COMET DUST COMPOSITION EXPLORED BY CHEMOMETRIC METHODS USING MASS SPECTRAL DATA FROM COSIMA/ROSETTA

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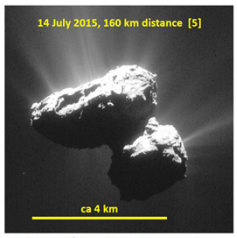
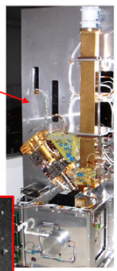
- **COSIMA** [1] was operated on-board of spacecraft **Rosetta**;
  - collected ca. 35,000 **cometary dust particles**;
  - imaged them (size determination and categorization) [2, 3];
  - measured ca 34,000 mass spectra [4] on ca. 400 particles.
- A set of selected **mass spectra** has been evaluated
  - by various chemometric methods,
  - to characterize the **homogeneity** and **composition** of the particles, and to search for **CHNO containing substances**.



Comet 67P/Churyumov-Gerasimenko
Orbit: 1.2 – 5.7 AU from sun, 6.4 years; rotation 12.76 h; density 0.4-0.5 g/cm³; albedo 5 % reflectance (very black).

Rosetta spacecraft (ESA)
Total 3000 kg, incl. 100 kg lander *Philae*, 165 kg instruments, 1700 kg propellant (methyl-hydrazine + N_2O_4). 3 m x 2 m x 2 m; solar panels 32 m wide; dish antenna 2.2 m .

2 Mar 2004 launch
6 Aug 2014 arrival (100 km)
Escorting the comet, typ. 10 – 200 km distance, 1.5 – 4.8 AU from Earth, 1.2 – 3.8 AU from sun.
12 Nov 2014 *Philae* landing
30 Sep 2016 controlled end of mission by impact on comet (2 m/s), switch-off.



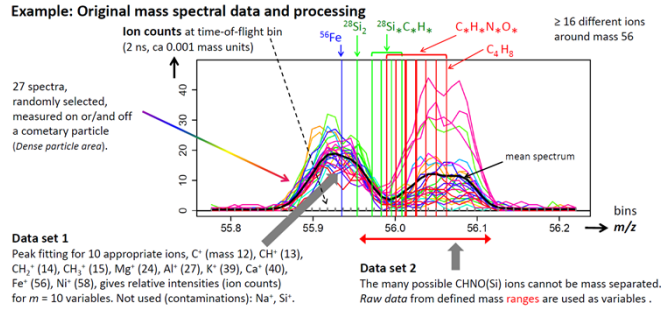
Cometary particle(s)
Named *Kerttu*, ○ SIMS spot size ca 50 µm x 70 µm

Assembling the instrument **COSIMA** [1] for operation on-board of **Rosetta.**
- ☐ Comet particle collection (targets 1 cm x 1 cm, typ. Au).
- ☐ Imaging (1024 x 1024 pixel, 14 µm resolution).
- ☐ **SIMS** measurements Secondary ion mass spectrometry with TOF (time-of-flight) analyzer, single ion counting in 2 ns flight-time bins; mass resolution ca 1400 at *m/z* 100 (50%); mass range up to 6500 Dalton .

Typ. spectrum: 2.2 minutes, 42,000 bins for *m/z* 0 – 300.

20 kg, 20 W

Example: Original mass spectral data and processing



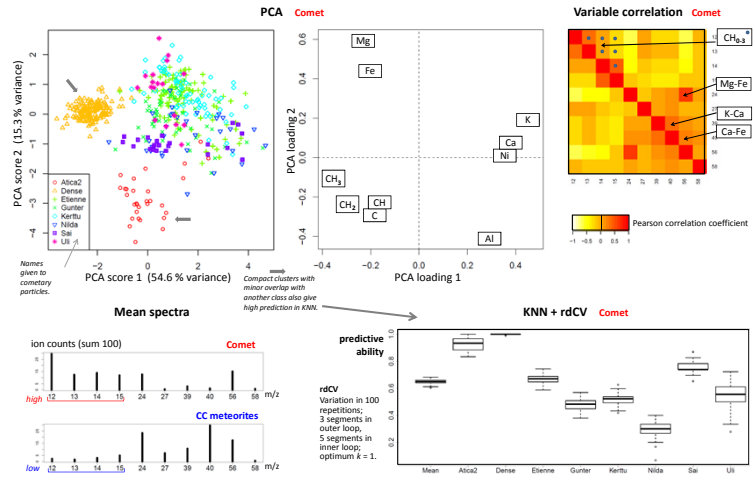
Homogeneity and composition of cometary particle surfaces

Data

- ❍ *n1* = 516 spectra from 8 cometary particles.
- ❍ *n2* = 674 reference spectra from 4 meteorites (❖). (CC; carbonaceous chondrites *Allende, Lancé, Murchison, Renazzo*), considered being similar to cometary material.
- ☐ *m* = 10 variables (**data set 1**), compositional data (CoDa); only relative values or ratios are relevant; processed by centered log-ratio transformation (CLR) [6] : x_{ij} (CLR) = log(x_{ij} /**G**(x_i)) with **G**(x_i) for the geometric mean of all variables of observation (spectrum) *i*; with values x_{ij} = 0 replaced by artificial noise >0 (uniformly distributed).

Methods

- PCA for visualization of the homogeneity or (diversity) of the cometary particle surfaces.
- KNN with rdCV (repeated double cross validation [7]) for a quantitative estimation of the separation of the spectra measured on the 8 cometary particles (and on meteorites).
- Correlation coefficient (Pearson) matrix for the 10 variables.
- Comparison of the mean spectra (normalized to sum 100) for cometary material and CC meteorites.
- ❖ Meteorite samples: COSIMA laboratory twin instrument.



Results

- Cometary particle surfaces show varying compositions (e. g., carbon-rich, Mg+Fe-rich, Mg+K+Fe-rich).
- Highest positive correlations appear between the carbon-containing ions, and for the pairs Mg-Fe, K-Ca, and Ca-Fe.
- Cometary materials have considerably higher carbon contents than carbonaceous meteorites - interesting for discussions of their *similar* age or origin.
- Cometary material is significantly different (based on the 10 used ion signals) than the CC meteorites, yielding e. g., 100% correct discrimination by KNN + rdCV..

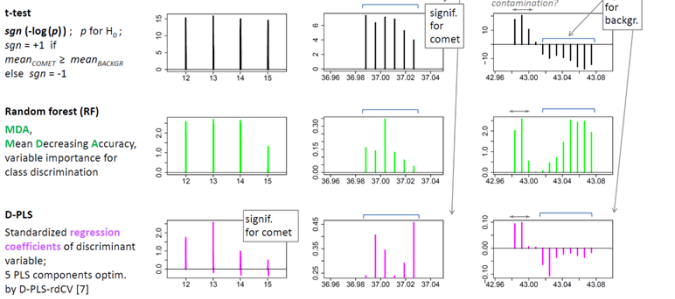
Search for CHNO containing substances on cometary particle surfaces

Data

- ❍ *n1* = 30 spectra measured at a cometary particle (*Sai*).
- ❍ *n2* = 60 spectra measured at Au background.
- ☐ *m* = 665 variables (**data set 2**), ion counts for 665 mass bins, covering all 322 possible ion formulae with C, H, N, O in the mass range 12 to 72. Normalized to sum=100.
- ◆ The 2 object classes are well separated (PCA, KNN).

Methods

- Search for marker variables indicating ions from CHNO compounds in cometary material (significant higher intensities at cometary particle than at background).
  - Statistical t- and u-test (-log(*p*)).
  - Random forest (MDA, mean decreasing accuracy).
  - D-PLS (regression coefficients of linear discriminant variable).



Tentative interpretation

☞ Ions, probably **from the cometary material**:
{ } not separable by mass; coded as **obvious** or *guess*
C^+; CH^+; {CH_2^+, N^+}; {CH_3^+, NH^+}; $C_2H_2^+$; {$C_2H_3^+$, CNH^+}; C_3^+; C_3H^+; {$C_3H_2^+$, C_2N^+}; {CH_2CN^+, $C_3H_4^+$}; CO_2^+; C_4^+; ...

☞ Ions, probably from background: saturated or lowly unsaturated CH ions: e. g., $C_3H_{5-9}^+$, $C_4H_{7-9}^+$, $C_5H_{7-12}^+$

Results

- Cometary particle surfaces contain CH(NO) compounds.
- No distinct organic substance classes are evident from the data; a complex mixture of unsaturated organic compounds may be present.
- These results from multivariate data evaluation do not contradict the presence of high molecular weight structures [8].
- The applied methods for characterizing the variable importance are complementary. For the used data, t-test and u-test yield almost identical results, and appeared more user-friendly (in terms of interpretability) than RF or DPLS.

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