Cometary Particle Surfaces Characterized by Chemometric Evaluations of Secondary Ion Mass Spectra

Varmuza Kurt [1*], Filzmoser Peter [1], Hilchenbach Martin [2], Kissel Jochen [2], Stenzel Oliver [2], Merouane Sihane [2], Paquette John [2], Hornung Klaus [3], Cottin Hervé [4], Fray Nicolas [4], Isnard Robin [4], Engrand Cécile [5], Briois Christelle [6], Thirkell Laurent [6], Modica Paola [6], Langevin Yves [7], Baklouti Donia [7], Bardyn Anais [8], Siljeström Sandra [9], Silén Johan [10], Rynö Jouni [10], Lehto Harry [11], Schulz Rita [12]

[1] **Vienna University of Technology**, Institute of Statistics and Mathematical Methods in Economics, Research Unit Computational Statistics, Vienna, Austria
[2] Max Planck Institute for Solar System Research, Göttingen, Germany
[3] Universität der Bundeswehr München, LRT-7, Neubiberg, Germany
[4] Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université Paris Est Créteil et Université Paris Diderot, Créteil, France
[5] CSNSM, CNRS-IN2P3, Université Paris Sud, Université Paris-Saclay, Orsay, France
[6] Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Université d'Orléans et du CNES, Orléans, France
[7] Institut d'Astrophysique Spatiale, Université Paris Sud, Orsay, France
[8] DTM, Carnegie Institution of Washington, Washington, DC, USA
[9] Bioscience and Materials, Research Institute of Sweden, Stockholm, Sweden
[10] Finnish Meteorological Institute, Helsinki, Finland
[11] Finnish Tuorla Observatory, Department of Physics and Astronomy, University of Turku, Piikkiö, Finland
[12] European Space Agency, Noordwijk, The Netherlands

Instrument **COSIMA** on board of the ESA mission **Rosetta** collected cometary particles with 20 - 1000 µm diameter at distances of 10 - 1500 km from comet **Churyumov-Gerasimenko** (67P) between August 2014 and September 2016.

More than **30,000 particles** were documented by images.

About **33,900 secondary ion mass spectra** were measured (time-of-flight mass analyzer) by COSIMA and sent to Earth.

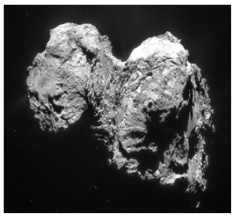
Sets of selected positive SIMS spectra were evaluated by univariate and multivariate statistical techniques.

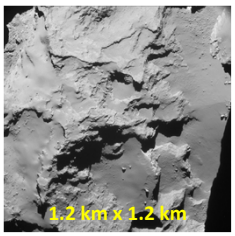
Aims of the data analyses and result shown here are:

- characterization of carbon-containing substances on the surface of cometary particles,
- determination of atomic ratios,
- search for different chemical compositions of the particles collected at various distances from the sun.

Comet *67P*

Name: 67P / Churyumov-Gerasimenko (*Chury*)
Size: 6 km x 4 km x 2 km; *Density:* 0.53 g/cm^3
Orbit: 6.44 years; 1.24 AU (perihel) – 5.7 AU (aphel)
1 AU (Astronomical Unit) = 150 000 000 km,
~ mean distance Earth – Sun
Rotation: 12.76 h
Albedo: ca 5% ("black like charcoal") [14]



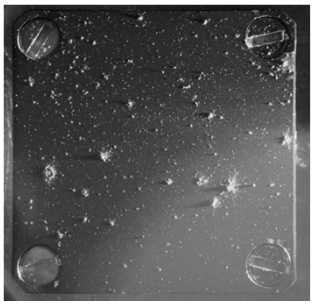


Cometary dust particles

About 1400 dust particles (30 000 fragments) of 10 – 1000 µm size have been collected on metal targets [4] (1 cm x 1 cm, see picture) by the COSIMA instrument.

Distances to the comet typically between 10 – 150 km.

Distance to Sun: 1.24 – 3.83 AU.



Spacecraft Rosetta (ESA)

Launch: 2 March 2004 (Kourou), Ariane 5. More than 10 years journey.

Arrival at comet (ca 100 km): 6 Aug 2014, 2.8 AU from Earth.

First mission to rendezvous with a comet. Escorting the comet at typical distances of 10 – 200 km [2].

Nov 2014: lander *Philae* reached the surface of comet.

Aug 2015: nearest to Sun (perihel, 186 .10^6 km).

30 Sep 2016: end of mission by controlled touch down at comet & shut down.

Mass spectrometer COSIMA onboard of Rosetta

- Collected dust particles on metal targets (Au, Ag).
- Analyzed them by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The mass resolution of ca 1400 (half peak) at *m/z* 100 separated several inorganic and organic ions with the same mass number. About 30,000 full spectra have been sent to ground [1,5].
- Primary ions: ^{115}In, 3 ns shots, 8 keV, 1.5 kHz.
- Typical 225,000 shots per spectrum.
- Measurement spot: 30 µm x 50 µm.
- Secondary ions (positive & negative): 3 keV, 2-stage ion reflector.
- 26,300 time bins (4 ns) for m/z 0 - 300.
- COSISCOPE camera: 1024 x 1024 pixel (14 µm diameter) [3].

* kurt.varmuza@tuwien.ac.at, http://www.lcm.tuwien.ac.at/vk/

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Selected Results – Based on COSIMA Data

Organics

- ❑ Organic material on the surface of cometary particles is macromolecular [6].
- ❑ No specific organic compounds could be identified on cometary particles.
- ❑ Cometary particles appear different from the meteorite type carbonaceous chondrites (CC meteorites) [9].
- ❑ Cometary material contains more (organic) carbon than CC meteorites.
- ❑ Atomic ratios estimated from SIMS data:
  C/Si ~ 5 [7] C/N ~ 30 [8]
  C/H ~ 1 [11]

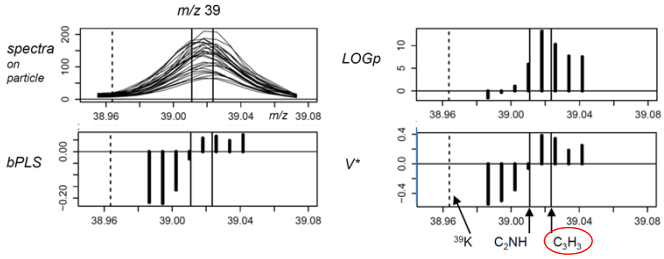
The **mineralic composition** of the cometary material is similar to that of chondritic meteorites, however, with the more volatile rock-building elements C, S, Na, K, Cu, Li enriched in the comet [9].

Unsaturated CH-ions

have been found to be characteristic in the mass spectra of cometary material. The presence of $C_3H_{0\text{-}4}^+$, C_4^+, etc. indicates unsaturated organic compounds [10].

Methods used to characterize the importance of variables for a discrimination between the two classes (1) comet particle spectra and (2) background spectra are [17]:

- **t-test:** comparing class means, criterion *LOGp* = sgn [-log(*p*)]
- **D-PLS:** standardized regression coefficients of discriminant variable
- **Random Forest:** criterion *MDA* (Mean Decreasing Accuracy)
- **Robust Pair-wise Log-Ratios (rPLR):** criterion V*, developed for the identification of biomarkers, based on all ratios of all variables [12].



Distance between collection area and Sun may affect the composition of particle surfaces

Collection of cometary particles occured at various distances between comet and Sun. Is the **composition** of the particles dependent on the distance to the Sun – and may this be reflected in the mass spectral data? A first approach.

Data: *n* = 3095 mass spectra, *m* = 11 peak heights (C^+, CH^+, CH_2^+, CH_3^+, Mg^+, Al^+, $C_2H_3^+$, K^+, $C_3H_3^+$, Ca^+, Fe^+).

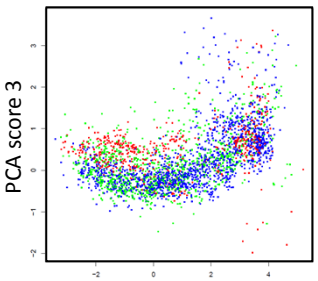
Distance to Sun (mean in the sampling interval): 2.16 – 3.6 AU

3 classes: **<2.5 AU (n_1=579)**; **2.5 – 3.1 AU (n_2=1023)**; **>3.1 AU (n_3=1493)**

Methods

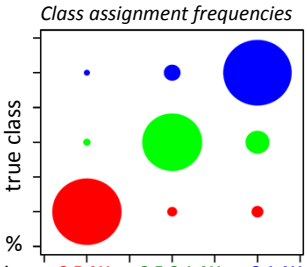
(a) Robust PCA [14] with data transformed by the centered log-ratio method (compositional data) [13].

(b) KNN classification with repeated double cross validation (rdCV) [16]. Peak heights normalized to constant sum.



PCA indicates some separation of the classes.

These preliminary results indicate that the chemical composition of the cometary particles may depend on the distance between collection area and Sun.



KNN gives 67 – 78 % correct assignments to the classes.

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* kurt.varmuza@tuwien.ac.at, http://www.lcm.tuwien.ac.at/vk/

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Cometary particle surfaces - characterized by chemometric evaluation of secondary ion mass spectra

K. Varmuza[1], P. Filzmoser[1], M. Hilchenbach [2], J. Kissel[2], O. Stenzel[2], S. Merouane[2], J. Paquette[2], K. Hornung[3], H. Cottin[4], N. Fray[4], R. Isnard[4], C. Engrand[5], C. Briois[6], L. Thirkell[6], P. Modica[6], Y. Langevin[7], D. Baklouti[7], A. Bardyn[8], S. Siljeström[9], J. Silén[10], J. Rynö[10], H. Lehto[11], R. Schulz[12]

[1] Vienna University of Technology, Institute of Statistics and Mathematical Methods in Economics, Research Unit Computational Statistics, Vienna, Austria

[2] Max Planck Institute for Solar System Research, Göttingen, Germany

[3] Universität der Bundeswehr München, LRT-7, Neubiberg, Germany

[4] Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université Paris Est Créteil et Université Paris Diderot, Créteil, France

[5] CSNSM, CNRS-IN2P3, Université Paris Sud, Université Paris-Saclay, Orsay, France

[6] Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Université d'Orléans et du CNES, Orléans, France

[7] Institut d'Astrophysique Spatiale, Université Paris Sud, Orsay, France

[8] DTM, Carnegie Institution of Washington, Washington, DC, USA

[9] Bioscience and Materials, Research Institute of Sweden, Stockholm, Sweden

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