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Comet and meteorite particle surface characterization by multivariate data analyses using TOF-SIMS data from COSIMA/Rosetta

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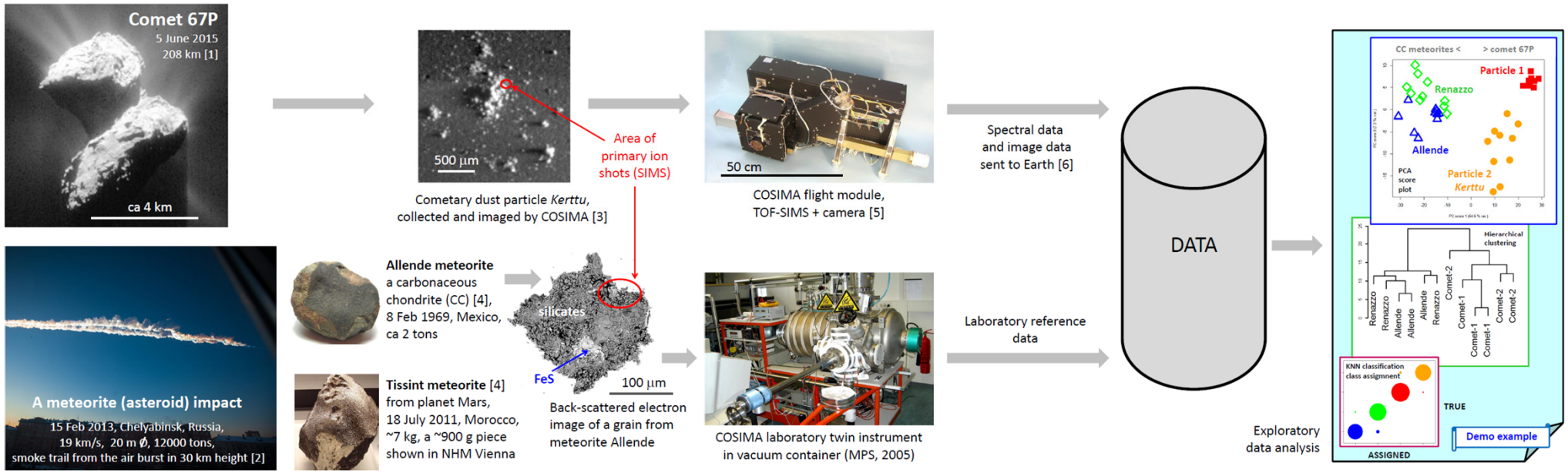
- Cometary dust particles have been collected and analyzed near comet 67P by the COSIMA instrument (TOF-SIMS, on-board of ESA/Rosetta).
- Meteorite samples have been used as references and have been analyzed by a laboratory twin instrument of COSIMA.
- The mass spectra have been evaluated by chemometric methods to characterize the elemental/chemical composition of the samples.



1 Introduction

COSIMA - Cometary Secondary Ion Mass Analyser - [5] is one of the instruments on-board of the ESA spacecraft **Rosetta**, which escorted comet 67P/Churyumov–Gerasimenko from Aug 2014 until Sep 2016. During these two years, COSIMA collected about 35,000 dust particles from the coma of the comet, imaged them, and measured mass spectra on the surfaces of about 400 particles. More than 1000 images and 34,000 mass spectra were sent to Earth.

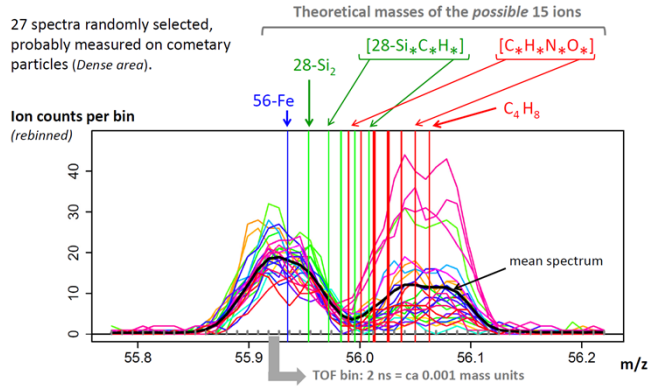
Meteorite samples are from the collection of the **Natural History Museum (NHM) Vienna**, and comprise carbonaceous chondrites (**CC**, carbon-rich, used here as the closest available equivalent to comet material), ordinary chondrites (**OC**), and a meteorite ejected from the planet Mars (**MM**) by an asteroid impact.

This work explores the multivariate diversity and similarity of meteorite samples and comet samples, based on mass spectral signals from selected positive secondary ions (elemental ions and simple CH-ions), measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS) as implemented in COSIMA.

2 Mass spectrometer COSIMA

- Primary ions: ^{115}In, 3 ns shots (ca 1000 ions), 1500 shots per second, 8 kV; measurement spot on sample ca 50 µm x 70 µm [5].
- Secondary ions (positive or negative): 3 kV acceleration, ion reflector, ion counter (2 ns time bins), up to ca 6500 Dalton, mass resolution about 1400 at *m/z* 100.
- Typical per spectrum: 200,000 primary ion shots; registered secondary ions (m/z <700.5) per shot: 0.2 - 1 (median 0.6) positive, and 0.4 - 1.4 (median 0.7) negative.
- Targets for dust collection: 1 cm x 1 cm, Au black, Ag.
- COSISCOPE microscope /camera: 1024 x 1024 pixel (14 µm diameter).
- Mass of instrument 20 kg; power consumption 20 W.

TOF-SIMS spectra measured by COSIMA on-board of Rosetta



Spectra measured: **2016** March 10 (ca 230.10^6 km from Earth)
Complete spectrum: 3 minutes; 225,000 primary ion shots
Instrument built: 1997 - **2002**
Last service: **2004** (launch)

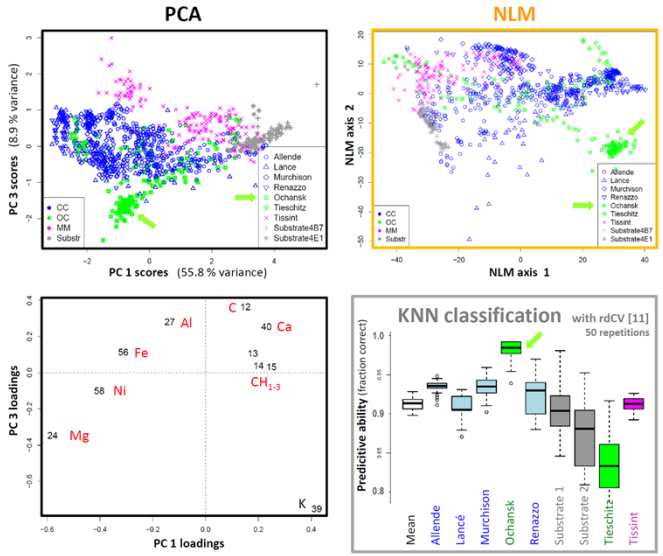
3 Mass spectral data processing

- Raw spectrum: ion counts for 130,000 TOF bins (sent to Earth).
- Calibration of mass scale; rebinning to fixed mass bins (42,000 bins for m/z 0 – 300).
- Recognition of mass peaks by a fitting procedure.
- Selection of ***n* spectra** measured *on-grain* or *off-grain* (substrate), supported by *one-class classification* [7, 8].
- Selection of ***m* = 10 peaks** for most abundant isotopes of **C^+, CH^+, CH_2^+, CH_3^+, Mg^+, Al^+, K^+, Ca^+, Fe^+, Ni^+** thus trying to avoid signals from contaminations, e.g., Na-salts.
- Subtraction of contributions from polydimethylsiloxane (PDMS).
- Matrices ***X*** (*n* objects × *m* variables) used for data evaluation.

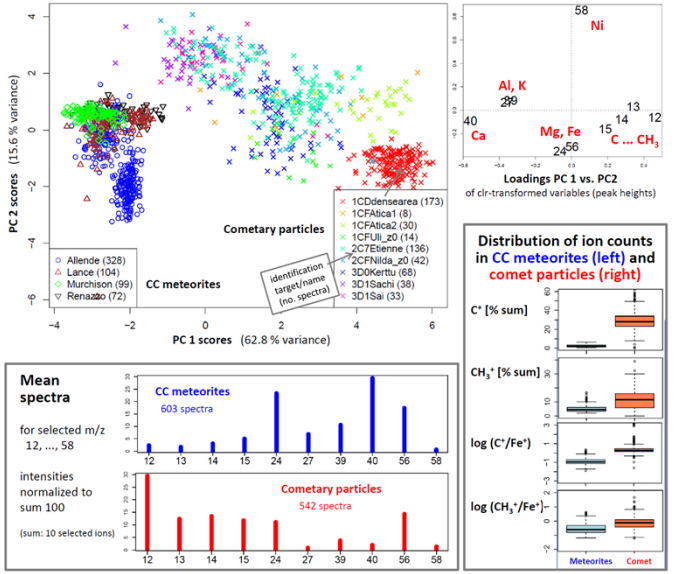
4 Chemometrics

- ❑ Matrices ***X*** contain **compositional data** (CoDa); only relative values or ratios are relevant.
- ❑ To avoid artifacts (e.g., accidental correlations of variables), appropriate transformed data have been used. A basic approach is the **centered log-ratio transformation (CLR)**:
  x_{ij} (CLR) = $\log(x_{ij} / G(x_i))$ with $G(x_i)$ for the geometric mean of all variables of observation (spectrum) *i* [9].
- ❑ PCA, principal component analysis; NLM, Sammon's nonlinear mapping; KNN, k-nearest neighbor classification [9].
- ❑ All computations with **software environment R** [10].

5 Meteorites



6 Cometary particles and CC meteorites



7 Summary

- The investigated meteorite samples show a distinct **clustering** with the used ten variables, reflecting the different meteorites.
- The **heterogeneity** of the meteorite samples appears similar when applying the complementary methods PCA, NLM and KNN.
- Cometary material shows only **weak similarities** (based on the used 10 variables) with the investigated meteorite samples.
- **Cometary material has higher contents of carbon** (measured by the ions C^+, CH^+, CH_2^+ and CH_3^+ in relation to the other considered ions) than carbonaceous chondrites - thus confirming previous results [12].

References

[1] http://www.esa.int/spaceinimages/Images/2015/06/Comet_on_5_June_2015_NavCam (C) ESA/Rosetta/NavCam – CC BY-SA IGO 3.0
[2] https://en.wikipedia.org/wiki/Chelyabinsk_meteor
[3] Hilchenbach M. et al.: Conference *Comets: A new vision after Rosetta/Philae*, Toulouse, 14-18 Nov 2016
[4] Meteoritical Bulletin Database 2017, http://www.lpi.usra.edu/metbull.php
[5] Kissel J. et al.: Space Sci. Rev., **128**, 823 (2007)
[6] Hilchenbach M. et al.: The Astrophysical Journal Letters, **816**: L32 (2016)
[7] Xu Y., Brereton R.G.: J. Chem. Inf. Model., **45**, 1392 (2005)
[8] Pomerantsev A.L.: J. Chemom., **22**, 601 (2008)
[9] Varmuza K., Filzmoser P.: Introduction to multivariate statistical analysis in chemometrics, CRC Press, Boca Raton, FL, USA (2009)
[10] R, A language & environment for statistical computing, R Development Core Team, www.r-project.org (2017)
[11] Varmuza K., et al.: Chemom. Intell. Lab. Syst., **138**, 64 (2014)
[12] Fray N. et al.: Nature **528**, 72 (2016)

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