

EPSC2017  
**LF4 abstracts**

## Origin of cometary and chondritic refractory organics: Ion irradiation experiments

E. Quirico<sup>1</sup>, M. Faure<sup>1</sup>, A. Faure<sup>1</sup>, D. Baklouti<sup>2</sup>, P. Boduch<sup>3</sup>, H. Rothard<sup>3</sup>, E. Ballanzat<sup>3</sup>, E. Dartois<sup>2</sup>, R. Brunetto<sup>2</sup>, L. Bonal<sup>1</sup>, P. Beck<sup>1</sup>, B. Schmitt<sup>1</sup>, J. Duprat<sup>4</sup> and C. Engrand<sup>4</sup>.

<sup>1</sup>Université Grenoble Alpes, CNRS, Institut de Planetologie et Astrophysique de Grenoble (IPAG), UMR 5274, Grenoble F-38041, France, email: [eric.quirico@univ-grenoble-alpes.fr](mailto:eric.quirico@univ-grenoble-alpes.fr) <sup>2</sup>Institut d'Astrophysique Spatiale, CNRS / Université Paris Sud, Bâtiment 121, 91405 Orsay, France. <sup>3</sup>CIMAP-Ganil (CEA CNRS UMR6252, ENSICAEN, Univ. Caen Normandie) Caen France. <sup>4</sup>Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse (CSNSM), Université Paris-Sud, UMR 8609-CNRS/IN2P3, F-91405 Orsay, France

### Abstract

The formation process of Refractory Organic matter present in chondrites and Interplanetary Dust Particles (IDPs) of cometary and asteroidal origin is a debated issue. Earlier studies have advocated a formation step in a hot environment, however the potential role of ion irradiation has been so far poorly constrained. We present here experimental simulations that address this issue, comprising thermal degradation and ion irradiation experiments conducted at GANIL (Caen France) and CSNSM (Orsay France). We show that unlike thermal reactions, ion irradiation might lead to ROM-like material under very stringent conditions on both the nuclear dose and the nature of precursor. These very narrow conditions suggest that forming ROM without any action of thermal reactions is extremely difficult in astrophysical environments, either ISM or the proto-solar disk.

### 1. Introduction

Refractory organic matter (ROM) – termed Insoluble Organic Matter (IOM) in chondrites – is a polyaromatic carbonaceous solid ubiquitous in cometary dust and primitive chondrites. The origin of this material is still a debated issue. While the high D/H fractionation points to a formation step in low-T conditions, the polyaromatic structure might require an energetic input as thermal processing and/or ions irradiation [1-4]. We report here experimental simulations in order to test both these processes for producing kerogen-like materials from various precursors: polyethylene glycol (PEG1450), sucrose, lignine, cellulose and a Me-OH soluble extract of lignite.

### 2. Results and Discussion

Thermal degradation experiment were run at IPAG with a tubular furnace maintained under secondary vacuum, over the range 300-1000 °C. Low-energy (LE-) irradiations were performed on the IRMA beamline at CSNSM (Orsay-France) with fluences up to  $4.10^{14}$  ions/cm<sup>2</sup> [C 40 keV, Ne 170 keV], and high-energy (HE-)irradiation at GANIL (Caen-France) [Zn 590 MeV, C 12 MeV, Ni 12 MeV]. Infrared spectra were collected *in situ* during irradiation. Raman spectroscopy (514 and 244 nm) was performed *ex situ* to characterize the polyaromatic structure of the samples. Both IR and Raman data allowed comparison with IOM/ROM from chondrites/cometary dust. Heating experiments resulted in the carbonization of the insoluble precursors lignine, cellulose and sucrose. PEG 1450 fully sublimated during warming, and no data were collected from the lignite extract. The carbonization process resulted in carbon enrichment (H and O loss), along with aromatization and growth of aromatic units. Samples obtained at 400°C during ~1h were found fairly similar to chondritic IOM, showing similar functional groups and polyaromatic structures. Nevertheless, they were not strictly similar and a weak, but significant precursor effect was observed. We also suspect that kinetic effects were at play. In contrast, LE-irradiations failed in providing relevant analogs. All precursors were transformed into an almost amorphous carbonaceous material above a critical nuclear dose of ~ 10 eV/atome. No progressive structural transition was observed. HE-irradiation provided a more complex picture. Irradiated PEG1450 and lignite-extract led to insoluble dark solids whose composition was controlled by the electronic dose. They showed a global composition similar to IOM, but also critical differences (e.g. acetylinic group C≡C, which is absent in IOM) (Fig. 1, 2). In addition, these samples were fluorescent and fragile, precluding the

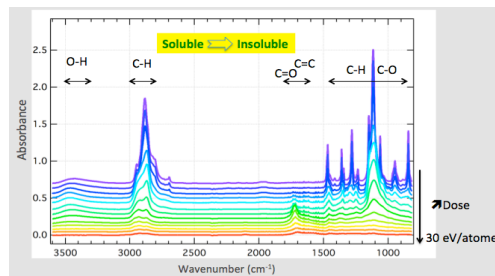
collection of Raman data. We infer their  $sp^2$  structure was very dissimilar from a polyaromatic structure. In contrast, HE-irradiation of lignine and sucrose led to polyaromatic samples, but more disordered than that of IOM. This precursor effect is consistent with previous studies on polyimide and soots [5], suggesting that the final structure is strongly controlled by the structure of the precursor.

### 3. Conclusion

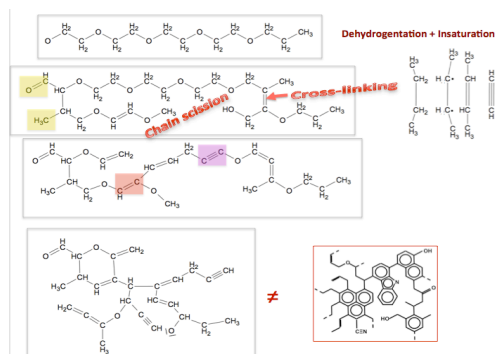
These results show that heating processes provide fair ROM-like polyaromatic solids, and kinetics and precursor effects might even improve these analogs. In contrast, LE-irradiations lead to amorphous carbonaceous material, structurally dissimilar to ROM. HE-irradiation is a plausible chemical route to transform simple species into an insoluble solid, but its respective structure and composition would be dissimilar from ROM. Producing a ROM material would require highly aromatic precursor, but even in this case fitting ROM composition appears very difficult. Finally, our experiments support the view that thermal processing was likely a step of the formation process of ROM.

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**Figure 1:** Infrared spectra of PEG1450 during a high energy irradiation (electronic regime).



**Figure 2:** A schematic view of the structural and chemical evolution of the PEG1450 polymer under high-energy irradiation. A macromolecular insoluble material is finally formed, but it is dissimilar to a polyaromatic structure (in red box).

# FTIR Reflectance Studies of Synthetic Glasses with Planetary Compositions: Mid-Infrared Data for the ESA/JAXA BepiColombo Mission

A. Morlok (1), S. Klemme (2), I. Weber (1), A. Stojic (1), M. Sohn (3), H. Hiesinger (1)

(1) Institut für Planetologie, Wilhelm-Klemm Strasse 10, 48149, Germany ([morlok@uni-muenster.de](mailto:morlok@uni-muenster.de))

(2) Institut für Mineralogie, Corrensstraße 24, 48149 Münster, Germany (3) Hochschule Emden/Leer, Constantiaplatz 4, 26723 Emden, Germany

## Abstract

We present mid-infrared diffuse reflectance spectra of analog materials with planetary compositions (Mercury, Mars, Venus, Moon, Earth) as part of a database for the MERTIS (Mercury Radiometer and Thermal Infrared Spectrometer) instrument on board of the ESA/JAXA BepiColombo mission. First results of glasses showing varying degrees of crystallisation are presented. Best results for glassy planetary materials are achieved with low Mg contents, which allows fast quenching. Materials with MgO well over 30 wt% result in mostly crystalline analogues.

## 1. Introduction

The ESA/JAXA BepiColombo mission to Mercury includes a mid-infrared spectrometer (MERTIS-Mercury Radiometer and Thermal Infrared Spectrometer). This unique instrument allows us to map spectral features in the 7-14  $\mu\text{m}$  range, with a spatial resolution of  $\sim 500$  meter [1-4]. For the interpretation of the data which are expected after arriving at Mercury in 2024, we produce mid-infrared spectra for a database at the IRIS (Infrared and Raman for Interplanetary Spectroscopy) laboratory ([http://www.uni-muenster.de/Planetology/en/ifp/ausstattung/iris\\_spectra\\_database.html](http://www.uni-muenster.de/Planetology/en/ifp/ausstattung/iris_spectra_database.html)).

Material on the surface of Mercury was exposed to heavy impact cratering throughout its history [4]. Glass lacks an ordered microstructure and represents the most amorphous phase of a material, typical for events generated by events involving high shock pressure and temperatures [5,6]. Using synthetic analog materials based on the observed chemical composition of planetary bodies allows us to produce

infrared spectra of materials from which no samples in form of meteorites are available so far.

In addition to studies of glass with the average composition of distinct surface regions on Mercury, we present additional spectra based on synthetic glasses with bulk composition of mantle or crustal regions of the other terrestrial planets. In this presentation, we show the first results for such analog glasses for surface materials from Venus [7] and the Moon [8,9].

## 2. Samples and Techniques

Glasses were synthesized equivalent to the chemical composition of mantle and crustal units of Mercury, Venus, Earth, Moon and Mars based on remote sensing, meteorite and model data [7,8,9]. Mixtures of major oxides ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ) and carbonates ( $\text{CaCO}_3$ ) were prepared. The finely ground powder was slowly heated to  $1000^\circ\text{C}$  to decarbonate and subsequently vitrified in a vertical furnace at  $\sim 1400^\circ\text{C}$ - $1600^\circ\text{C}$  for 2h and quenched immediately afterwards. The resulting glasses will be characterized using EMPA and SEM before the spectral studies.

*Infrared Spectroscopy:* For the FTIR diffuse reflectance analyses, powder size fractions 0-25  $\mu\text{m}$ , 25-63  $\mu\text{m}$ , 63-125  $\mu\text{m}$  and 125-250  $\mu\text{m}$  were measured. For mid-infrared analyses from 2-20  $\mu\text{m}$  we used a Bruker Vertex 70 infrared system with a MCT detector. Analyses were conducted under low pressure (3 mbar) to avoid atmospheric bands. Additional FTIR microscope analyses of thin sections are also planned for polished thick sections. For in-situ mid-infrared specular reflectance analyses we will use a Bruker Hyperion 1000/2000 System at

the Hochschule Emden/Leer. We used a 1000×1000  $\mu\text{m}$  sized aperture, for each spectrum; 128 scans were added.

**Raman Spectroscopy:** In order to characterize the glasses and inclusions, Raman analyses will be conducted using an Ocean Optics IDR-Micro Raman system. The laser excitation is 532 nm in a range from 200  $\text{cm}^{-1}$  to 2000  $\text{cm}^{-1}$ .

### 3. Results

The first series of spectra for glasses based on the chemical composition of the surface of Venus and Moon show simple spectra typical for amorphous materials. A single, strong RB is at 10.6  $\mu\text{m}$  (CF 8.1  $\mu\text{m}$ ) for the venusian surface glass (Fig.1), 10.5  $\mu\text{m}$  for Lunar highland glass (CF 8.0-8.2  $\mu\text{m}$ ) and 10.6  $\mu\text{m}$  (CF 8.2-8.3  $\mu\text{m}$ ) for the lunar mare glass. Interestingly, the glasses show no recognizable Transparency Feature (TF), in contrast to natural glasses like tektites and impact melts [10].

The spectrum based on starting material with the chemical composition of the bulk silicate Moon (Fig.2), however, shows clear crystalline RB features at 10.6  $\mu\text{m}$  and 10.1  $\mu\text{m}$ , and weaker features at 9.7  $\mu\text{m}$ , 11.9  $\mu\text{m}$ , and 16.2  $\mu\text{m}$ . These bands are typical for forsterite [11,12]. A TF in the finest grain size fraction is found at 12.5  $\mu\text{m}$ . The CF is between 8.2 and 8.5  $\mu\text{m}$ .

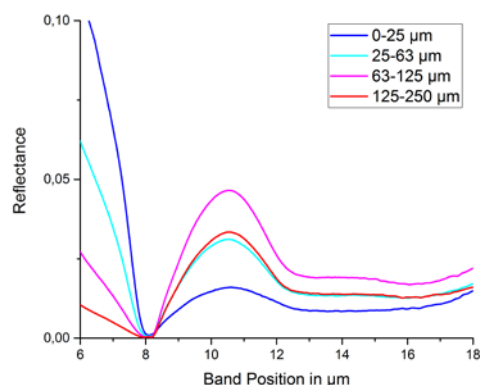
### 4. Summary and Conclusions

The CF and RB features for the synthetic glasses of lunar and Venusian surface composition are typical for basaltic material [10, 13]. The synthetic glasses have comparatively low Mg contents (below 10 wt% MgO), which allows fast quenching of the materials. The bulk silicate Moon glass, on the other hand, has a MgO content of 35.1 wt%, which resulted in mainly crystalline material with forsterite olivine content [11].

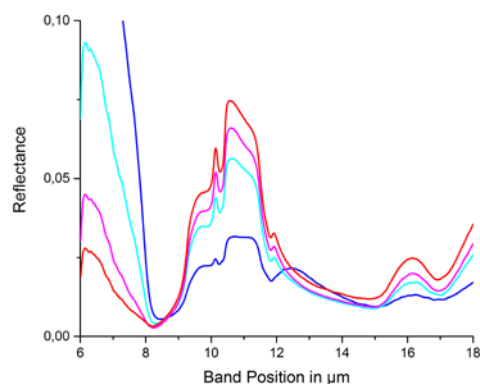
Future analyses in this part of our project will include similar glasses with compositions of terrestrial and martian surface and mantle.

### Acknowledgements

This work is supported by the DLR funding 50 QW 1302 in the framework of the BepiColombo mission.



**Figure 1:** Example for spectra of glassy materials: FTIR spectrum of glass based on chemical composition averaged from analyses of the surface of Venus of Venera and Vega missions [7].



**Figure 2:** Example for results of materials dominated by crystalline material: FTIR spectrum of recrystallized glass with the chemical composition of the bulk silicate moon [9], dominated by crystalline olivine features [10].

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# Composition of micrometeorites compared to carbonaceous chondrites and comet 67P/Churyumov-Gerasimenko

**S. Günther** (1,2), S. Merouane (1), M. Hilchenbach (1) and C. Engrand (3)  
(1) Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany (2) Geowissenschaftliches Zentrum der Georg-August-Universität Göttingen, Germany (3) CSNSM CNRS/IN2P3-Univ. Paris Sud 8609, Orsay, France  
(guenther@mps.mpg.de)

## Abstract

Three Antarctic Micrometeorites (AMMs) from the Concordia collection and four different types of carbonaceous chondrites were analyzed by Raman spectroscopy and EDX analysis to compare their organic and mineralogical composition. One of the AMMs shows organic material and a mineralogy that is very similar to cometary material. The organic material detected in two of the carbonaceous chondrite samples is also very unprocessed and rather similar to the organic material of comets.

## 1. Introduction

These AMMs are submillimeter-sized dust particles collected in the Antarctic snow. Some of these micrometeorites could have formed in the outer solar system and brought to the inner solar system by comets [1]. Former chemical analyses identified several micrometeorites to be very similar to CM and CR carbonaceous chondrite groups [1]. CI and CM chondrites are the least thermally altered meteorites with a chemical composition close to the solar composition [2]. They have suffered a moderate to high aqueous alteration on their parent bodies [3].

## 2. Methods

The three micrometeorite samples analyzed are fragments of larger AMMs and have sizes of 38  $\mu\text{m}$  x 67  $\mu\text{m}$  x 32  $\mu\text{m}$ ; 23  $\mu\text{m}$  x 20  $\mu\text{m}$  x 11  $\mu\text{m}$  and 23  $\mu\text{m}$  x 20  $\mu\text{m}$  x 29  $\mu\text{m}$ . For the analysis they were deposited on gold targets. The carbonaceous chondrites samples, also fragments of larger meteorites, have sizes from 45  $\mu\text{m}$  x 45  $\mu\text{m}$  x 17  $\mu\text{m}$  to 700  $\mu\text{m}$  x 300  $\mu\text{m}$  x 20  $\mu\text{m}$ . They were pressed on a gold target to have an almost flat surface. All samples were analyzed by Raman Spectroscopy and Raster Electron Microscopy.

The samples were analyzed by confocal Raman Spectroscopy using a Witec Alpha 3000 microscope with a spatial resolution of 1  $\mu\text{m}$  and a power between 0.5-3.5 mW. The power was set as low as possible to avoid damaging the organic material. A 3D scan was used to produce a topographic view of the particles with steps between 0.25  $\mu\text{m}$  and 2  $\mu\text{m}$  in the lateral dimension and 1  $\mu\text{m}$  in depth.

The EDX analyses were performed at a pressure of  $2.1 \times 10^{-5}$  mbar with an acceleration voltage of 15-20 kV. Element mappings were acquired with a resolution of 300-500 raster points. Individual spectra were taken with 60-200 live seconds in order to measure their bulk composition. The mappings were acquired with 600 -12,600 live seconds.

## 3. Results

As a first step using both the Raman spectra and the EDX analyses we can identify the mineralogy of the AMMs (Tab.1).

Tab. 1: Identified components of the AMMs with detailed chemistry.

	DC 06-07-45-7	DC 06-07-162	DC 06-09-249
<b>Identified compounds</b>	Pargasite Anorthite Troilite Pyroxene Olivine Hematite Organics	Pyroxene Magnetite Sulfates Organics	Pyroxene Maghemite Hematite
<b>Detailed chemistry</b>			
Pyroxene	En <sub>97.5</sub> Fs <sub>2.5</sub> to En <sub>70</sub> Fs <sub>30</sub> + hints for very Ca-rich Px	En <sub>44</sub> Fs <sub>50</sub> Wo <sub>50</sub>	En <sub>50</sub> Fs <sub>50</sub> to En <sub>90</sub> Fs <sub>10</sub>
Olivine	Fo <sub>37±19</sub> to Fo <sub>99±16</sub>	-	-
Sulfates	-	(Na,K) <sub>2</sub> SO <sub>4</sub>	-



## 4. Discussion

The mineralogy of DC 06-07-45-7 mostly consists of rather unaltered components like very Mg-rich olivine and pyroxene, troilite, anorthite and organics that have not been much processed by aqueous alteration. These organics are very similar to the organics that were observed in Interplanetary Dust Particles (IDPs) (Fig. 1).

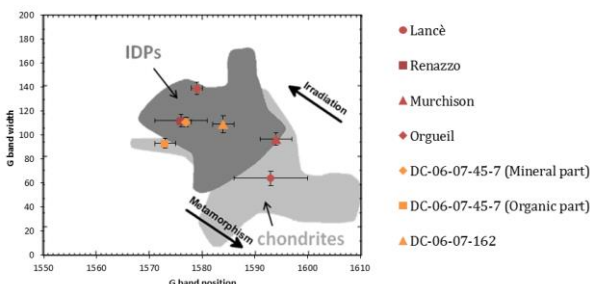


Fig. 1: Modified plot from Brunetto et al. [4]. G band parameters for meteorites and IDPs are compared to our samples. The G band parameters change with the degree of thermal alteration.

DC-06-07-162 still contains organic material that was slightly more processed by thermal alteration than DC-06-07-45-7 (Fig. 1). The mineralogy is typical for a hydrothermally altered object. That particle could have undergone aqueous alteration on its parent body, similarly to CI and CM chondrites. DC 06-09-249 contains no organic material and has a very processed mineralogy. It is likely coming from a larger parent body, or has entered in the Earth's atmosphere at a very high velocity.

Pargasite that has been detected in particle DC-06-07-45-7 is an amphibole that is very rare in chondrites and that has not been reported so far in micrometeorites. It is very common in larger parent bodies from which achondrites might originate and requires temperatures about 600°C to be formed [5]. Looking at the whole composition of our particle we can exclude an achondritic origin. Some studies [6] claim that pargasite could be formed by solar nebula processes from pyroxene with water. That would be more consistent with our particle composition.

Among these AMMs, particle DC-06-07-45-7 is the particle showing most similarities with cometary materials, in particular with particles of comet 67P/Churyumov–Gerasimenko. It has a similar porous morphology as these particles [7] and also contains complex organic material [8]. It also shows

the typical mineralogy of cometary material: anhydrous silicates, sulfides, and inclusions of Ca-Al silicates.

## 5. Conclusion

The analysis of the AMMs already shows a broad and diverse mineralogy implying different degrees of alteration on their parent bodies. This shows that the micrometeorites retrieved in Antarctic ices originate from a diversity of objects and a comparison of their composition with well-known meteorites as well as cometary data from space missions (e.g. Stardust, Rosetta) is necessary to assess their possible origin.

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# Laboratory spectral reflectance studies aimed at providing clues to composition of refractory phases of comet 67P/CG's nucleus

**L.V. Moroz** (1,2), K. Markus (1,2), G. Arnold (2), D. Henckel (2), D. Kappel (2), U. Schade (3), M. Ciarniello (4), B. Rousseau (5), E. Quirico (6), B. Schmitt (6), F. Capaccioni (4), D. Bockelee-Morvan (5), G. Filacchione (4), S. Erard (5), C. Leyrat (5), A. Longobardo (4) and the VIRTIS Science Team  
(1) Institute of Earth and Environmental Science, University of Potsdam, Potsdam, Germany ([Liubov.Moroz@dlr.de](mailto:Liubov.Moroz@dlr.de)), (2) German Aerospace Center (DLR), Berlin, Germany, (3) HZB for Materials and Energy, Berlin, Germany, (4) INAF-IAPS, Rome, Italy, (5) LESIA-Observatoire de Paris, Meudon, France, (6) Université Grenoble Alpes, IPAG, Grenoble, France.

## Abstract

We present 0.3-5  $\mu\text{m}$  reflectance spectra of well-characterized powdered crystalline materials (Fe-sulfides, Mg-silicates), natural complex hydrocarbons and their mixtures that can serve as spectral analogues of comet 67P/CG's refractory phases. We study the ability of Fe-sulfides to suppress absorption bands of other cometary refractory components and to affect spectral slopes and reflectance values of the 67P/CG surface at different wavelengths from the near-UV to the IR. We investigate the evolution of organic absorption bands as a function of sulfide content in the mixtures and the possibility for detection of individual C-H stretching bands in reflectance spectra of 67P/CG.

## 1. Introduction

Visible and InfraRed Thermal Imaging Spectrometer (VIRTIS) onboard Rosetta orbiter revealed that the surface of comet 67P/CG is dark from the near-UV to the IR and is enriched in refractories such as organic and opaque components [1,2]. The broadness and complexity of the ubiquitous absorption feature around 3.2  $\mu\text{m}$  suggest a variety of cometary organic constituents [2]. For example, complex hydrocarbons can contribute to the feature between 3.2 and 3.5  $\mu\text{m}$  and to the low reflectance of the surface in the visible [2,3]. Fine-grained opaques (Fe-sulfides, Fe-Ni alloys) are likely responsible for the low IR reflectance and low contrast of the 3.2  $\mu\text{m}$  absorption band [1,2]. Other non-icy constituents that may contribute to spectral reflectance properties of the 67P surface include amorphous and crystalline silicates. To derive compositional information from VIRTIS spectra of the 67P surface, it is important to

understand possible spectral contributions of relevant refractory phases to the reflectance curves of the comet surface.

## 2. Samples and Methods

Fe-sulfides used here include three terrestrial pyrrhotites ( $\text{Fe}_{1-x}\text{S}$ ) and a troilite ( $\text{FeS}$ ) from troilite nodules of the Muonionalusta iron meteorite. Bulk samples were crushed, ground and dry-sieved to several size fractions. Two sets of ortho- and clinoenstatites ( $\text{En}_{100}$ ) were synthesized by K. Markus and R. Housley. Synthetic Fe-free forsterites and diopsides were provided by R. Housley. The samples were chemically and mineralogically characterized. The well-characterized kerite sample PAM#42 (#8450 in [3];  $\text{H/C(at.)}=1.15$ ) was used as a spectral analogue for cometary macromolecular refractory organic material. Troilite and pyrrhotite <25  $\mu\text{m}$  separates were mechanically mixed with the kerite <25  $\mu\text{m}$  separate. A similar set of orthoenstatite-pyrrhotite mixtures was prepared as well. Optical microscopy and SEM/BSE imaging of thin sections and ImageJ software were employed to characterize grain size distribution of mineral and kerite powders, as well as the mixtures. Analysis of the measured reflectance spectra and microscopic images showed that the desired state of mixing was not achieved, especially for kerite-sulfide mixtures. The second set of mixtures was prepared by manual grinding of the original mixtures in an agate mortar. Biconical reflectance spectra (0.3-18  $\mu\text{m}$ ) were acquired at Planetary Spectroscopy Laboratory (DLR, Berlin) in vacuum at  $i=e=15^\circ$  using a Bruker VERTEX 80v FTIR-spectrometer equipped with a Bruker variable angle reflectance accessory.



### 3. Results and Conclusions

All powders of Mg-silicates used in this study are very bright, spectrally flat and nearly featureless in the visible and near-infrared. Steep near-UV drop-off is observed in all spectra despite very low contents of Fe and other transition elements.

Fe-sulfide powders are spectrally diverse in terms of reflectance and spectral slopes, and no specific spectral differences exist between pyrrhotites and troilite. Analysis of microscopic images suggests that the observed spectral diversity is associated with particle size variations rather than compositional ones. Overall reflectance of all samples decreases with decreasing particle size, as expected.

Reflectance spectra of fine-grained kerite-sulfide and orthoenstatite-sulfide intimate mixtures show that fine-grained Fe-sulfides (troilite and pyrrhotite) are very efficient darkening agents from the near-UV to IR, which can explain the very low IR reflectance of the 67P nucleus. Coarse-grained sulfides are much less effective darkening agents than fine-grained ones.

Our results show that spectral reflectance of the ubiquitous dark material on the surface of 67P is mostly controlled by fine-grained opaques and organic refractories, while silicate components play a less significant role and are unlikely to contribute significantly to the VIRTIS spectra and to the observed spectral variations across the 67P surface.

The shape of VIRTIS reflectance spectra of 67P/CG's nucleus in the visible spectral range is consistent with the presence of organics containing polyaromatic hydrocarbons together with fine-grained Fe-sulfides (troilite and/or pyrrhotite). The above three conclusions are consistent with those obtained by [4] based on their spectral studies of coal-pyrrhotite and coal-pyrrhotite-silicate mixtures.

Analysis of reflectance spectra of kerite-sulfide mixtures shows that Fe-sulfides intimately mixed with other phases significantly influence shapes and relative contrasts of absorption bands of other species.

Despite the very low IR reflectance of 67P, the band contrast of its broad complex absorption centered near 3.2  $\mu\text{m}$  is rather significant. This suggests that the carriers of the individual absorption bands contributing to this feature likely possess very intense absorption bands in this spectral range.

The broad absorption feature in 67P surface spectra shows fine structure (Figure 1), in particular, several reflectance minima whose positions coincide with those of aromatic C-H stretch (3.275  $\mu\text{m}$ ),  $\text{CH}_3$  antisymmetric stretch (3.375  $\mu\text{m}$ ),  $\text{CH}_2$  antisymmetric stretch (3.42  $\mu\text{m}$ ), and  $\text{CH}_3$  symmetric stretch (3.48  $\mu\text{m}$ ) [3]. If the band assignments are correct, then the observed relative contrasts might imply higher content of aromatic C-H and higher  $\text{CH}_3/\text{CH}_2$  ratio in 67P organics compared to the kerite sample used in this study, which has carbon aromaticity (*fa*) of 0.5 [3]. Further work is needed to clarify which species contribute to the broad complex 3.2- $\mu\text{m}$  band in the VIRTIS spectra.

### Acknowledgements

We thank I. Büttner for assistance in sample preparation and R. Housley for kindly providing his synthetic silicate powders. L.V.M. and K.M. acknowledge the DFG grant MO 3007/1-1.

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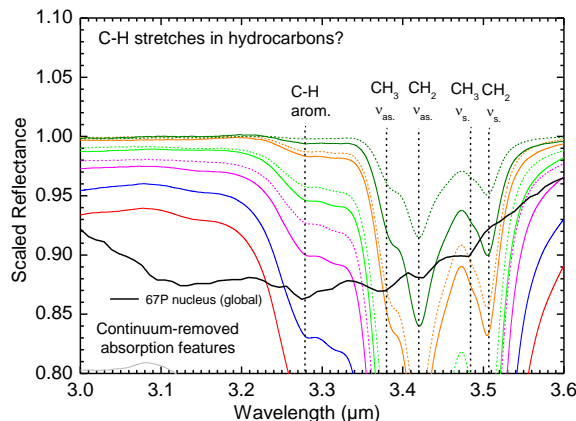


Figure 1: Continuum-removed absorption features of kerite-sulfide mixtures and in an average VIRTIS-M surface spectrum after geometric and thermal correction. Solid lines – kerite-pyrrhotite mixtures; dotted lines – kerite-troilite mixtures. Kerite volume percentages in the mixtures: red – 95; blue – 90; magenta – 80; green – 70; orange – 50; olive – 30.

# ‘Peeling a comet’: Layering of comet analogues

**E. Kaufmann** and A. Hagermann

School of Physical Sciences, The Open University, Milton Keynes, UK, (erika.kaufmann@open.ac.uk / Fax: +44(0)1908 655 667)

## Abstract

Many comet models define the nucleus surface as a strict boundary (e.g. [1]; [2]), others as a dynamic transitional zone (see e.g. [3]). A series of experiments has been performed at the Open University to gain more insight into which of the two is the more realistic approach.

## 1. Introduction

Our current understanding of the physics of comets is based on data from several space missions (e.g. Giotto, Deep Impact and most recently Rosetta), the predictions of theoretical models and the results of laboratory experiments. Some of the data and images obtained from cometary missions have raised questions that cannot be answered without improving the established theoretical models – a process that should be based on experimental results.

Several series of comet simulation experiments have been done in the past. For example KOSI (KOMETEN Simulation, German for comet simulation), the most extended campaign, was performed in the late eighties and early nineties of the last century [4]. Although those experiments provided new insight in the physics and morphology of cometary analogue materials, the set-up was quite complex and made it difficult to analyze the results in a quantitative manner.

To minimize these difficulties we decided to start our series of experiments using samples that only contain two components – H<sub>2</sub>O ice and carbon particles (carbon black).

To investigate the influence of subsurface solar light absorption by dust, we added varying quantities of carbon particles to samples of porous ice. The samples are irradiated for several hours, temperature

and hardness profile are measured and the change of the surface structure is recorded.

## 2. Experiments

We investigated mixtures of H<sub>2</sub>O ice and carbon black with different initial temperatures, mixing ratios and sample heights under vacuum conditions. The basic set-up for all experiments was the same: a cylindrical container consisting of two Perspex halves fixed on a cooled base plate inside an environmental chamber was filled with the sample material. The sample with an initial height  $h_0$  was cooled down to a given minimum temperature  $T_0$ , while the chamber was depressurised. After the temperature gradient inside the sample had stabilised, the samples were irradiated using a solar simulator and the temperature profile inside the sample was measured. Additionally, a time lapse record of the morphology of the sample during the irradiation phase was obtained using a set of commercial off-the-shelf webcams.

### 2.1 Hardness measurements

After the experiments, the sample was cut in halves and the hardness profile of the sample along the vertical axis was measured using the method described by [5]. The samples were already slightly harder than the original material due to sintering before the irradiation was started. At that time the hardness is constant along the z-axis.

The original sample material was a loose aggregate of particles with a hardness of about 4 -6 kPa. After the samples were cooled in a depressurised surrounding and irradiated for about 18 hours each of the samples got significantly harder with a soft layer including the surface, a harder layer beneath and a more soft one closer to the bottom of the sample.

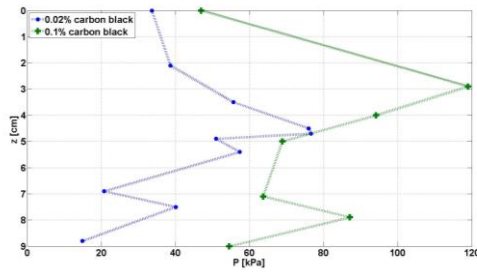


Figure 1: Example of hardness profiles after 18 hours of irradiation for two different H<sub>2</sub>O/carbon black mixtures, Surface:  $z = 0\text{cm}$ ,  $h_0 = 15\text{cm}$ ,  $T_0 = 173\text{K}$ .

## 2.2 Surface structure

During the irradiation process the surface has changed significantly. Figure 2 shows the sample surface at the beginning of the irradiation phase (left) and after 18 hours of irradiation (right). Particle emission starts immediately after the light is turned on, a significant change of the surface can already be observed within the first 10 minutes of irradiation.

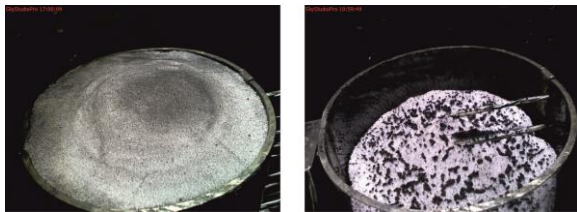


Figure 2: Change of the surface structure after 18 hours of irradiation. Sample includes 0.2% carbon black.  $T_0 = 173\text{K}$ ,  $h_0 = 15\text{cm}$ .

## Summary and Conclusions

The results of the experiments carried out so far show that all samples were hardened considerably by exposure to solar light. The higher the amount of light-absorbing carbon particles, the harder the samples became.

The hardest layer can be found 3 - 7cm below the surface where the sample temperature is  $\sim 203\text{K}$  to  $207\text{K}$ .

Changing the base temperature of the sample has less effect on the hardness than changing the carbon particle percentage.

For low carbon particle content the material close to the base barely changes compared to the original material in terms of hardness.

Particle emission starts immediately after the irradiation starts and conglomerates of carbon black built on the surface.

The dramatic surface hardening by insolation combined with the drastic change in surface structure (even if only a marginal amount of carbon particles are added to the ice sample) suggests that cometary models should treat the nucleus surface as an interactive transitional zone to better represent cometary processes.

## Acknowledgements

This project is funded by STFC under grant number ST/L000776/1.

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# Evolution of ice/dust mixtures upon sublimation of ice, implications for comets and larger icy objects

O. Poch (1), A. Pommerol (1), B. Jost (1), Z. Yoldi (1), N. Carrasco (2, 3), C. Szopa (2), N. Thomas (1)

(1) Physikalisches Institut and NCCR PlanetS, University of Bern, Switzerland ([olivier.poch@gmail.com](mailto:olivier.poch@gmail.com)),

(2) Université Versailles St-Quentin; Sorbonne Universités, UPMC Univ. Paris 06; LATMOS, CNRS, France

(3) Institut Universitaire de France

## 1. Introduction

The surfaces of many objects in the Solar System comprise substantial quantities of water ice either in pure form or mixed with minerals and/or organic molecules. Sublimation is a process responsible for shaping and changing the reflectance properties of these objects. This peculiar process is not known enough and requires experimental studies.

## 2. Methods

We present laboratory data on the evolution of the structure and the visible and near-infrared spectral reflectance of icy surfaces made of mixtures of water ice and non-volatile components (complex organic matter and silicates), as they undergo sublimation of the water ice under low temperature and pressure conditions [1,2]. We prepared icy surfaces which are potential analogues of ices found on comets, icy satellites or trans-neptunian objects (TNOs). The experiments were carried out in the SCITEAS simulation setup built as part of the Laboratory for Outflow Studies of Sublimating Materials (LOSSy) at the University of Bern [3].

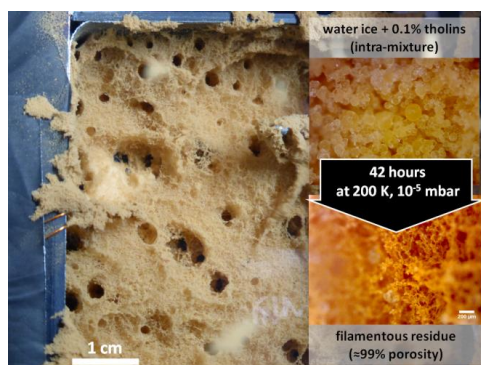


Figure 1: Formation of a dry foam-like porous organic matrix after sublimation of the water ice [1].

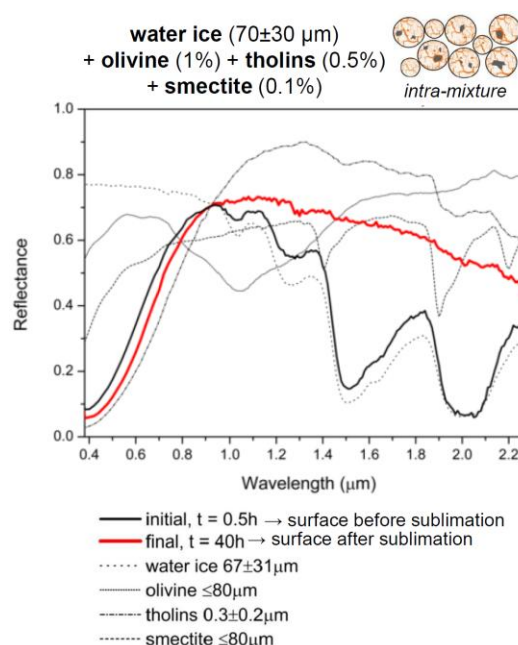


Figure 2: Reflectance spectra of a sample surface before and after sublimation [2].

## 3. Results

As the water ice sublimated, we observed *in situ* the formation of a sublimation lag deposit, or sublimation mantle, made of the non-volatiles at the top of the samples (Figure 1). The texture (porosity, internal cohesiveness etc.), the activity (outbursts and ejection of mantle fragments) and the spectrophotometric properties (Figure 2) of this mantle are found to differ strongly depending on the chemical nature of the non-volatiles, the size of their particles, the way they are mixed with the volatile component and the dust/ice mass ratio. The results also indicate

how the band depths of the sub-surface water ice evolve during the build-up of the sublimation mantle.

These data provide useful references for interpreting remote-sensing observations of Rosetta [4], Dawn [5], and also New Horizons.

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# The Katol (L6-7): A unique chondrite with evidences for shock-induced melting and post-shock annealing

D. Ray, S. Ghosh and **A.D.Shukla**<sup>#</sup>

Physical Research Laboratory, Ahmedabad 380 009, India (dwijesh@prl.res.in)

<sup>#</sup>presenting author

## Abstract

Troilite-metal nodules (TMN) bearing Katol chondrite is classified as L6-7(S2). Its complex thermal-shock history includes highly thermal metamorphism in the host chondrite and extreme shock metamorphism and subsequent post-shock annealing in the TMN. The latter exhibits numerous shear melt veins (SMV) with quenched metal sulphide melt (QMSM) textures, maskelynite and ringwoodite. Subsequent healing in response to post-shock annealing induces degenerated plessites and undulose extinction of olivine grains which are intensely fractured and filled with QMSM.

## 1. Introduction

The Katol chondrite is one of the recent meteorite showers (May 22, 2012) in India. This unique chondrite hosts an unusual piece of TMN [1,2]. The silicate part of the chondrite is highly recrystallised and hardly any relict chondrule is discernible. Based on homogeneity of olivine (Fa 25.1, PMD: 2.37), low-Ca pyroxene (Fs 21.2, PMD: 0.82) and coarse plagioclase grains (generally > 100µ), Katol resembles to highly equilibrated petrologic type. There are no significant shock features except impact induced fracturing in olivines and pyroxenes and diaplectic plagioclase are recorded. In contrast, TMN is an impact melt product of mainly troilite and metal including high pressure silicate polymorphs. In this communication, we will discuss the nature of newly identified SMVs, microstructures of plessite within Fe,Ni alloy in order to understand the TMN shock history and post-shock annealing.

## 2. Microstructures

### 2.1 Quenched Metal-Sulphide Melt

QMSM is the major component of the TMN (Fig. 1). Texturally it looks like a metal-sulphide mosaic due to quenched droplets and irregular blebs of metals within the troilite host (Fig. 2). The SMVs

with different scales and in bifurcating pattern are the preferred sites of such quenched melts. (Fig. 1,2).

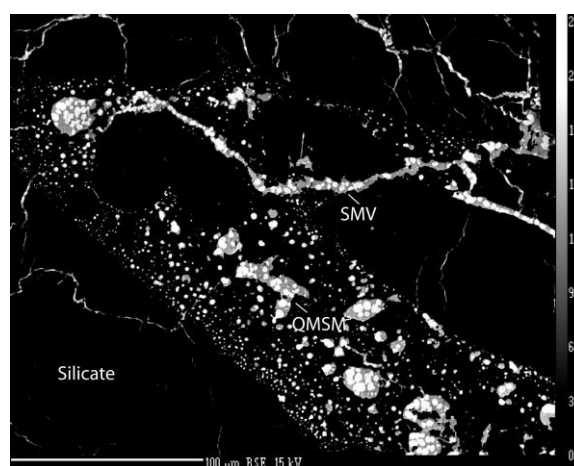


Figure 1: BSE image of QMSM and veins of SMV.

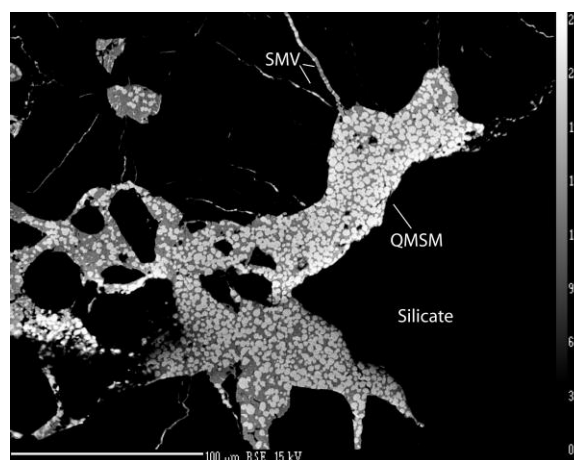


Figure 2: Irregularly branched SMVs showing caught-up silicate fragments in QMSM.

### 2.2 Metallography

Apart from isolated grains, a few coarse kamacite-taenite assemblages are found to occur adjacent to shock melt vein. The most interesting feature is the



finely crenulated taenite bands within kamacite in the plessite regions (Fig. 3,4) with well developed outer-taenite rim. The Ni content of kamacite within the plessite is comparatively low (Ni: 3.5-5.35 wt%), where as the outer taenite rim shows high Ni content (Ni:48.11 wt%).

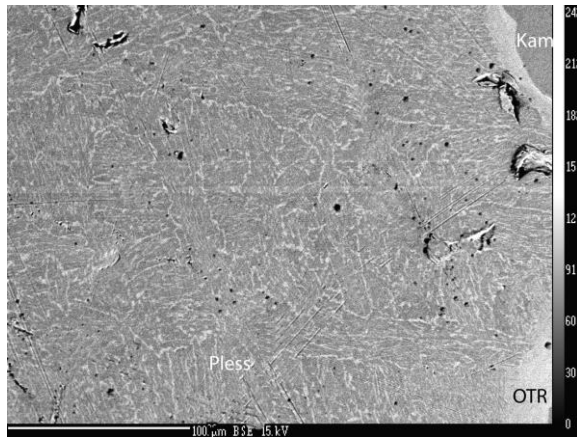


Figure 3: Fine crenulations within plessite (Pless). OTR:Outer taenite rim, Kam: Kamacite

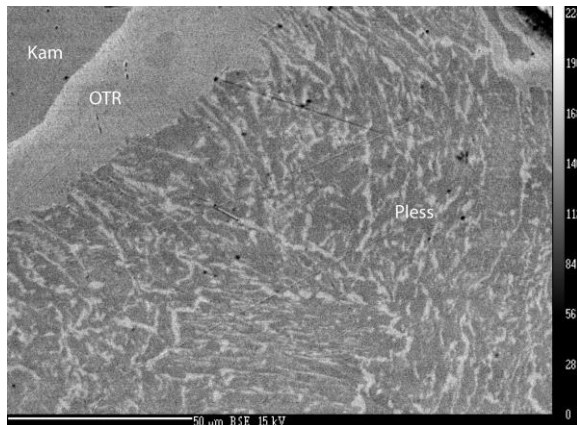


Figure 4: Degenerated plessite (in high mag) OTR:Outer taenite rim, Kam: Kamacite.

### 2.3 Post-shock annealing

Annealing is a slow recovery process through cooling of the shock-induced heat generated in the target rocks. Effects of post-shock annealing are more common in ordinary chondrites and commonly represent low shock stage despite previously experienced relatively higher shock [3]. Presence of shock-melted plagioclase glass, numerous shock-melt veins, high pressure polymorphs suggest that Katol

attained a maximum shock pressure up to S6. Subsequent annealing developed polycrystalline troilite, degenerated plessites and part healing of crystalline damage in olivine grains in the form of undulose extinction.

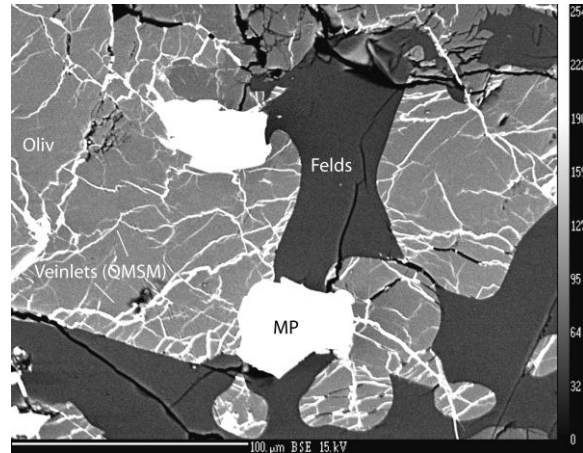


Figure 5: Fractures filling within olivine (Oliv) by QMSM. MP: Melt pockets, Felds: Feldspar

## 3. Summary and Conclusions

Based on microstructures, it appears that the impact generated hot, molten metal-troilite (Fe-Ni-S) melt was injected into the major shear veins and adjoining fractured silicates. TMN comprising SMVs filled with QMSM is a product of high energy, localised impact. Post-shock annealing lowered down the shock stage (S2) in silicates and degenerated the plessite. Finally, annealing healed and sealed the fractures in olivine grains by QMSM (Fig. 5).

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# Berlin Reflectance Spectral Library (BRS�)

**D. Henckel** (1, 2), G. Arnold (1, 3), D. Kappel (1), L.V. Moroz (1, 3) and K. Markus (1, 3)

(1) German Aerospace Center (DLR), Berlin, Germany ([daniela.henckel@gmx.de](mailto:daniela.henckel@gmx.de)), (2) Free University of Berlin, Institute of Geological Science, Berlin, Germany, (3) Institute of Earth and Environmental Science, University of Potsdam, Potsdam, Germany

## Abstract

The Berlin Reflectance Spectral Library (BRS�) provides a collection of reflectance spectra between 0.3 and 17  $\mu\text{m}$ . It was originally dedicated to support space missions to small solar system bodies. Meanwhile the library includes selections of biconical reflectance spectra for spectral data analysis of other planetary bodies as well. The library provides reference spectra of well-characterized terrestrial analogue materials and meteorites for interpretation of remote sensing reflectance spectra of planetary surfaces. We introduce the BRS�, summarize the data available, and access to use them for further relevant applications.

## 1. Introduction

Laboratory spectra of minerals, mineral mixtures and meteoritic samples are the basis for analysis of remote sensing spectra, e.g., to study surface composition or surface texture. The spectral library was originally created as the Rosetta Spectral Library (RSL) and was constantly extended comprising data relevant to various space missions like the Dawn mission or ExoMars. The BRS� is a separate DLR library complementary to the Planetary Emissivity Library (PEL) [1].

## 2. Spectra and sample information

The BRS� provides reflectance spectra of different analogues (terrestrial minerals, rocks, refractory organic materials, and meteorites) for small bodies like comets or asteroids and planetary bodies like Mars and Mercury. The spectra cover the wavelength range between 0.3 and 17  $\mu\text{m}$ . Measurements at longer wavelengths are planned to be integrated in a next step. The spectral library includes spectra of bulk and powdered materials. The spectra were recorded at the Planetary Spectroscopy Laboratory (PSL) [1], the Infrared and Raman for Interplanetary

Spectroscopy (IR/IS) at the University of Münster and the Complex Irradiation Facility (CIF) [2] at the DLR Bremen. The samples are measured at biconical geometry with varying incidence and emergence angles.

A DLR ID number (PAM#, Planetary Analogue Materials) is assigned to each spectrum of an analogue material. It allows tracking all sample information, spectral data and the measurement path.

BRS� provides chemical analyses (RFA, XRD or microprobe) for all spectrally characterized samples.

Over 300 different analogue materials are currently available at the DLR laboratory in Berlin. They include various phyllosilicates, mafic minerals, synthetic Fe-free mafic silicates [3], sulfides, sulfates, carbonates, oxides, hydroxides, synthetic salts, organic materials like solid oil bitumens [4] and meteorites (in particular C-chondrites).

## 3. Structure of the spectral library

The BRS� is a Microsoft Access database continuously extended by recent laboratory spectral data. The spectral library is divided into two parts, the public one that contains the post-processed data for external users and the part two comprising the raw data accessible only for internal use or upon request. For the BRS� public part over 200 post-processed spectra are included so far. For internal use 2500 raw datasets are available. In addition, both parts provide sample information on grain size, sample origin, sample type, chemical composition and measurement set-up (instrument, incidence/emergence /phase angles, resolution). The internal part of the database includes more detailed information on a sample to track the preparatory path and sample storage as well as the complete measurement set-up (standard, beamsplitter,

detectors, scan number, filter, pre-amplifier and others).

A README file available to all users comprises relevant information on how to cite and use the BRSL. It summarizes details of the laboratory set-up (instrument description), the general database structure, the measurement standard set-up, and information on the general measurement procedure.

The data provided by BRSL are available in the standard file formats. Spectral reflectance data (pre- and post-processed) are available as ASCII-files. Reflectance spectra plots (Figure 1) are available as png-files. Sample images (Figure 2) are provided as jpeg-files. Chemical analyses are available as pdf- and ASCII-files (tables). The public part of BRSL will be accessible via the VESPA service at <http://vespa.obspm.fr/planetary/data/epn/query/all/> to search and download the data. This service is provided by the Europlanet H2020 Research Infrastructure project funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 654208.

## 4. Conclusion and further work

The BRSL is a library of UV/VIS/IR reflectance spectra which provides a user with input data and sample information to support analysis of remote sensing reflectance spectra of solid solar system objects. The data sets are easily accessible and can be downloaded.

BRSL is complementary to the Berlin Planetary Emissivity Library (PEL) and complements existing databases with data relevant to small solar system bodies and dwarf planets.

The work on the spectral library is still ongoing and the dataset is continuously updated. Currently BRSL is optimized to follow user requests. By the end of June 2017, the spectral library will be implemented into the VESPA service and thus, available to interested public users.

## Acknowledgements

We acknowledge the VESPA team for their help and guidance to develop and establish our service in their network.

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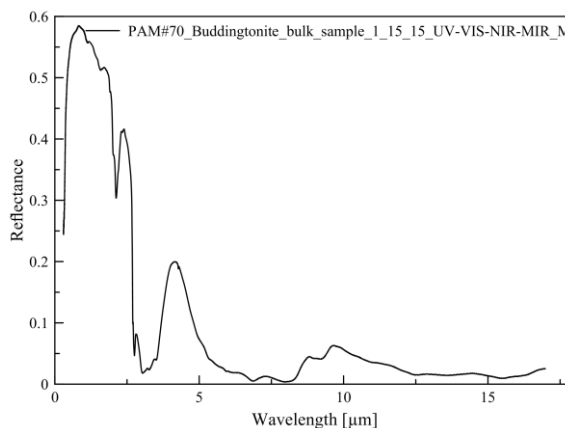


Figure 1: BRSL: Example of visualized reflectance spectrum. The figure shows a reflectance spectrum of buddingtonite (bulk sample) between 0.3 and 17  $\mu\text{m}$ .

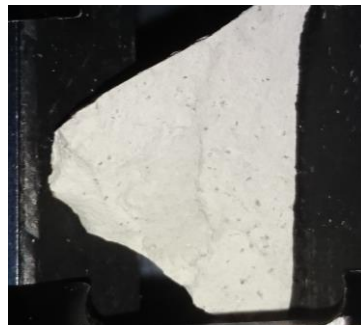


Figure 2: BRSL: Example of sample image (corresponding to Fig. 1). The figure shows an image of a bulk sample of buddingtonite, an ammonium-feldspar.

# Interpretation of VIRTIS/Rosetta surface spectra of comet 67P from laboratory reflectance measurements of cometary analogues, including iron sulphides

**Batiste Rousseau** (1), S. Érard (1), P. Beck (2), É. Quirico (2), B. Schmitt (2), O. Brissaud (2), F. Capaccioni (3), G. Filacchione (3), D. Bockelée-Morvan (1), C. Leyrat (1), M. Ciarniello (3), A. Raponi (3), D. Kappel (4), G. Arnold (4), L. V. Moroz (4, 5) and the VIRTIS Team

(1) LESIA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06, Univ. Paris Diderot, Sorbonne Paris Cité, 5 place Jules Janssen, 92195 Meudon, France ([batiste.rousseau@obspm.fr](mailto:batiste.rousseau@obspm.fr)), (2) Université Grenoble Alpes, CNRS, Institut de Planetologie et Astrophysique de Grenoble (IPAG), France, (3) INAF-IAPS, Istituto di Astrofisica e Planetologia Spaziali, Rome, Italy, (4) Institute for Planetary Research, DLR, Berlin, Germany, (5) Institute of Earth and Environmental Science, University of Potsdam, Potsdam, Germany

## Abstract

The Rosetta spacecraft has been orbiting the comet 67P from August 2014 to September 2016 with the aim to understand better the activity, the evolution and the surface processes of the nucleus. The VIRTIS spectrometer [1] has acquired reflectance spectra from two channels: VIRTIS-M, an imaging-spectrometer, ranging from 0.25  $\mu\text{m}$  to 5.1  $\mu\text{m}$  with  $\sim 2$  nm and  $\sim 10$  nm resolution (resp. in the VIS and IR) and VIRTIS-H, a point spectrometer ranging from 1.9  $\mu\text{m}$  to 5.1  $\mu\text{m}$  with a  $\sim 10$  times higher spectral resolution than VIRTIS-M. The goal of this study is to reproduce the spectral behavior of the surface as observed by VIRTIS in the range 0.4  $\mu\text{m}$  – 2.7  $\mu\text{m}$ . For this purpose, we measured reflectance spectra of cometary analogs produced in the lab from iron sulphides, coal and silicates.

## 1. Introduction

Cometary nuclei are among the most pristine objects in the Solar System, having experienced no differentiation and moderate evolution during their lifetime. Their study helps to better understand the first stages of the formation of planetary bodies and the dynamics in the primitive nebula. Observations of cometary nuclei [2,3], dust sample returns [4] and collection of Interplanetary Dust Particles [5] give us important information about the composition of cometary surfaces while a number of experiment many experiments [6, 7] tried to reproduce the physical mechanisms of the activity in presence of ice and dust. Here we try to infer the global composition of the surface by comparing laboratory measurements to VIRTIS data.

## 2. Methods

Observations dedicated to study the dust in the coma made by the GIADA, COSIMA and MIDAS instruments on board Rosetta [8, 9, 10] have indicated particle size distribution extending to the sub- $\mu\text{m}$  scale. The development of new grinding techniques at IPAG allows us to produce particles with sizes  $< 0.4 \mu\text{m}$  for a series of tested materials: organic matter (coal), iron sulphides (pyrite, pyrrhotite) and silicates (olivine, pyroxene). Various compositions (coal+sulphide, coal+silicates, coal+sulphide+silicate...) and mixing modalities (intimate/linear) were tested in our mixtures as well as different grain sizes. Reflectance measurements at standard observation geometry (incidence =  $0^\circ$ , emergence =  $30^\circ$ ) were made with a spectro-gonio-radiometer in order to understand the effect of these parameters and to reproduce as good as possible the VIRTIS spectra. A set of measurements at various observation geometries was also acquired.

## 3. Results

**Pure phases ( $< \mu\text{m}$ ):** spectral effects of grain size variation were tested for pure sub-micrometric phases. While silicates and coal experience brightening with decreasing size (see Fig 1. for coal), Fe-sulphides get darker (Fig. 2). This influences the spectral shape of mixtures.

**Mixtures - effect of composition:** we use powders with sub-micrometric grains to realize different mixtures. Coal+silicate and pyrrhotite+silicate do not fit the VIRTIS spectra. A mixture of coal+33wt% of pyrrhotite provides a good fit ('A' – blue spectrum on Fig. 3). However, coarser grains are needed in this case.

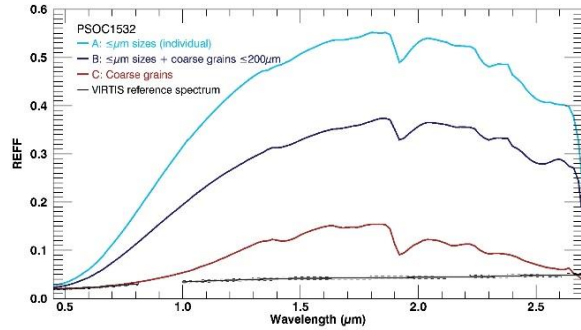


Figure 1: spectra of pure coal PSOC1532 powders with various grain sizes

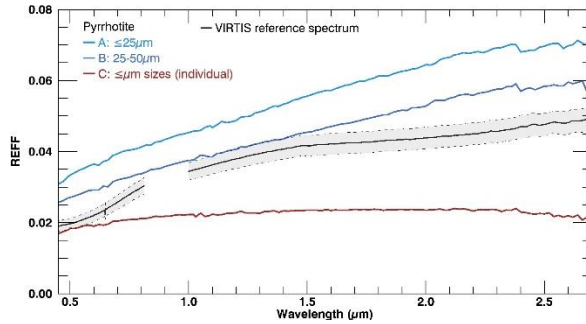


Figure 2: spectra of pure pyrrhotite ( $Fe_{1-x}S$ ) powders with various grains sizes

**Effect of mixing modalities (Fig. 3):** spectral slopes and IR reflectance of intimate mixtures of coal and pyrrhotite are smaller with respect to the values inferred by VIRTIS ('B' – red spectrum, Fig. 3). In mixtures with coating of pyrrhotite over coal, the spectral slope is bluer and the reflectance value is higher but still does not fit the VIRTIS one ('C' – green spectrum, Fig. 3). Conversely, in the VIS, the fit is fairly good in both cases. The presence of silicate plays a minor role in these mixtures (intimate and coating, Fig. 4).

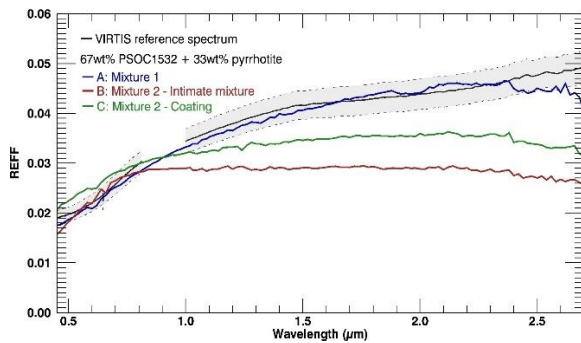


Figure 3: mixtures of coal and pyrrhotite against mean VIRTIS spectrum. See text for details

## 4. Summary and Conclusions

Our measurements indicate that sub-micron particles are needed to reproduce the spectral properties of the surface of 67P. This is particularly true concerning pyrrhotite which is able to darken spectra in the IR only with small grain sizes, unlike the used coal [11]. Our measurements highlight the importance of the effects of mixing modalities (intimate mixture, coating) and grain size. Some scattering properties could be better determined with multi-angular acquisition. Finally, this work may be relevant to the study of primitive asteroid types, in particular C and D-types which exhibit albedo properties similar to 67P in the VIS and NIR range.

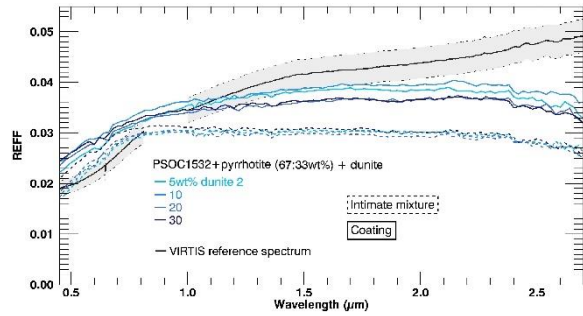


Figure 4: mixture of coal, pyrrhotite and various proportions of silicates. Intimate (solid) and coating (dotted)

## Acknowledgements

The authors would like to thank the following institutions and agencies, which supported this work and the development of the VIRTIS instrument: Italian Space Agency (ASI-Italy), Centre National d' Etudes Spatiales (CNES, France), Deutsches Zentrum für Luft und Raumfahrt (DLR, Germany). Université Grenoble Alpes (UGA) and CNES are acknowledged for their support to instrumental facilities and activities at IPAG.

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# Microimaging VIS-IR spectroscopy comparison between two shergottites

P. Manzari, S. De Angelis, M.C. De Sanctis, Istituto di Astrofisica e Planetologia Spaziali, INAF-IAPS, via Fosso del Cavaliere, 100 – 00133, Roma, ([paola.manzari@iaps.inaf.it](mailto:paola.manzari@iaps.inaf.it))

## Abstract

Micro-imaging spectroscopy is the new frontier of non destructive investigation methods on planetary materials and analogues. With the aim of supporting the measurements by Ma\_MISS spectrometer onboard future Exomars 2020 mission, spectral investigations are ongoing on meteorites and Mars analogues by means of the Spectral Imager (SPIM). In this abstract, we compare the measurements obtained with SPIM on two shergottite slabs: North West Africa 8657 and Dar Al Gani 489 trying to highlight the spectral differences between these two meteorites.

## 1. Introduction

Several studies in these last years showed that micro-imaging spectroscopy is the new frontier of non destructive investigation methods both for the spectral characterization of planetary materials and analogues [1, 2] and for validating remote sensed data on planetary and terrestrial surfaces. In this respect, the effectiveness of the SPIM (Spectral Imager) high resolution spectrometer for spectral characterization of meteorites was previously discussed [4,5]. As a short term goal, the interpretations of VIS-IR spectra related to Mars meteorites and analogues will support the Ma\_MISS (Mars Multispectral Imager for Subsurface Studies) measurements during the next ExoMars 2020 mission. Ma\_MISS is a miniaturized visible/near-infrared imaging spectrometer in the range 0.4-2.2  $\mu\text{m}$  with 20nm spectral sampling devoted to observe the lateral wall of the borehole generated by a drilling system [6]. In the present abstract we show results about the spectral characterization of two shergottite slabs NWA 8657 and DAG 489 by means of SPIM spectral imager.

## 2. Experiment set up and samples

The imaging spectrometer installed in SPIM is a spare of the spectrometer on Dawn spacecraft. It

works in the 0.22-5.05  $\mu\text{m}$  spectral range, with a spatial resolution of 38x38  $\mu\text{m}$  on the target [7]. Both analyzed meteorites are basaltic shergottites. Their petrographical composition slightly differ: Dar al Gani 489 (DaG) is composed of olivine megacrysts up to 5 mm set in a fine-grained groundmass of pyroxene, maskelynitized plagioclase and mesostasis [8]. Minor phases reported include chromite, ilmenite, whitlockite, Cl-apatite, pyrrhotite. North West Africa 8657 mainly consists of 64.3 vol% pyroxene and 32.8 vol% maskelynite with minor opaque minerals, 1.6 vol%, and phosphates, 1.3 vol%. The accessory ilmenite, ulvospinel, pyrrhotite, merrillite, apatite and quartz [9].

## 3. Results

In fig.1, SPIM images collected on the two meteorite slabs are showed. The average spectra related to the slabs are in Fig.2. The comparison between the two samples shows clearly the different composition of pyroxenes. The spectrum of DAG489 is marked by a signature typical of low-Ca pyroxenes with two major features centered at 0.98-0.99 and 1.98-2  $\mu\text{m}$ . In the spectrum of NWA8657 the 1 and 2  $\mu\text{m}$  band are centered at longer wavelengths. This means a prevalence of Ca-rich pyroxenes [10] in NWA 8657 with respect to DAG 489.

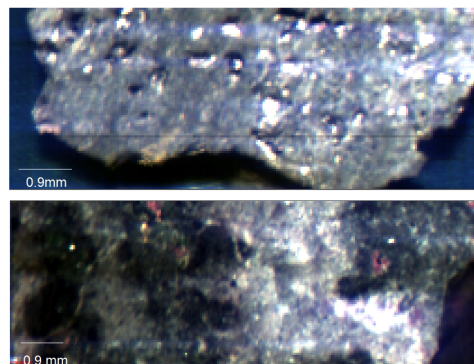


Fig.1 RGB (0.680 $\mu\text{m}$ ;0.560 $\mu\text{m}$ ;0.468 $\mu\text{m}$ ) images of NWA8657 (top) and DAG 489 (bottom) collected by means of the SPIM, SPectral IMager.



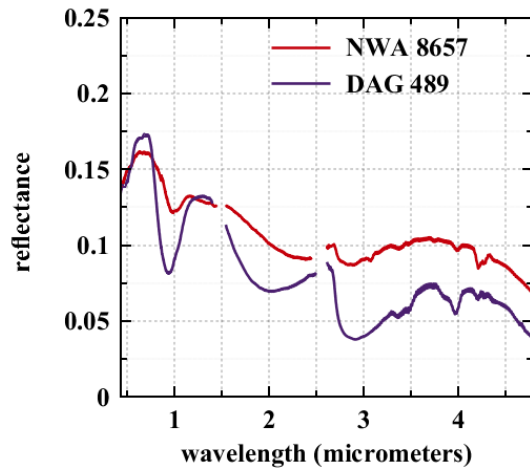


Fig.2 Average spectra related to NWA 8657 and DAG 489 investigated slabs.

On the basis of the results on NWA8657 by SEM, a preliminary spectral investigation pixel by pixel on DAG489 slab was performed. Aside the pyroxenes, the slab shows clearly spectra of maskelynite/glass, carbonates and opaques (Fig.3).

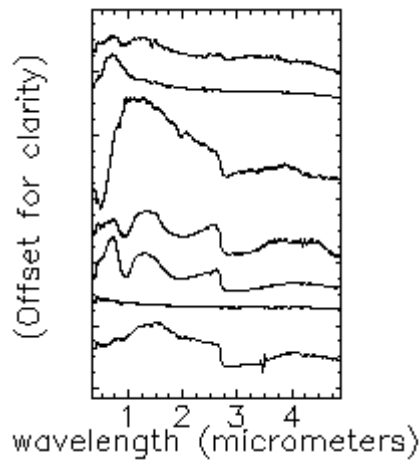


Fig.3 Spectral classes found in DAG489 slab

During this first look the occurrence of hydrated mineral phases was revealed in DAG489. These spectra are characterized by the 1.91, 2.78 $\mu$ m absorptions due to H<sub>2</sub>O stretch. A deeper look at the features of these spectra showed some absorptions like 3.87, 3.97, 4.20, 4.7 $\mu$ m that are typical of SO<sub>4</sub> combinations and overtones [11] (fig.4).

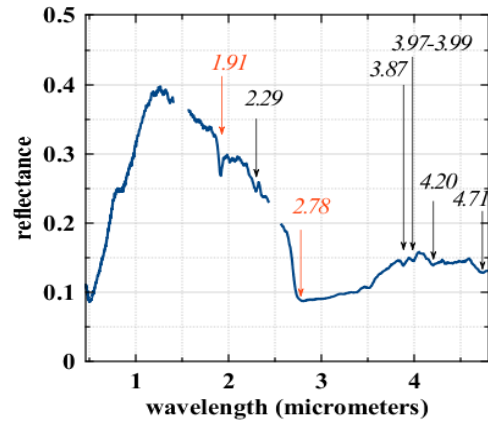


Fig.4 Spectrum of hydrated phase characterized by H<sub>2</sub>O (red arrows) and SO<sub>4</sub> absorptions combination and overtones (black arrows)

## 4. Summary and Conclusions

This preliminary investigation on two basaltic shergottites show that they are different in the pyroxene composition, being DAG489 composed of low Ca pyroxenes respect to NWA8657. Moreover, respect to NWA8657, DAG489 show the occurrences of some pixel spectra characterized by absorptions at 1.9 and 2.8  $\mu$ m that are due to water contents and that in some grains are found together with features related to SO<sub>4</sub> groups. Further investigations are ongoing for a more reliable spectral characterization and in order to support MaMiss spectrometer during the Exomars2020 mission.

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# Near- and mid-infrared spectroscopy of icy planetary/cometary analogue matter

**Z. Yoldi** (1), O. Poch(1), B. Jost (1), O. Brissaud (2), E. Quirico (2), P. Beck (2), B. Rousseau (3), A. Pommerol (1), B. Schmitt (2) and N. Thomas (1).

(1) Physikalisches Inst., University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland ([zurine.yoldi@space.unibe.ch](mailto:zurine.yoldi@space.unibe.ch))

(2) Institut de Planétologie et d'Astrophysique de Grenoble, Université Grenoble Alpes - CNRS, Grenoble, France.

(3) LESIA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06, Univ. Paris Diderot, Sorbonne Paris Cité, 5 place Jules Janssen, 92195 Meudon, France

## 1. Introduction

The complexity of natural surfaces makes the quantitative inversion of optical remote-sensing data a considerable challenge. Physical and numerical light scattering models such as the one developed by Hapke [1] rapidly show their limitations when confronted to the results of well controlled laboratory experiments. Therefore, libraries of good quality spectra of well characterized samples are crucial to enhance the scientific return from remote-sensing missions. This is problematic in the case of icy materials as the samples are difficult to prepare with good reproducibility and have a tendency to evolve with time as the ice can sublime, sinter, or re-condense. In addition, the laboratory setups needed to hold the samples and perform the spectral measurement must be adapted to work at the very low temperature required to limit the evolution of the samples.

The Planetary Imaging Group (PIG) in Bern has developed a series of Setups for the Preparation of Icy Planetary Analogues (SPIPA) that are used to prepare water ice samples, pure or mixed with contaminants, in a reproducible way [2, 3].

Although difficult, measurements of icy samples are highly desirable at a time when ambitious European missions are operated, about to arrive or currently been designed to study the surfaces of objects containing significant amounts of water ice. Of particular relevance here are the recent Rosetta mission, the Exomars TGO Orbiter –already inserted into Mars orbit, and the JUICE Orbiter which will be launched toward the Jovian system in 2022. These experiments have been performed with the spectrogonio radiometer [4] of the Europlanet 2020-RI's Cold Surface Spectroscopy Facility (<https://cold-spectro.sshade.eu/>) at IPAG, Grenoble, France.

## 2. Samples

We have measured about 30 reflectance spectra from 0.7 to 4  $\mu\text{m}$  of 10 different samples including pure water ice particles of different grain sizes, and their mixtures with anthracite dust. All the measurements have been made at 173K. The geometry of measurement was kept constant at 0° incident angle and 30° emission angle. Three different size distributions for ice have been produced and measured (Figure 1): SPIPA-A [2], with an average grain diameter  $4.5 \pm 2.5 \mu\text{m}$ ; SPIPA-B [3], with a diameter of  $70 \pm 30 \mu\text{m}$  and SPIPA-C, with a diameter distribution between 5 and 100  $\mu\text{m}$ . We have also studied water ice/dust mixtures with different dust-to-water mass ratios (0.01 and 0.1) and using different methods to mix the ice and the dust (intra- and inter- mixtures).

## 3. Results

We have performed a systematic study showing how the particle sizes, the dust concentration and/or the way the water is mixed with the dust (intra- or inter-particle mixtures) influence the shape/depth of the absorption bands, the level of reflectance of the continuum, and the amplitude of the Fresnel reflection peak. The reflectance spectra of pure water ice particles are shown in Figure 2. These spectra indicate how different size distributions influence the shape/depth of the water absorption bands (at 1.05, 1.28, 1.5, 2  $\mu\text{m}$ ), and the shape of the spectrum between 2.5 to 4  $\mu\text{m}$ . In particular, a Fresnel reflection peak centered at 3.1  $\mu\text{m}$  is detected for SPIPA-B, but is absent when micrometer-sized particles (SPIPA-A) are present on the surface. Alternatively, the bump of reflectance centered at 3.7  $\mu\text{m}$  is indicative of the presence of micrometer-sized particles and is absent for particles of 70  $\mu\text{m}$  (SPIPA-B). Figure 3 indicates how the way the water and the

dust are mixed together, how the concentration of dust and how the size of the water ice particles, affect the reflectance of the water ice (i.e. the shape/depth of the absorption bands, brightness, amplitude of the Fresnel reflection peak etc.).

All measured data will be made available to the community through publication in our BYPASS database of the SSHADE database infrastructure (under development).

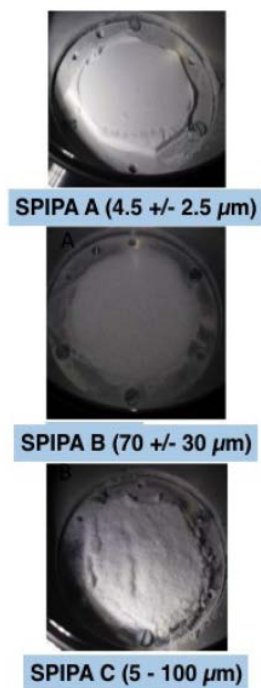


Figure 1: The three different ices produced are shown in their sample holders. For each one, the averaged diameter size or the size distribution is shown.

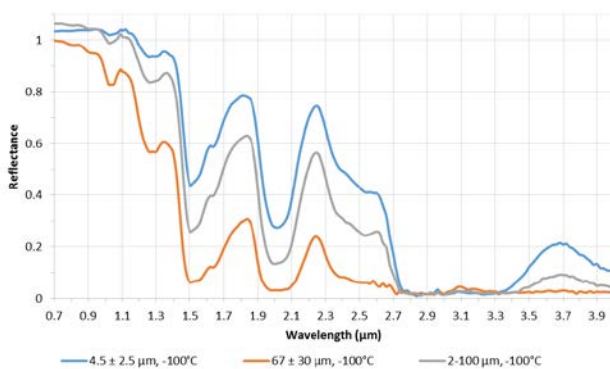


Figure 2: Reflectance spectra of surfaces of pure water ice particles with different sizes. In blue SPIPA-A, in orange SPIPA-B and in grey SPIPA-C.

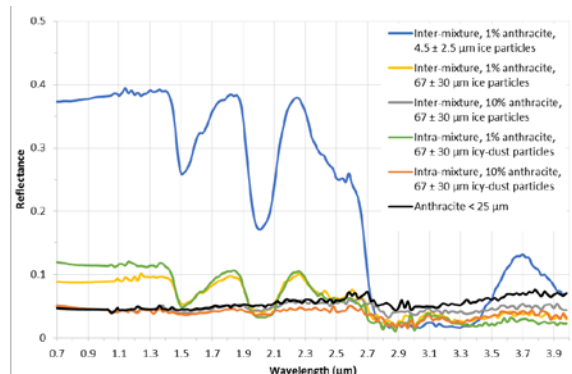


Figure 3: Reflectance spectra of surfaces mixtures of water ice and anthracite particles.

## Acknowledgements

This collaborative work was funded by the Transnational Access program (project n°10972) within the Europlanet 2020 Research Infrastructure. Europlanet 2020 RI has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N°654208.

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## Carboxylic acids at the surface of comet 67P/CG?

I.Istiqomah (1), E. Quirico (1), A. Faure (1), P. Theulé (2), O. Poch (3), P. Beck (1), L. Bonal (1), B. Schmitt (1), M. Ciarniello (4), G. Filacchione (4), F. Capaccioni (4), S. Erard (5), D. Bockelée-Morvan (5), C. Leyrat (5), G. Arnold (6), A.Barrucci (5), M.T. Capria (4), M-C DeSanctis (4), A. Longobardo (4), L. Moroz (6), E. Palomba (4), F. Tosi (4) and the VIRTIS Team

(1)Université Grenoble Alpes, CNRS, Institut de Planetologie et Astrophysique de Grenoble (IPAG), Grenoble, France, (istiqomah.istiqomah@univ-grenoble-alpes.fr), (2)Physique des Interactions Ioniques et Moléculaires (PIIM), Marseille, France, (3) NCCR Planets, Physics Institute, University of Bern, Switzerland, (4) INAF-IAPS, Rome, Italy, (5) LESIA, Meudon, France, (6) Institute of Planetary Research, DLR, Germany

### Abstract

A broad feature centered at 3.2  $\mu\text{m}$  has been detected in the reflectance spectra of comet 67P/Churyumov-Gerasimenko collected by the VIRTIS/Rosetta imaging spectrometer. This band points to the presence of semi-volatile organics, however to date no firm identification of molecular species has been done. In this study, we have focused on the experimental spectral characterization of carboxylic acids, which have been proposed as candidates for the 3.2  $\mu\text{m}$  broad band. We show that simple carboxylic acids are not viable candidates, because of their thermal stability in regard to the surface temperature, and/or due the shape/size of their 3  $\mu\text{m}$  band that does not fit VIRTIS spectra. We infer that if carboxyl groups are the main carrier of the 3.2  $\mu\text{m}$  band, it should be present in a low mass macromolecule, along with OH groups in side chains that favor hydrogen bond. A balance ratio between OH groups and aliphatics  $\text{CH}_2/\text{CH}_3$  must also be respected. Last, intimate mixtures do not fit VIRTIS data, and small spots of semi-volatiles on the surface of opaque material must be considered to account for 3.2  $\mu\text{m}$  band.

### 1. Introduction

The VIRTIS instrument (Visible InfraRed Thermal Imaging Spectrometer) aboard the Rosetta spacecraft has detected a broad feature centered at 3.2  $\mu\text{m}$  in the reflectance spectra of comet 67P/Churyumov-Gerasimenko, which might be consistent with the presence of semi-volatile organics, also possibly detected by the COSAC and PTOLEMY instruments [1-4]. Carboxylic acids have been proposed as candidates as these molecules in the liquid form display a broad absorption band that fit that of the 3.2  $\mu\text{m}$  band. In this study, we have focused on the experimental spectral characterization of pure and

mixed (with other organics) carboxylic acids, which have been proposed as candidates to account for the 3.2  $\mu\text{m}$  broad band [1-2]. Carboxylic acids are also the main component in the soluble organic fraction in primitive meteorites, with several tens of carboxylic, dicarboxylic and hydroxylated acids identified so far [5]. The thermal stability of these molecules has also been studied (desorption kinetics), in order to infer their presence at the surface of the nucleus.

### 2. Methods

Experiments have been run at IPAG with a Vertex 70v FTIR spectrometer equipped with a GLOBAL source and a DTGS detector for transmittance spectra. Thin films of low weight carboxylic acids were condensed as ices on a KBr window held at 25 K, and warmed up with a resistor and a PID controller (Lake Shore 331) until the sublimation of the acid. Carboxylic acids available in the solid state at room temperature were prepared with a spin coater, by deposition in a vacuum furnace and pellet. Mid-infrared spectra ( $4000 - 400 \text{ cm}^{-1}$ ) were collected with a  $4 \text{ cm}^{-1}$  spectral resolution. The reflectance spectra of mixture of carboxylic acid with graphite or basalt (as analogs of dark refractory cometary materials) were done using spectro-gonio radiometer in the spectral range 500-4200 nm.

### 3. Results

The experiment results of figure 1 shows that C1-C4 carboxylic acids with an aliphatic side chain display a broad feature in the 3  $\mu\text{m}$  region controlled by the –OH group, onto which are superimposed C-H stretching and combination modes. This band has however components towards long wavelengths (3.67-4.35  $\mu\text{m}$ ), which do not appear in VIRTIS spectra. Above C5, the prominent and sharp aliphatic massif at 3.4  $\mu\text{m}$  dominates the 3  $\mu\text{m}$  region and does not account for the broadness of the 3.2  $\mu\text{m}$  feature.

We also investigated dicarboxylic (C4 fumaric acid) and hydroxylated acids (C2 glycolic and C3 lactic acids). The presence of several –OH groups leads to a broadening of the 3  $\mu$ m feature with respect to their related monocarboxylic acids, however side bands between 3.67 and 4.35  $\mu$ m are still present.

Figure 2 presents the reflectance spectra of mixture of hydroxylated carboxylic acids with basalt and graphite. Graphite with sub-micrometric grain has very low reflectance and is used as an analog of refractory grains. There is not any features appeared on granular mixture and dissolved mixture. As another way to see the features of hydroxylated acid in reflectance spectra, we changed the graphite to basalt, which is brighter than graphite. We also observed that basalt hydration could not be suppressed and we need to improve this issue. And the results from reflectance spectra support a surface composed of refractory dark materials along with small semi volatiles patches geographically distributed [6-7].

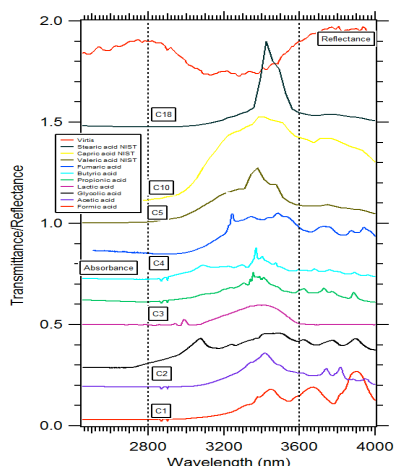


Figure 1: Comparison of a reflectance spectrum of VIRTIS with transmission spectra of carboxylic acids

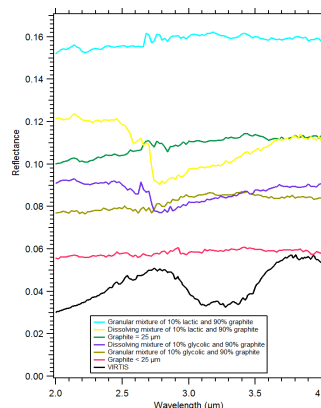


Figure 2: Reflectance spectra of graphite and mixtures of hydroxylated acids with graphite

## 4. Conclusions

In this study, we have reported on the transmittance and reflectance spectra of carboxylic acids. Simple carboxylic acids are not thermally stable (sublimation temperature around 200K) and they do not fit the spectrum of comet 67P/CG. Large carbon chain is also not spectrally match so the balance ratio between COOH and OH groups in side chain is mandatory to produce a broad band. Small spots of ice on the surface of opaque material must be considered to account for 3.2  $\mu$ m band.

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# Meteorite collection at the Faculty of Mining and Geology, Belgrade, Serbia – forgotten gems

**A. Zdravković\***<sup>1</sup>, Kristina Šarić<sup>1</sup>, and Ana Černok<sup>2</sup>; <sup>1</sup>Faculty of Mining and Geology, University of Belgrade, Serbia  
\*corresponding author (alena.zdravkovic@rgf.bg.ac.rs), <sup>2</sup>Open University, School of Physical Sciences, Walton Hall, MK7 XX, United Kingdom

## Abstract

Here we describe a collection of 36 meteorites within the Collection of Rocks and Minerals at the Faculty of Mining and Geology, University of Belgrade. At the end of the XIX century, the Mineralogical Cabinet of Great School of Belgrade (precursor of Belgrade University) received a gift of 30 samples from a French collector and nobleman Charles Adrien marquis de Mauroy and 3 samples from the Collection of the Mining Institute of the empress Catherine II. Among the aforementioned examples, all but one from the so-called Russian collection are preserved. In addition to these, the collection contains a meteorite sample from Romania and three meteorites of unknown name and origin.

## 1. Historic background

Early meteoritics in Serbia has been initiated after the witnessed fall of Sokobanja meteorite in 1877. The meteorite was named after the location where it was recovered – Sokobanja, in central-eastern Serbia. One of the team members investigating the fall and recovering the material was Prof. Josif Pančić (1814-1888), a sciences professor at the Great School of Belgrade (Beogradska Velika Skola). A series of subsequent meteorite falls (Jelica in 1889, Čačak in 1919, and Dimitrovgrad in 1947), has contributed to further developments of meteorite collection in Serbia, as well as to sample exchanges with foreign museums. Josif Pančić was very active and respected scientist across Europe, and with his collaborations and private efforts, he collected 95 world well known meteorites. Unfortunately, most of this collection went missing during the WWI [2]. On the good side, rather quick development of geological sciences in Serbia at the end of the XIX century has helped retain an evidence of the original meteorite collections. Due to internationally affirmed pioneers (Josif Pančić, Jovan Žujović, Sava Urošević) in

geology, many meteorites from the missing collection were recorded throughout European and world archives and most of the exchanged samples are still kept in famous museums worldwide (e.g. Smithsonian or Vienna collection). In total, 52 meteorites are today stored in the Collection of Rocks and Minerals, as well as in the Paleontological collection of the Belgrade University. The most exceptional are the two meteorite collections that were donated to the Mineralogical Museum of High school (precursor of Belgrade University) in 1899. via St. Petersburg Mining Institute of the empress Catherine II (precursor of Saint Petersburg State University). Above mentioned collections are: three samples of meteorites donated by the Museum of the Mining Institute in Saint Petersburg and 30 samples of meteorites donated by the French nobleman, collector and honored member of the Mineralogical Emperor Society in Saint Petersburg. In course of time, the two University collections have lost the samples of the Serbian recorded falls, which are now stored in the Natural History Museum, Belgrade.

### 1.1 Collection donated by St. Petersburg's Mining Institute

In 1899, at the meeting of the Serbian geological Society, Sava Urošević presented two exceptional collections of minerals and meteorites that were donated to the Mineralogical Museum of the High School [4]. One of them was the collection of 1525 samples of minerals including three samples of meteorites donated by the St. Petersburg's State Mining Institute of the empress Catherine II. An honoured mining ingenier M. Melnikoff, conservator of the Mining Institute Museum in St. Petersburg, signed an accompanying catalogue written in french. Samples were numbered according to their original catalogue number within the russian collection. Besides numbering, each sample in that catalogue contained information on the sample's name and the locality from which it was collected. Meteorites



donated to the serbian collection had numbers 36, 37 i 38, but meanwhile the one with the number 36 went missing. Descriptions of these three meteorites in the original catalogue were as follows. **36:** *Fer météorique aveque troilite (pesant 284 gr.), Trouvé, en 1890, pres de la village Augustinowka, gouv. de Ecatherinoslaw dans l'argile alluvial);* **37:** – Palasite with olivine (65,6 g) *Fer météorique aveque olivine - (Pallassite de Krassnojarsk), Trouvé, en 1749 par Pallass, en Sibérié, 400 kilomètres de Krassnojarsk, pres de la rivière Oubei );* **38:** (težine 268 g) *Fer météorique, Trouvé, en 1889 au placer de Pétropawlovsk sur la rivière Toubil ar.d'Artchinsk, g. d'Jenisseisk.*

## 1.2. Collection donated by Marquiz de Mauroy

Collection of 30 meteorite samples were also donated to the Mineralogical Museum of the Great school in 1899. by a French nobleman and honored member of the Mineralogical Emperor Society in Saint Petersburg, Marquis de Mauroy (*Marquis Adrien Charles de Mauroy, 1848 – 1927*) [4]. At the end of XIX century, marquize de Mauroy's meteorites collection was the second largest collection in the world [3]. The donated collection represents the small fragments of Mauroy's numerous collection, which it has personally donated to the Vatican Observatory in Italy ten years later [1], [4]. This collection did not possess a catalogue, and the samples were not numbered. A revision of the collection was therefore not directly based on the original samples description but rather on facts announced at the Meeting of the Serbian geological Society, which was held a century ago (in 1899). It was confirmed that the samples and labels with French handwriting are truly donated by Marquise de Mauroy. The samples weight written on the labels was also very useful. Now it is known that due to circumstances, the original catalog of the entire Mauroy's collection from 1909. is located in the Vatican Observatory in Italy with majority of collector's samples. The cooperation with their curator Mr. Guy Consolmagno in 2013. was helpful for our numbering of the samples and confirming the names on the labels. All 30 samples from this donation are kept at the Museum of Rocks and Minerals, in Belgrade.

## 1.3. Individual samples and labels

There are four additional meteorites in the Collection of rocks and minerals. Among them is the meteorite sample named Mocs, Cluj from Romania with handwritten etiquette with all necessary data. On the label on its surface is written "Mocs 25 g", and on the etiquette with details written on Serbian: *Meteorite, Lithite, Chantonite, fall 3.02.1972., Mocs, Kluž, Romania, weith 24,55, No 32.* Two iron meteorite samples, different in shape and in weight without any data and labels (P80 Fe-meteorite 202g and P81 Fe-meteorite 48,8g), and one obviously non iron meteorite sample which is still unclassified (11,5 cm long), are also held in our collection. Individual label from the period between two World wars pointing out that the Fe-meteorite with the name Arva Megye was present or is still present in the Collection.



Figure 1. Unclassified meteorite sample (11,5 cm)

## 2. Summary and Conclusions

Most the meteorites within this Collection have been classified, apart from three samples for which the name and description went missing. However, these meteorites haven not been subjected to any other scientific investigations in past decades. We have a plan to prove their authenticity by using modern mineralogical methods supported through the Open University.

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## The 2017 joint Italian – Iranian expedition to Lut desert for meteorite recovery

V. Moggi Cecchi (1), L. Cecchi (1), G. Pratesi (2), G. Giuli (3), M. Nemati (4), M. Di Martino (5), R. Serra (6)

(1) Museo di Storia Naturale dell'Università di Firenze, Firenze, Italy, email: vanni.moggicecchi@unifi.it (2) Dipartimento di Scienze della Terra dell'Università di Firenze, Firenze, Italy (3) Scuola di Scienze e Tecnologia, Università di Camerino, Camerino, Macerata, Italy (4) Department of Geology, Shahid Bahonar University, Kerman, Iran (5) INAF – OATO, Torino, Italy (6) Museo del Cielo e della Terra, San Giovanni in Persiceto, Bologna, Italy

### Abstract

A field trip in the Lut Desert has been realized in march 2017 by the University of Firenze and the Shahid Bahonar University of Kerman.

### 1. Introduction

Lut desert extends in an area of about 240 x 80 km in the south – east region of Iran. High temperatures, very little precipitation rate (less than 50mm/year) and high amounts of evaporation are some of the main properties of Lut Desert. Previous expedition in this area confirmed that it is suitable for preservation of meteorites and their recovering [1-4]. According to the international agreement signed between the University of Firenze and the Shahid Bahonar University of Kerman, a first field trip to Lut Desert and related fieldwork for searching and collecting meteorites has been realized from 10 to 25 march 2017.

### 2. Field trip details

The explored area was a part of the Kalut desert (Figure 1), that is the north west part of the Lut Desert. This area is characterized by the presence of 50-100 meters high ridges consisting of loess deposits. These reliefs have been modeled by the action of wind forming long channels oriented north-west to south-east. During the expedition 45 specimens of meteorites and several doubtful stones have been recovered in the field. The weight of the samples ranges from few grams to one kilo with a total amount of 3670 grams.



Figure 1: Trail of the field trip.



Figure 2: the biggest specimen recovered.

## Acknowledgements

We wish to acknowledge the Lut Travel Agency of Kerman for support and logistic in the organization of the field trip.

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# IR Spectroscopy of ammoniated phyllosilicates and mixtures with relevance for dwarf planet (1) Ceres

S. De Angelis (1), M. Ferrari (1), S. Stefani (1), A. Raponi (1), M.C. De Sanctis (1), G. Piccioni (1), E. Ammannito (2)  
(1) Institute for Space Astrophysics and Planetology, IAPS-INAF, Rome Italy, ([simone.deangelis@iaps.inaf.it](mailto:simone.deangelis@iaps.inaf.it)) (2) Italian Space Agency – ASI, Rome, Italy

## Introduction

The surface composition of (1) Ceres has been revealed with great detail by VIR spectrometer high resolution observations [1] on board Dawn spacecraft [2]. Spectroscopic observations in the infrared range 1-5  $\mu\text{m}$  have showed an average surface composition consisting of a mixture of Mg-phyllsilicate, (Mg,Ca)-carbonate, a dark absorbing phase and  $\text{NH}_4$ -phyllsilicates [3], and bright areas locally composed by mixtures of Na-carbonates, phyllsilicates, a dark phase and ammonium compounds [4]. The reproduction in laboratory of such mineral mixtures is thus of interest in order to better constraint and interpret remote-sensing observations. In this work we focus on the preparation and IR spectroscopic measurements in laboratory of  $\text{NH}_4$ -phyllsilicates and mineral mixtures.

## 1. Sample preparation and experimental setup

A set of 8 phyllsilicates were chosen from Clay Minerals Society, grinded and dry sieved to a fine grain size ( $d < 36 \mu\text{m}$ ). Ammonium phyllsilicates were then prepared following a procedure similar to what described in Bishop et al. 2002 [5]. All powders were immersed in excess (10:1 vol/mass) solutions of ammonium hydroxide (30%  $\text{NH}_3$  in  $\text{H}_2\text{O}$ ) for several days, centrifuged and decanted: this cycle was repeated more times, and finally samples were dried. Splits of these samples were separated and treated with a leaching procedure. Other endmembers, concerning the average mixture, were prepared in the form of  $d < 36 \mu\text{m}$ -powders, specifically antigorite, (Ca,Mg)-carbonate and magnetite. A set of 8 different mixtures has been then prepared, keeping fixed antigorite, dolomite and magnetite, and varying the  $\text{NH}_4$ -clay mineral constituent.

All end-members have been spectrally characterized by means of visible/infrared spectroscopy. Spectra in the VNIR have been acquired with a FieldSpec Pro in the 0.35-2.5  $\mu\text{m}$  range, with 6 mm spatial resolution and spectral resolution  $3 \div 8 \text{ nm}$ . Fourier Transform Infrared Spectrometer (FTIR-PLAB) Vertex-80 was used in reflectance mode to acquire spectra of powders, with spectral resolution  $2 \text{ cm}^{-1}$ , spatial aperture of about 6 mm, in the spectral range 1.3-14  $\mu\text{m}$ , using an MCT detector. Each acquisition was performed by summing 256 scans in order to increase S-N ratio. Reflectance spectra were acquired from all endmembers, and separately from phyllsilicates,  $\text{NH}_4$ -phyllsilicates and “leached”  $\text{NH}_4$ -phyllsilicates, and finally from mixtures.

Clay minerals endmembers		
<b>Sepiolite</b>	SEPSP1	
$(\text{K}_{0.01})[\text{Mg}_{5.54} \text{Al}_{0.35} \text{Mn}_{0.02} \text{Fe}^{2+}_{0.04} \text{Fe}^{3+}_{0.14}][\text{Si}_{7.90} \text{Al}_{0.1}]\text{O}_{20}(\text{OH})_4$		
<b>Rectorite</b>	RAR1	
$(\text{Na,Ca})\text{Al}_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$		
<b>Nontronite-1</b>	NAU1	
$(\text{M}^{+}_{1.05})[\text{Si}_{6.98} \text{Al}_{1.02}][\text{Al}_{0.29} \text{Fe}_{3.68} \text{Mg}_{0.04}]\text{O}_{20}(\text{OH})_4$		
<b>Nontronite-2</b>	NAU2	
$(\text{M}^{+}_{0.72})[\text{Si}_{7.55} \text{Al}_{0.45}][\text{Fe}_{3.83} \text{Mg}_{0.05}]\text{O}_{20}(\text{OH})_4$		
<b>Illite-1</b>	IMT2	
$\text{K}_{0.65} \text{Al}_2\text{O}[\text{Al}_{0.65} \text{Si}_{3.35} \text{O}_{10}](\text{OH})_2$		
<b>Illite-2</b>	ISCZ1	
<b>Montmorillonite</b>	SCA3	
$(\text{Mg}_{0.45} \text{Ca}_{0.15} \text{Na}_{0.26} \text{K}_{0.01})[\text{Al}_{2.55} \text{Fe}^{3+}_{0.12} \text{Mn}_{\text{tr}} \text{Mg}_{1.31} \text{Ti}_{0.02}][\text{Si}_{7.81} \text{Al}_{0.19}]\text{O}_{20}(\text{OH})_4$		
<b>Hectorite</b>	SHCA1	
$(\text{Mg}_{0.56} \text{Na}_{0.42} \text{K}_{0.05})[\text{Mg}_{4.60} \text{Li}_{1.39} \text{Mn}_{\text{tr}} \text{Ti}_{0.01}][\text{Si}_{7.75} \text{Al}_{0.17} \text{Fe}^{3+}_{0.05}]\text{O}_{20}(\text{OH})_4$		

Tab.1. Clay minerals endmembers.

## 2. IR Spectral measurements: results

In fig.1 an example of spectra acquired on nontronite endmember (NAU-1) is shown, in which the non-

treated sample (blue line) is compared with the  $\text{NH}_4$ -treated sample (green). The full spectral coverage has been subdivided in five ranges for clarity, specifically 0.35-2.5  $\mu\text{m}$  (FieldSpec) and then 1.3-2.5  $\mu\text{m}$ , 2.5-4.1  $\mu\text{m}$ , 4-6 and 6-14  $\mu\text{m}$  for FTIR data. The ammoniated sample is characterized by the occurrence of several new features in four of the five displayed ranges, although a global change in the overall spectrum is visible in the full range; namely a substantial decrease in reflectance level is observed, together with a reduction of spectral contrast. New absorption bands putatively attributable to  $\text{NH}_4^+$  ions appear near 2 and 2.1  $\mu\text{m}$ , near 3.1  $\mu\text{m}$  and at 7  $\mu\text{m}$ .

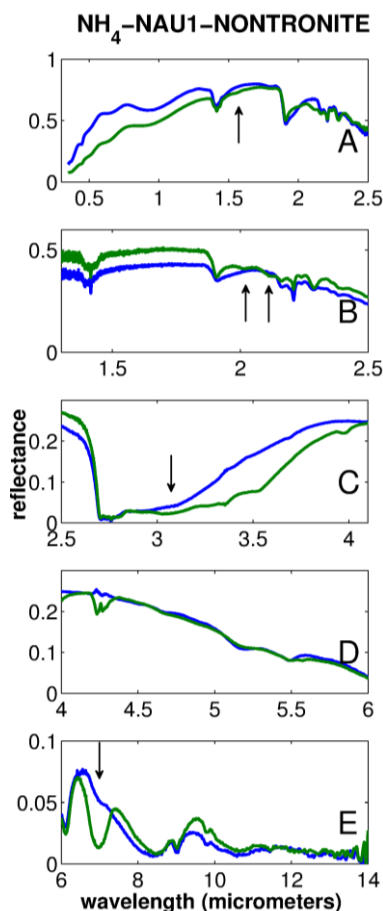


Fig.1. Nontronite NAU-1. Untreated sample (blue line) vs  $\text{NH}_4$ -treated sample (green line). A: 0.3-2.5  $\mu\text{m}$ . B: 1.3-2.5  $\mu\text{m}$ . C: 2.5-4.1  $\mu\text{m}$ . D: 4-6  $\mu\text{m}$ . E: 6-14  $\mu\text{m}$ . The  $\text{NH}_4^+$  3.1- $\mu\text{m}$  band here appears as a bump overlapped with the water band at 3  $\mu\text{m}$ , which is difficult to remove unless heating the sample in vacuum.

In fig.2 the VIR average spectrum of Ceres (purple line) [3] is compared with mixture spectra measured with FTIR. Here the mixture is composed by serpentine-antigorite, dolomite, magnetite and  $\text{NH}_4$ -

NAU1 (nontronite). Laboratory spectra show a good matching with VIR spectrum; the agreement is better for what concerns the OH<sup>-</sup> 2.7  $\mu\text{m}$ -band of serpentine and the 4  $\mu\text{m}$ -band of carbonate. The feature near 3.1  $\mu\text{m}$  due to  $\text{NH}_4^+$  in laboratory spectra is evident, although additional adsorbed water is present in the sample and influences the band.

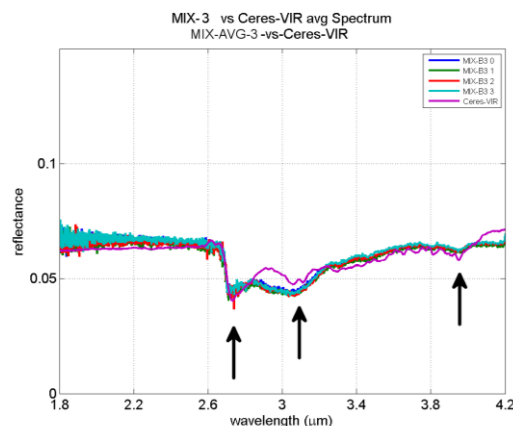


Fig.2. Dawn-VIR average spectrum of Ceres (purple line) vs Mixture AVG-3 laboratory spectra. Arrows indicate, from left to right, absorptions in the mixture due to antigorite (2.72  $\mu\text{m}$ ),  $\text{NH}_4^+$ + $\text{H}_2\text{O}$  (3-3.1  $\mu\text{m}$ ) and dolomite (4  $\mu\text{m}$ ).

### 3. Summary and Conclusions

Treatment of phyllosilicates with ammonia shows that different minerals behave in different ways:  $\text{NH}_4^+$  ions are easily accepted by several crystal structures (nontronite, montmorillonite), while other structures accept these ions with difficulty. Laboratory spectra of the mixture show a good agreement with VIR spectrum. Further work is ongoing to remove adsorbed water from phyllosilicates, in order to facilitate  $\text{NH}_4^+$  inclusion in mineral structures, and to separate  $\text{NH}_4^+$  and OH<sup>-</sup> absorption features in the 3- $\mu\text{m}$  spectral region.

### Acknowledgements

The experiment is funded by ASI.

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# FT-IR and $\mu$ -IR analysis of Carbonaceous Chondrite meteorites characterization as possible analogue of next sample returned materials

**F. Dirri** (1), M. Ferrari (1), E. Palomba (1), A. Longobardo (1), S. Stefani (1), A. Rotundi (1,2), A. Galiano (1), L. Nardi (1)  
(1) Institute for Space Astrophysics and Planetology, Via del Fosso del Cavaliere 100, 00133, Rome, Italy  
([fabrizio.dirri@iaps.inaf.it](mailto:fabrizio.dirri@iaps.inaf.it)); (2) Dipartimento di Scienze e Tecnologie, Università di Napoli "Parthenope", CDN, IC4, 80143, Naples, Italy.

## Abstract

In this work, the Fourier Transform Infrared Spectroscopy (FT-IR) and Infrared  $\mu$ -spectroscopy ( $\mu$ -IR) techniques have been applied on four Carbonaceous Chondrites (CC) meteorites, as possible analogues of the Hayabusa2 and Osiris-REx space missions asteroid targets. The analysed CC meteorites belong to CV, CI and CM classes. Chondrules, CAIs, and mineral inclusions, have been identified and analysed in detail in the spectral region 8-14  $\mu$ m ( $\mu$ -IR analysis). CC packed powders have been analysed using a FT-IR spectrometer in the spectral range of 2-14  $\mu$ m. The absorption bands, Christiansen and Reststrahlen features, of the main minerals have been identified. We plan to compare the FT-IR spectral results with C-type asteroids data collected by in-flight spectrometers (e.g. 1Ceres, 10Hygeia etc.).

## 1. Introduction

Different types of analysis were performed to characterise returned asteroidal and cometary samples, and meteorites [1,2,3]. The mineralogy and composition of an extraterrestrial body is the key to know its geological evolution. For this purpose, remote-sensing infrared spectrometers are mounted onboard space probes [4]. To support space data interpretation is fundamental their comparison with spectra acquired on extraterrestrial samples that can be considered analogs of the space mission targets. Waiting for the best analogs, i.e. samples that will be returned from primitive asteroids targets by Hayabusa 2 and Osiris Rex missions [5,6], we applied FT-IR and  $\mu$ -IR techniques to four CC meteorites, as possible analogues of 101955 Bennu (B-type) and 162173 Ryugu (C-type).

## 2. Samples and Analysis

We analysed four CC samples: 1) Murchinson (CM2 group) and 2) NWA8267 (CM2 group), characterized by small chondrules and refractory inclusions [7]; 3) NWA2086 (CV3 group) with considerable amount of large mm-size chondrules and Calcium Aluminum Inclusions (CAIs), many surrounded by igneous rims [8], 4) Orgueil (CI1 group) characterized by the absence of chondrules and refractory inclusions and with a high degree of hydration [9]. A preliminary analysis was performed on CC samples using a Stereo Microscope (Leica M205c) equipped with a digital camera in order to select the sample regions characterized by a significant mineralogical heterogeneity. Spectra have been acquired with  $\mu$ -IR Microscope (mod. Bruker Hyperion 3000) and analysed in the spectral range of interest: 8-14  $\mu$ m on the selected regions (Fig.1). The Christiansen features and Reststrahlen bands of the main minerals have been identified and summarized in Table 1.

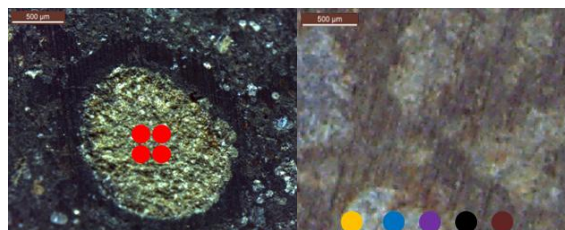


Figure 1. Examples of selected regions analysed with the  $\mu$ -IR technique. *Left*: NWA8267 (CM2). *Right*: NWA2086 (CV3).

To support the identification of minerals detected in selected features by  $\mu$ -IR analysis, packed powders of meteorite samples were analyzed by FT-IR spectroscopy. FT-IR analysis was performed using a Bruker Vertex 80 Spectrometer with a MCT-detector (which is liquid nitrogen cooled) obtaining the bi-directional reflectance in the spectral range 2-14  $\mu$ m.



The measurement configuration for data acquisition was with incidence ( $i$ ) and emission angle ( $e$ ) of  $30^\circ$ . The acquired spectra are shown in Fig. 2.

Table 1: Bands identified by means of  $\mu$ -IR technique.

Meteorite	NWA2086	Murchison	NWA8267	Orgueil
Type and class	CV3	CM2	CM2	CI
Analysed region	Chondrule, Matrix	Inclusions	Chondrule, Matrix	Matrix
Christiansen feature ( $\mu\text{m}$ )	8.2	8.4, 9.2	8.5	8.9
Main spectral bands ( $\mu\text{m}$ )	9.1, 10.5, 11.2, 12	9.10, 10.4, 10.5, 11, 11.5, 12.2	9.1, 10.5, 11.6	9.5, 10.10, 11.3, 11.9

### 3. Results and future perspectives

The data acquired with  $\mu$ -IR technique (Fig. 2, on *Left*) on CCs matrix, chondrules and CAIs inclusions indicate that the spectral bands:

- in Murchison can be ascribed to the Fe-rich olivine, to a pyroxene mixture and phyllosilicates [7];
- in NWA8267 can be assigned to a mixture of pyroxene with the predominance of the Ca-rich member [10];
- in NWA2086 can be ascribed to olivine, Ca-rich plagioclase and pyroxene [8];
- in Orgueil can be ascribed to serpentine, saponite, and Fe-rich olivine [9].

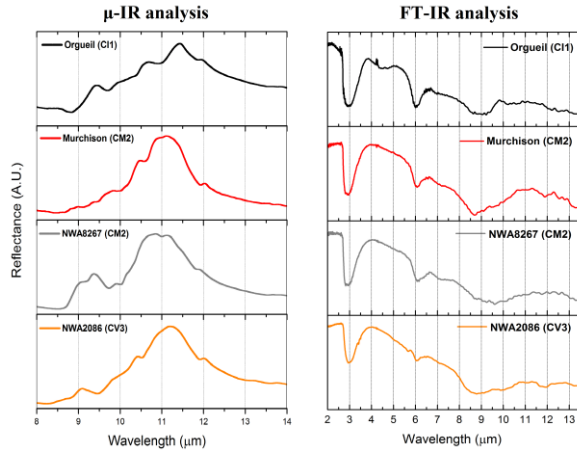


Figure 2. The spectra obtained by  $\mu$ -IR (*left*) and FT-IR (*right*) spectroscopy on the four CC meteorites.

The spectral data acquired with FT-IR analysis on CC powders show a distinct absorption band between 2.8 and  $3\ \mu\text{m}$  which is attributed to the OH stretching

band and a weak absorption band at  $3.4\ \mu\text{m}$  which can be attributed to the presence of organics [11]. These features are weaker in CM and CI than in CV3 sample for which clear absorption bands can be observed between 3.3 and  $3.5\ \mu\text{m}$ .

We plan to compare, in the near future, the CCs spectral data obtained between 2 and  $4.2\ \mu\text{m}$  with C-type asteroids spectra, e.g. 1Ceres, 10Hygeia, to find similar spectral features. In addition, Field Emission-Scanning Electron Microscope with Energy Dispersive Spectroscopy (FE-SEM/EDS) measurements will provide chemical information of meteorite samples and high resolution images of the inclusions morphology. This technique, combined with  $\mu$ -IR and FT-IR analysis will provide a comprehensive mineralogical framework for the CC meteorite selected samples, which will help the returned samples characterization of next sample return missions.

### Acknowledgments

This work is supported by the Italian Space Agency, PRIN-MIUR and Regione Campania. We would like to thank the PLab researchers (IAPS-INAF) for making available their instrumentation. This research has been performed using the spectra from ASTER database (courtesy of the JPL).

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# FT-IR and $\mu$ -IR characterization of HED meteorites in relation to infrared spectra of Vesta-like asteroids

M. Ferrari (1), F. Dirri (1), E. Palomba (1), S. Stefani (1), A. Longobardo (1) and A. Rotundi (2,1)

(1) Institute for Space Astrophysics and Planetology, IAPS-INAF, Via del Fosso del Cavaliere 100, 00133, Rome, Italy.  
 (2) Dipartimento di Scienze e Tecnologie, Università degli Studi di Napoli "Parthenope", CDN, IC4; 80143 Naples, Italy.  
[marco.ferrari@iaps.inaf.it](mailto:marco.ferrari@iaps.inaf.it)

## Abstract

We present the results of the FT-IR and  $\mu$ -IR study of three Howardite-Eucrite-Diogenite meteorites (HEDs) [1] compared to the spectroscopic data collected by VIR onboard Dawn spacecraft [2]. The origin of this group of achondrites is thought to be linked to the asteroid 4 Vesta [3], hypothesis lately reinforced by the data provided by the Dawn mission [4].

## 1. Introduction

In order to acquire a fuller grasp of remotely sensed compositional data, it is fundamental to compare them to analogue samples analyzed by means of spectroscopy techniques. Here we report a FT-IR and  $\mu$ -IR spectroscopy combined study of three HED meteorite samples: 1) NWA 7159, a monomictic brecciated eucrite consisting of exolved orthopyroxene and anorthite with accessory silica polymorph and ilmenite; 2) NWA 7490 a diogenite with a cumulate texture dominated by orthopyroxene, with Ca-plagioclase, minor olivine and chromite and troilite as accessory minerals; 3) NWA 2698, an howardite with eucritic pyroxene.

## 2. Experimental set up

For the FT-IR analyses on meteorites powder we used a Fourier transform interferometer (mod. Bruker Vertex 80) operating in the range of 0.8 to 2.4  $\mu$ m using the InGaAs detector and from 2 to 14  $\mu$ m with the MCT detector. All spectra were acquired with an incidence angle ( $i$ ) of 30° and an emission angle, ( $e$ ) of 30°. For  $\mu$ IR-spectroscopy, we used a microscope (mod. Bruker Hyperion 3000) connected to the Vertex 80 interferometer, this set-up (working range 2-14  $\mu$ m) is able to acquire spectra in reflection mode on single feature with minimum dimensions of 50  $\mu$ m.

## 3. Discussion

The FT-IR analysis performed on meteorite powders provided bulk information on the mineralogy of the samples. The mid-IR reflectance spectra of the three analysed achondrites are showed in figure 1.

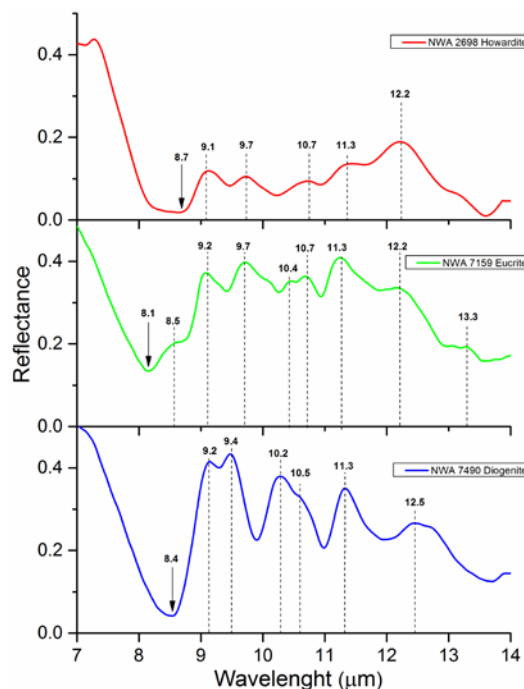


Figure 1: Reflectance spectra of NWA 7490, NWA 7159 and NWA 2698; the Christiansen features are marked by arrows, while the Reststrahlen features are marked by dotted line.

The position of the Christiansen feature and of the main bands are summarised in table 1. The spectrum of NWA 2698 meteorite (red in fig. 1) shows the bands at 9.1, 10.7 and 11.3  $\mu$ m that can be attributed to pigeonite, whereas the bands at 9.7 and 12.2  $\mu$ m are ascribed to calcium plagioclase. The Christiansen feature at 8.7  $\mu$ m is consistent with the presence of pyroxene. The bands at 9.2, 10.4, 10.7 and 11.3  $\mu$ m in the spectrum of NWA 7159 meteorite (green in

fig.1) can be attributed to pigeonite. The bands at 8.5, 12.2 and 13.3  $\mu\text{m}$  are due to the presence of anorthite, in agreement with the value of the Christiansen feature at 8.1 $\mu\text{m}$ .

Table 1: Result of the IR characterization of the constituents present in the three analysed meteorites.

Sample	Christiansen feature ( $\mu\text{m}$ )	Main spectral bands ( $\mu\text{m}$ )	Mineral
NWA 2698	8.7	9.7 and 12.2	anorthite
		9.1, 10.7 and 11.3	pigeonite
NWA 7159	8.1	9.2, 10.4, 10.7 and 11.3	pigeonite
		8.5, 9.7, 12.2 and 13.3	anorthite
NWA 7490	8.4	12.5	anorthite
		9.2 and 12.5	forsterite
		9.4, 10.2, 10.5 and 11.3	hypersthene

The reflectance spectrum of NWA 7490 shows the bands at 9.4, 10.2, 10.5 and 11.3  $\mu\text{m}$  attributable to pyroxene hypersthene. The band at 9.1  $\mu\text{m}$  can be attributed to Mg-olivine whereas the band at 12.5  $\mu\text{m}$  can be due to the contribution of both Mg-olivine and anorthite. The Christiansen feature is in the range of the pyroxene values. If the FT-IR analysis on meteorites powder provided bulk information on the samples, the  $\mu$ -IR analysis provided reflectance spectra of single minerals, corroborating the results of the bulk composition and excluding possible alteration of the principal minerals. By means of combined analyses we obtained a comprehensive mineralogical framework for the HEDs. It was proven that the mineralogical heterogeneity of the HED meteorites is consistent with the spectroscopic diversity seen on Vesta, thus this study helps in better constraining and characterising the reflectance spectra performed on Vesta-like bodies. A complete characterization of these samples using techniques that provide mineralogical composition, such as XRPD, and techniques that provide chemical and textural information, such as SEM/EDS, are being considered for the future.

## 4. Summary and Conclusions

IR spectra acquired on the three HED meteorites indicate that:

- the pyroxene of NWA 2698 is a pigeonite in accordance with the composition of the eucritic

pyroxene, as reported in the Meteoritical Bulletin N°90;

- the NWA 7159 sample shows a predominant presence of anorthite, as confirmed by the value of Christiansen feature. The presence of pigeonite is in accordance with the pyroxene composition reported in the Meteoritical Bulletin N°104;
- the meteorite NWA 7490 shows the presence of Ca-plagioclase and Mg-olivine, in addition to the predominant occurrence of hypersthene, as reported in the Meteoritical Bulletin N°101.

Basing on the obtained results, the near-IR spectra of these HEDs are directly comparable to those acquired by the in-flight spectrometer on 4 Vesta asteroid (Fig. 2) [5].

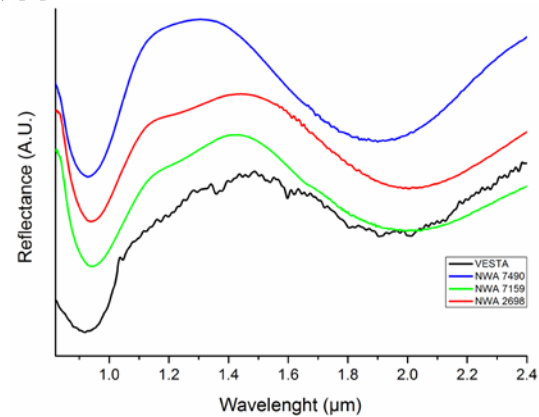


Figure 2: Near-IR reflectance spectra of NWA 7159, NWA 7490, NWA 2698 samples compared to the average spectrum of 4 Vesta asteroid [5].

## Acknowledgements

This work is supported by the Italian Space Agency, PRIN-MIUR and Regione Campania. We are grateful to the PLab (INAF-IAPS) for making available their instrumentation. This research uses spectra reproduced from the ASTER database (courtesy of the JPL) and the Berlin Emissivity Database (Helbert et al. 2007).

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# A compact low-temperature reflectance chamber for FT-spectroscopy experiments at the PSL

Y.M. Rosas Ortiz<sup>1,2</sup>, A. Maturilli<sup>1</sup>, J. Helbert<sup>1</sup> and D. Wendler<sup>1</sup>

(1) Institute of Planetary Research, German Aerospace Center DLR, Berlin, Germany, (2) Technische Universität Berlin, Department of Aeronautics and Astronautics, Berlin, Germany (yaquelin.rosasortiz@dlr.de)

## Abstract

We report on the ongoing development at the Planetary Spectroscopy Laboratories (PSL) group of a compact low-temperature, high vacuum, reflectance chamber; which, in combination with the existing high temperature setup and a Fourier transform infrared (FTIR) spectroscopy instrument will expand the PSL current unique capability of measuring emissivity spectrum of fine-grained powder materials from 1 to above 100  $\mu\text{m}$ , bulk materials and coatings at temperatures up to 1000K across the whole infrared wavelength range.

After this update, the PSL will cover an extremely wide range of temperatures; from emissivity spectra measurements up to 1000K and in the future for reflectance spectrum measurements down to cryogenic temperatures.

## 1. Introduction

The Institute for Planetary Research of the German Aerospace Center (DLR) has an expertise in spectroscopy of minerals, rocks, meteorites and organic matter, built up in more than 3 decades. In its facilities at the Planetary Spectroscopy Laboratories (PSL) a wide range of planetary analogue materials are routinely analyzed, with the available equipment the PSL having a unique capability to measure emissivity of fine-grained powder materials over a very wide spectral range, bulk materials and coatings at temperatures up to 1000K across the whole infrared wavelength range. Most of its previous work is based on emissivity measurements.

Following user demands PSL extended in the last years its spectral coverage down to the UV allowing now to measure bi-directional reflectance from

150nm to 300 microns with two identical Bruker VERTEX 80V spectrometer [2],[7].

At the PSL measurements for the characterization of asteroid and comet analogues by means emission and reflectance spectroscopy have already been performed [5] and reflectance spectra at room temperature has been measured [4].

The PSL now aims to extend its capability to perform reflectance measurements at low-Temperature environments, especially on the characterization of asteroid, cometary or solar system small bodies (SSSB) analogues. In the case of the main-belt asteroids and dwarf planet Ceres, the daytime surface temperature is between 200 and 300K (-73.15°C to 26.85°C) [11].

## 2. Low temperature: spectroscopy

Objects in space are subjected to its almost perfect vacuum, cold and solar radiation. For instance the maximum day-light temperature of the dwarf planet Ceres was estimated to be 235K [10], the surface temperatures distributions of Vesta is from 40K to 248K [3] and the surface temperatures of Asteroid 21 Lutetia reaches a maximum value of 245K [1].

Pronounced spectral effects at the lowest temperature of 80K are shown by Moroz et al. [8] in a reflectance spectra measurement of Olivine and orthopyroxene, which are very common rock-forming minerals in the Solar System. A measure of the temperature dependence of the reflectance spectra at the primitive surface of Ceres has been addressed by Beck et al. [12] to investigate the reflectance spectrum under decreasing temperatures (down to 93K).

Setting up a system for reflectance spectroscopy experiments at cryogenic temperatures represents a unique opportunity for the PSL.

### 3. Technical Approach

In the first concept phase various cooling systems have been evaluated. The cooling system has the main objective to cool down the sample surface down to cryogenic temperatures. The possibility of using a closed based cycle cooling by helium gas or liquid nitrogen with typical temperatures of 70-90K, to provide distributed cooling power for a cooling surface, is discussed. The nominal cooling capacity of the miniature cryocooler system currently at use at DLR is for example 65K [9]. It is expected to reach a cryogenic temperature within the range of 70K – 100K.

### 4. Experimental setup

At PSL, there are currently two instruments equipped with external chambers to measure emissivity. One of them is a vacuum chamber built to measure at very high temperatures and the second chamber (that can be cooled down to 0° C) is for measurements at low to moderate temperatures [6]. In the latter samples can be heated from room temperature to 150°C in a purging environment.

The new low-T chamber will be coupled to the newest Fourier transform infrared (FTIR) spectroscopy instrument Bruker Vertex 80 V equipped with aluminum mirrors for high efficiency down to the UV spectral range.

### 5. Summary and Conclusions

In summary, laboratory-spectroscopy investigations of minerals are key to support the interpretation of remote sensing data returned by the interplanetary missions.

A compact low-temperature reflectance chamber for FT-spectroscopy experiments at the PSL is currently under development. The expected cryogenic temperature to reach is approximately within the range of 70K – 100K. The potential experiments are promising. The current and future missions (e.g., NASA/DAWN and ESA/ExoMars 2020, NASA/EUROPA Multiple Flyby Mission, ESA/JUICE respectively) indicate the high potential usage of this development, which may result in many scientific or even commercial applications.

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