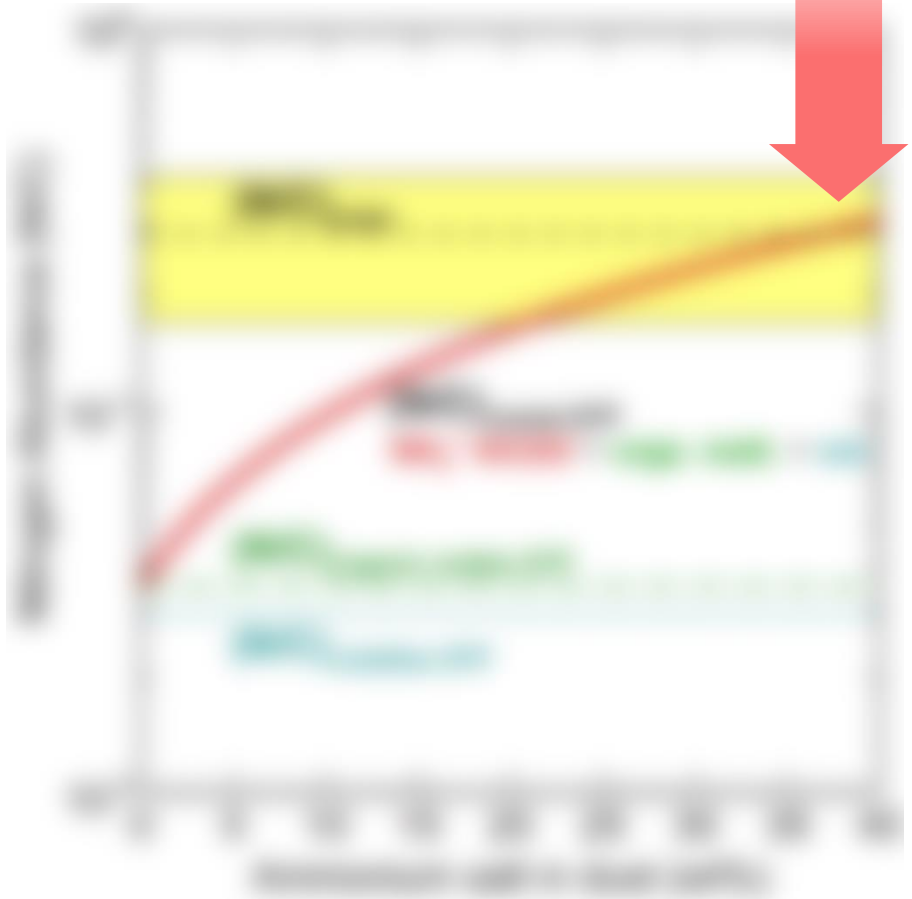
A New Cometary Reservoir of Nitrogen

➢ **Identification of a new reservoir of nitrogen**

Do NH_4^+ salts solve the problem of the missing nitrogen?

Distribution of N in comet 67P

Relative abundance of N



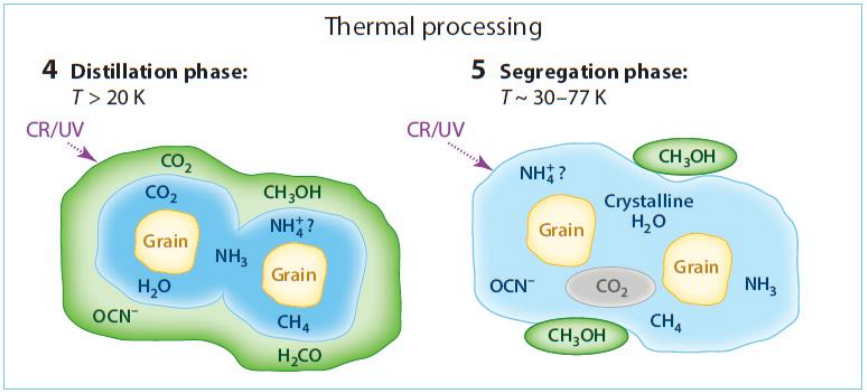
*Concentration of NH_4^+ salts of **few % up to about 40 wt%** in the cometary dust.*

Poch *et al.*, in revision

ORIGINS OF THE AMMONIUM SALTS

How are NH_4^+ salts formed?

Evolution of icy grains, Boogert *et al.* (2015)



Produced by **acid-base** reactions (10-30 K):

$NH_3 + HCOOH \rightarrow NH_4^+ + HCOO^-$

Produced by **nucleophilic addition** of NH_3 with CO_2:

$2NH_3 + CO_2 \rightarrow NH_4^+ + NH_2COO^-$

in solid ices + catalytic effect of **cosmic dust**
Theulé+ (2013), Potapov+ (2019)

When, Where they formed?

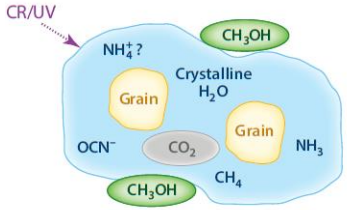
To answer these questions we need:

- **Kinetics of formation mechanisms** obtained via theoretical + experimental studies to improve models of evolution of icy grains
- **Observations**: search for spectral signatures (JWST)

- **interstellar ices**?
  and/or
- **protoplanetary disk**?
  and/or
- **in the comet**, during sublimation of ices?

Influences of the Ammonium Salts

NH_4^+ salts may potentially influence several properties of astrophysical ices



Chemical evolution

Solid phase

- Once formed in the ice, can ionic solids catalyse **reactions on their surface**?
- How do the salts evolve when submitted to **irradiation** (UV/cosmic rays)?

Gas phase

- **Adsorption/Desorption** on ionic solids versus ices: different affinities? catalysis?
- **Sublimation/Decomposition** of the salts: production of molecules in gas phase

Aggregation of grains

Stickiness/coagulation efficiency

- **Salty-ice grains stickier** than non-salty-ice grains?
- Salt-pure or salt-coated grains stickier than ice or silicates/organics grains?

Solid form of Nitrogen

- NH_4^+ salts are **solid up to > 200 K**
  $\Rightarrow$ providing N well inside the N_2 and NH_3 snow lines.

Conclusion and Perspectives

- **VIRTIS-M identified NH_4^+ salts on the nucleus of comet 67P**
- **These salts may represent the dominant reservoir of N in this comet**
- **Potential implications in** (Hänni+, EPSC-DPS 2019)
  - **Comae distributed sources** of gaseous molecules (Mumma+, EPSC-DPS 2019)
  - **Cosmochemistry**, for the cosmic cycle of nitrogen
  - **Planetary formation**: role of these salts in accretion mechanisms?

Open questions:

- What are the counter-ions of NH_4^+ in comet 67P?
- What is their exact concentration in comet 67P?
- NH_4^+ salts also present in other small bodies? in cosmo-materials?
- How, when and where did they formed?

SSHADE: THE EUROPEAN SOLID SPECTROSCOPY DATABASE INFRASTRUCTURE

B. Schmitt, Ph. Bollard, A. Garenne, D. Albert, L. Bonal, and the SSHADE Consortium Partners

IPAG & OSUG, Grenoble, France + 21 laboratories in 11 countries

(contact@sshade.eu)

- **Vis-IR Spectroscopy and spectro-imagery** are increasingly used in space missions to study the solid phases at their surface (ices, minerals, organic materials, …).
- **Infrared, Raman, fluorescence** and **X-ray micro-spectroscopies** are also used to study **planetary and cosmo-materials**, in the laboratory and onboard landers and rovers.
- **Laboratory spectra of a variety of natural or synthetic materials** are needed to analyze the observations of solids at the surface or in the atmosphere of solar system bodies.

What is SSHADE? https://www.sshade.eu + https://wiki.sshade.eu

SSHADE hosts a set of specialized databases provided by various research groups and dedicated to astrophysics, planetary & material sciences, and geosciences.

Content of SSHADE: Online since February 2018

The **SSHADE databases** cover laboratory, field and simulated spectral data including various levels of products (e.g. transmission, reflectance, optical constants, Raman, …)

- ✓ **Types of samples:** synthesized or natural ices, minerals, rocks, organic and carbonaceous materials, terrestrial analogues, extra-terrestrial samples (meteorites, IDPs, Lunar soils, …).
- ✓ **Spectral ranges:** mostly covering the X, VUV, UV, Vis, Near/Mid/Far-IR & sub-mm.

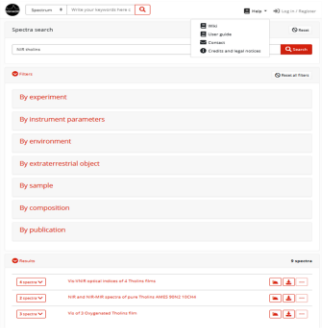
The SSHADE Projet and Consortium

- ✓ **SSHADE project:** within VESPA activity of Europlanet 2020-RI
- ✓ **SSHADE consortium**: 23 partners in 21 labs from 11 countries
- ✓ **SSHADE infrastructure host**: OSUG Data Center (UGA).

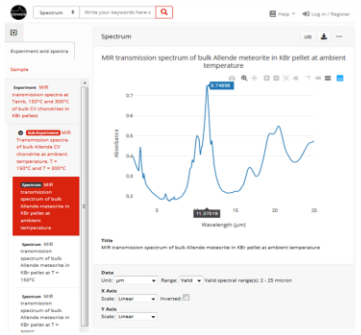
SSHADE interface : Search tools

The user can search **spectral data** or **publications** through two complementary forms:

- ✓ a simple **'Google-style' search bar**
- ✓ a number of **specialized filters** to refine the search



SSHADE search tools for spectra: bar + filters

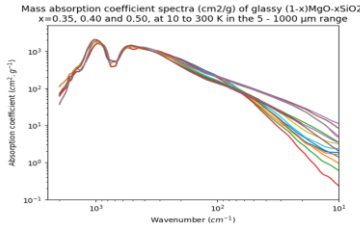


Interactive display for samples & spectra

STOPCODA database

IRAP (MICMAC team) - CNRS / Université Paul Sabatier, OMP, Toulouse

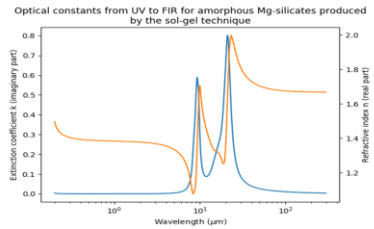
Expertise: infrared spectra of cosmic dust analogues at low temperature.



DOCCD database

AIU Observatory / Laboratory Astrophysics team - Friedrich Schiller University, Jena

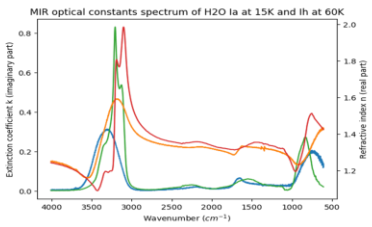
Expertise: UV to FIR complex refractive indices of solid materials relevant for cosmic dust.

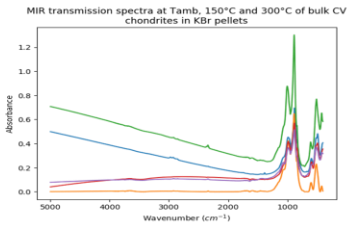


GhoSST database

IPAG (Planetology team) - CNRS / Université Grenoble Alpes. OSUG, Grenoble

Expertise: spectroscopy of solids of planetary and astrophysical interests: natural and synthetic solid samples with special focuses on low temperature ices & molecular solids, hydrated minerals, organics and carbonaceous materials, and cosmo-materials (meteorites, micro-meteorites & IDPs).





and many other databases…