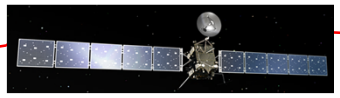
Mass spectrometry near comet 67P (Rosetta/COSIMA)

Kurt Varmuza[1]*, Peter Filzmoser[1], Irene Hoffmann[1], Martin Hilchenbach[2], Jochen Kissel[2], Sihane Merouane[2], John Paquette[2], Oliver Stenzel[2], Hervé Cottin[3], Nicolas Fray[3], Robin Isnard[3,4], Christelle Briois[4], Paola Modica[4], Laurent Thirkell[4], Cécile Engrand[5], Donia Baklouti[6], Yves Langevin[6], Anaïs Bardyn[7], Klaus Hornung[8], Sandra Siljeström[9], Jouni Rynö[10], Johan Silén[10], Rita Schulz[11], Franz Brandstätter[12], Ludovic Ferrière[12], Christian Koeberl[12,13]

[1] TU Wien, Institute of Statistics and Mathematical Methods in Economics, Vienna, Austria; [2] Max-Planck-Institute for Solar System Research, Göttingen, Germany; [3] Université Paris Est Créteil et Univ. Paris Diderot, LISA, UMR CNRS 7583, Créteil, France; [4] Université d'Orléans, Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS, Orléans, France; [5] Université Paris Sud, Centre de Sciences Nucléaires et de Sciences de la Matière, CNRS/IN2P3, Orsay, France; [6] Université Paris Sud, Institut d'Astrophysique Spatiale (IAS), CNRS, Orsay, France; [7] Carnegie Institution of Washington, Dept. Terrestrial Magnetism, Washington, DC, USA; [8] Universität der Bundeswehr, LRT-7, Neubiberg, Germany; [9] RISE Research Institutes of Sweden, Bioscience and Materials, Stockholm, Sweden; [10] Finnish Meteorological Institute, Helsinki, Finland; [11] European Space Agency (ESA), Scientific Support Office, Noordwijk, The Netherlands; [12] Natural History Museum Vienna, Austria; [13] University of Vienna, Department of Lithospheric Research, Vienna, Austria

1 The Project

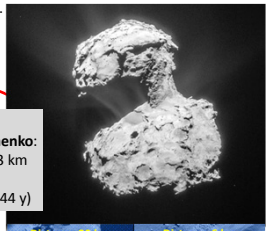
Launch: 2 Mar 2004, Ariane 5, Kourou, French Guaiana



Spacecraft **Rosetta** (ESA); 11 instruments + lander; size 2.8 m × 2.1 m × 2 m; 3 tons; 32-m-wide solar panel; 2.2 m dish antenna; fuel: me-hydrazine + N_2O_4

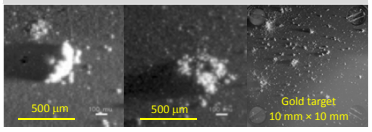
On the way
10 years, 5 months, 4 days
(31 months hibernation)

Arrival: 100 km from comet, 2.8 AU from Earth, 6 Aug 2014.
Escorting: typical distance 10 - 200 km, 1.5 – 3.8 AU from Earth.
End: 30 Sep 2016 (landing).
[1 AU ≈ 150 000 000 km]

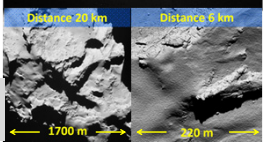


Comet 67P /Churyumov–Gerasimenko:
Size: ~ 6 km × 4 km × 3 km
Density: 0.53 g/cm³
Orbit: 1.24 - 5.7 AU (6.44 y)

Cometary dust particles. Collected by instrument COSIMA, 10 - 200 km from surface; imaged and analyzed by the TOF-SIMS mass spectrometer COSIMA. 1400 particles, 30 000 fragments, size 10-1000 µm [9].



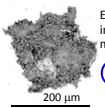
Particle pictures: MPS



Comet pictures: ESA, MPS

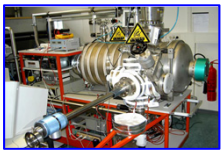
Sandy flat areas, boulders 30 m, canyons, cliffs (100 m)

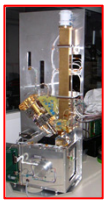
Meteorite Allende (example), from NHM Wien, carbonaceous chondrite (CC)



Electron microscope image (NHM) of a manually broken grain

COSIMA instrument in lab (MPS)





COSIMA instrument, on-board [8]

mass spectral data from **cometary particles**

mass spectral data from **meteorite samples**

Data evaluation, interpretation

2 TOF-SIMS instrument COSIMA

- Primary ions: $^{115}In^+$, 3 ns shots (~ 1000 ions), 1500 shots per second, 8 kV; measurement spot on sample ~ 35 µm x 50 µm.
- Secondary ions (positive or negative): 3 kV acceleration, ion reflector, ion counter (1.95 ns time bins), up to ca 6500 Dalton.
- Mass resolution (full width at half maximum peak height): 500 (m/z 12) – 1000 (m/z 73).
- Typical per spectrum 225,000 primary ion shots; registered secondary ions (m/z <700.5) per shot: 0.2 - 1 (median 0.6) positive ions, or 0.4 - 1.4 (median 0.7) negative ions.
- Targets for dust collection: 1 cm x 1 cm, Au black, Ag.
- COSISCOPE microscope/camera: 1024 x 1024 pixel (14 µm) [7].
- Mass of instrument on-board 20 kg; power consumption 20 W.

3 Multivariate data

SAMPLES (cometary particles and CC meteorites)

Cometary particle *Donia*	79 spectra	]	148 comet spectra
Kerttu	69		
Meteorite *Allende*	355	]	606 meteorite spectra
Lancé	119		
Murchison	132		
Total	***n* = 754 spectra (objects)**		

Selection: Multivariate one-class classification (by orthogonal and score distances, and by a KNN approach) with background spectra defining the single class. Combined with spectroscopic and experimental parameters [5, 11, 13]. Background subtracted.

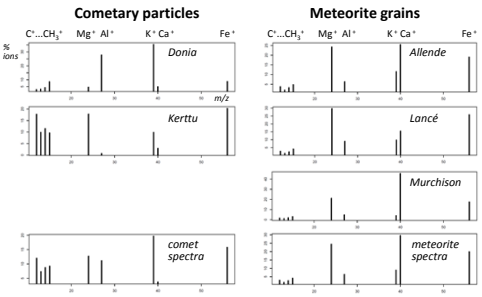
VARIABLES

Mass spectral peak heights for ***m* = 9** ion species:
C^+, CH^+, CH_2^+, CH_3^+, $^{24}Mg^+$, $^{27}Al^+$, $^{39}K^+$, $^{40}Ca^+$, $^{56}Fe^+$
Variables normalized to sum 100 per spectrum (% ions).

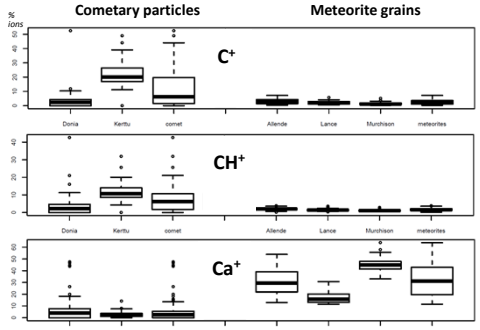
SOFTWARE

R. *A language and environment for statistical computing*. Vienna, Austria: R Development Core Team, Foundation for Statistical Computing, www.r-project.org (2018).

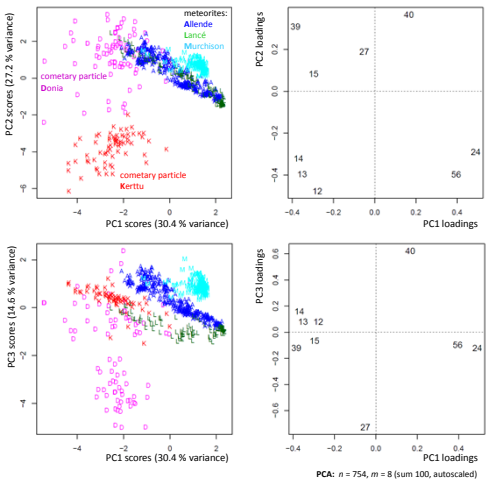
4A RESULTS: Mean spectra



4B RESULTS: Distributions of % ions



4C RESULTS: Principal Component Analysis (PCA)



PCA: n = 754, m = 8 (sum 100, autoscaled)

5 SUMMARY

Including data evaluations not mentioned here [2, 4, 6, 10].

- Cometary particles appear diverse and different from CC meteorites.
- Composition of cometary particles is close to that of chondritic meteorites but enriched in Si and C and depleted in Mg [12].
- Cometary particles show higher carbon contents than the carbon-rich meteorites (CC) Allende, Lancé, Murchison.
- Cometary particles consist of ~55% silicates and ~45% carbonaceous material (mass) [1].
- Carbonaceous material: mostly macromolecular substances [3].
- Ions $C_3H_{0-4}^+$, C_4^+, etc. indicate unsaturated organic compounds in cometary particles [14].

Details, more references, PDFs: http://www.lcm.tuwien.ac.at/comecs/

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References

[1] Bardyn A. et al.: MNRAS **469**, Suppl_2, S712 (2017)
[2] Engrand C. et al.: Rapid Commun. Mass Spectrom. **20**, 1361 (2006)
[3] Fray N. et al.: Nature **528**, 72 (2016)
[4] Fray N. et al.: MNRAS **469**, Suppl_2, S506 (2017)
[5] Hilchenbach M. et al.: The Astrophys. J. Lett., **816**: L32 (2016)
[6] Hornung K. et al.: Space Sci. Rev. **133**, 63 (2016)
[7] Langevin Y. et al.: Icarus **271**, 76 (2016)
[8] Kissel J. et al.: Space Sci. Rev. **128**, 823 (2007)
[9] Merouane S. et al.: MNRAS **469**, Suppl_2, S459 (2017)
[10] Schulz R. et al.: Nature **518**, 216 (2015)
[11] Silén J. et al.: Geosci. Instrum. Method. Data Syst. **4**, 45 (2015)
[12] Stenzel O. et al.: MNRAS **469**, Suppl_2, S492 (2017)
[13] Varmuza K. et al.: Chemom. Intell. Lab. Syst.**138**, 64 (2014)
[14] Varmuza K. et al.: J. Chemom. e3001 (2018)

* kurt.varmuza@tuwien.ac.at; www.lcm.tuwien.ac.at/vk/

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Poster at 29th MassSpec Forum Vienna, 20 – 21 Feb 2018, TU Wien, Vienna, Austria

Book of Abstracts

29th MassSpec Forum Vienna
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Getreidemarkt 9 1060 Vienna Austria

Posters will be set up during te whole MassSpec Forum Vienna.

6	Kurt Varmuza	TU Wien, A	Mass spectrometry near comet 67P (Rosetta/COSIMA)

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[5] Université Paris Sud, Centre de Sciences Nucléaires et de Sciences de la Matière, CNRS/IN2P3, Orsay, France
[6] Université Paris Sud, Institut d'Astrophysique Spatiale (IAS), CNRS, Orsay, France
[7] Carnegie Institution of Washington, Dept. Terrestrial Magnetism, Washington, DC, USA
[8] Universität der Bundeswehr, LRT-7, Neubiberg, Germany
[9] RISE Research Institutes of Sweden, Bioscience and Materials, Stockholm, Sweden
[10] Finnish Meteorological Institute, Helsinki, Finland
[11] European Space Agency (ESA), Scientific Support Office, Noordwijk, The Netherlands
[12] Natural History Museum Vienna, Austria

Introduction

The time-of-flight secondary ion mass spectrometer (TOF-SIMS) *COSIMA* on board of the *Rosetta* spacecraft has collected and analyzed dust particles near the comet 67P/Churyumov–Gerasimenko. Meteorite grains have been analyzed as reference samples using a laboratory twin instrument of *COSIMA*. Current results are summarized.

Methods

The *COSIMA* instrument collected on metal targets (mostly Au, 1cm x 1cm) about 1400 particles (size up to 1 mm, ~35,000 fragments) during the >2 years next to the comet (typical distance to the comet 10 - 200 km, typical exposure time 1 - 7 days). On about 250 particles TOF-SIMS spectra have been measured, and about 33,000 full spectra have been sent to Earth, together with images (1024 x 1024 pixel) of the targets. Additionally, about 6,000 spectra have been measured on 10 meteorite samples from the collection in the Natural History Museum Vienna. Spectral data interpretation was mainly based on ratios of secondary ion counts, correlation of signals, and multivariate (chemometric) methods.

Results

- Cometary particles consist of ~55% silicates and ~45% carbonaceous material (mass) [1].
- Carbonaceous material consists mostly of macromolecular substances [2].
- Presence of ions $C_3H_{0\text{-}4}^+$, C_4^+ in the spectra indicate unsaturated organic compounds [3].
- Elemental composition of cometary particles is close to that of chondritic meteorites but enriched in Si and C [4].

References

www.lcm.tuwien.ac.at/comecs/ (Project *CoMeCS*)

[1] Bardyn A. et al.: Carbon-rich dust in comet 67P/Churyumov-Gerasimenko measured by COSIMA/ Rosetta. *MNRAS (Mon Not Roy Astron Soc)* 2017; **469** (Suppl_2): S712-S722.
[2] Fray N. et al.: High-molecular-weight organic matter in the particles of comet 67P/Churyumov-Gerasimenko. *Nature* 2016; **528**: 72-74.
[3] Varmuza K. et al.: Significance of variables for discrimination - applied to the search of organic ions in mass spectra measured on cometary particles. *J. Chemometrics* 2018; in print.
[4] Stenzel O. et al.: Similarities in element content between comet 67P/Churyumov-Gerasimenko coma dust and selected meteorite samples. *MNRAS (Mon Not Roy Astron Soc)* 2017; **469** (Suppl_2): S492-S505.

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