One-class classification
for the recognition of relevant measurements
applied to
mass spectra from cometary and meteoritic particles

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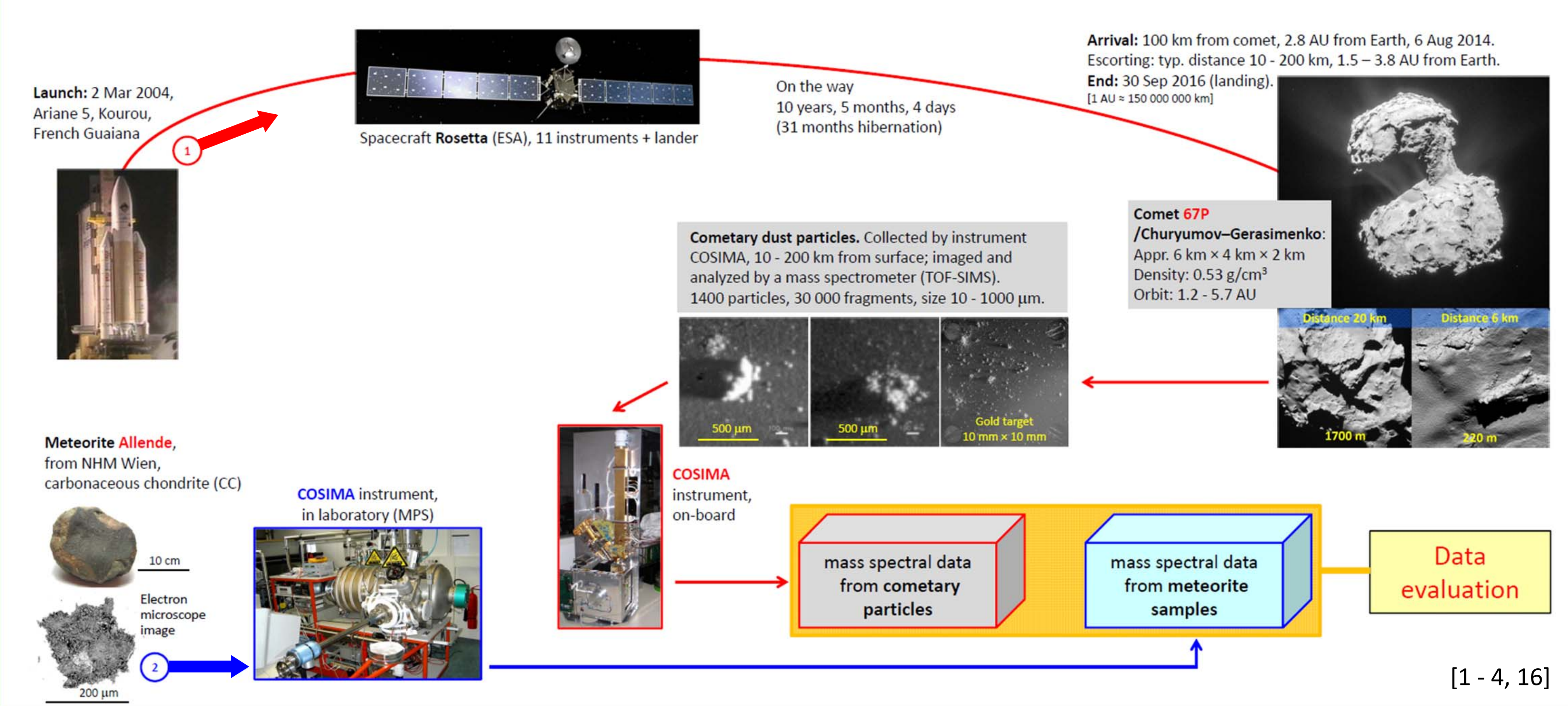
title

(1) Motivation / Rosetta project / COSIMA instrument

Data from deep space (comet), and laboratory (meteorites) → Multivariate statistics Chemoinformatics → Information about chemical composition of samples



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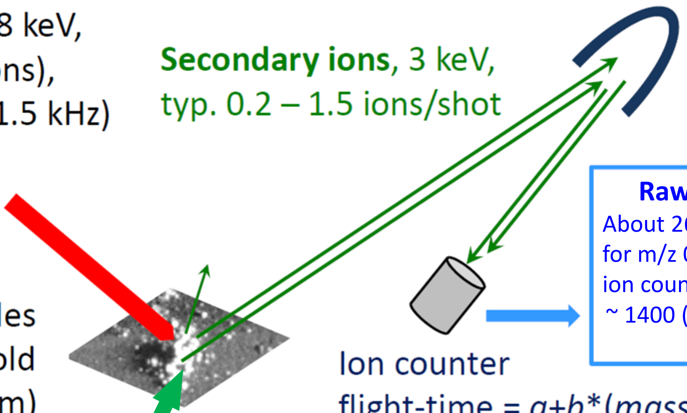
(2) Selection of potentially relevant spectra

measured on cometary particles or meteorite grains

COSIMA: TOF-SIMS / Time-Of-Flight Secondary Ion Mass Spectrometry

Primary ions, $^{115}In^{+}$, 8 keV,
3 ns shots (à 1000 ions),
typ. 225,000 shots (1.5 kHz)
per spectrum,
spot 30 µm x 50 µm

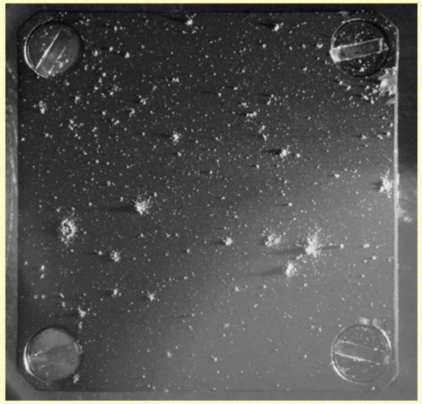
Secondary ions, 3 keV,
typ. 0.2 – 1.5 ions/shot



Raw mass spectrum
About 26,300 time (mass) bins for m/z 0 – 300 Dalton with ion counts. Mass resolution ~ 1400 (half peak height).

Cometary particles collected on a gold plate (1 cm x 1 cm)

Ion counter
flight-time = $a+b*(mass/z)^{0.5}$ [1]



Gold target (1 cm x 1 cm) with collected cometary particles.
Dec 2014 – Feb 2015, 20 – 140 km from comet (*COSIMA target 2CF*).

The position of the primary ion beam (~ 30 µm × 50 µm wide) has uncertainties up to ±70 µm. Therefore, an **evaluation of the spectra's origin** is necessary: From **background** (Au target material) or cometary **particle** (10 - 1000 µm size) ?

Strategies

- Ratios of selected ion counts, e.g., $C^{+}/CH_3^{+} > 1$
- **Multivariate methods are used here**

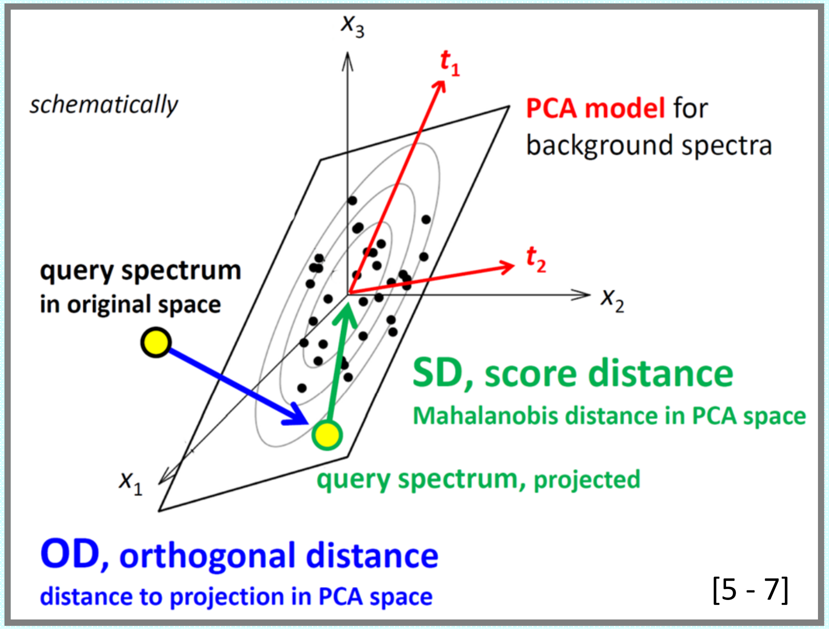
One-class classification

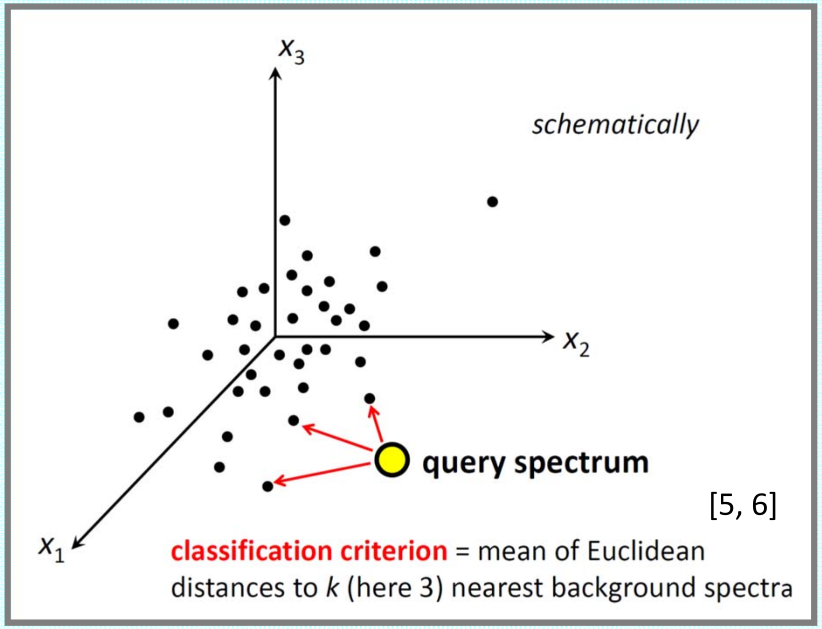
- ☐ Target class = background spectra
- ☐ Combination of
  - PCA approach (distances of query spectrum to PCA model)
  - KNN approach (mean distance of query spectrum to *k* background spectra)

SIMS data

(3) One-class classification

PCA approach combined with KNN approach





Classification

A query spectrum is NOT assigned to the background class, that means is considered potentially relevant if

- $OD > OD_{CUT}$ *. AND .* $SD > SD_{CUT}$
- *. AND .*
- mean KNN distance > KNN_{CUT}

CUToff values are typically 0.90 quantiles of empirical distributions + *safety addition*

(4) Data and Methods

Data

Variables. $m = 9$ mass spectral peak heights (ion counts) for C^+, CH^+, CH_2^+, CH_3^+, Mg^+, Al^+, K^+, Ca^+, Fe^+ (most abundant isotopes); for organics and inorganics.

Objects. $n = 1152$ spectra
55 from background for comet data (space),
121 from background for meteorite data (laboratory),
275 from 3 cometary particles (or neighborhood),
701 from 3 meteorites (Allende, Lancé, Murchison)

Preprocessing

Transformation (scaling). Because of the compositional data type (relative ion abundances are relevant) the **centered log-ratio** transformation (**clr**) has been applied (for PCA and KNN) [8].

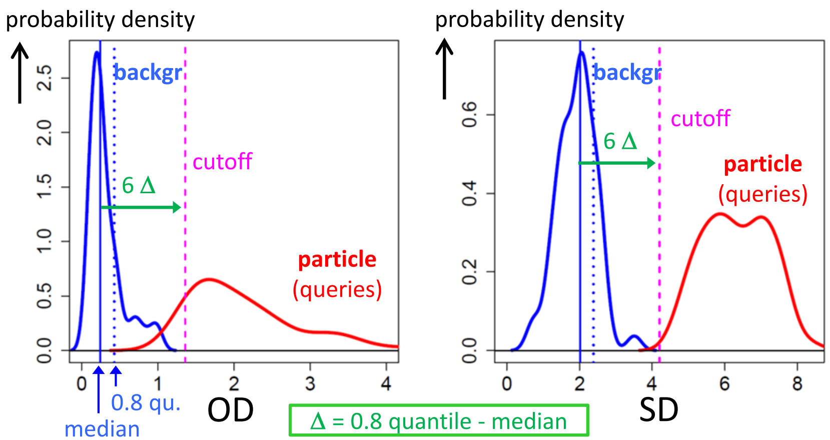
$$_{\text{CLR}}x_j = \ln[x_j / G(\boldsymbol{x})]$$

G, geometric mean of $x_1 \ldots x_m$; $j = 1 \ldots m$

PCA. Robust [9], minimum 90% variance preserved (typically 4 components).

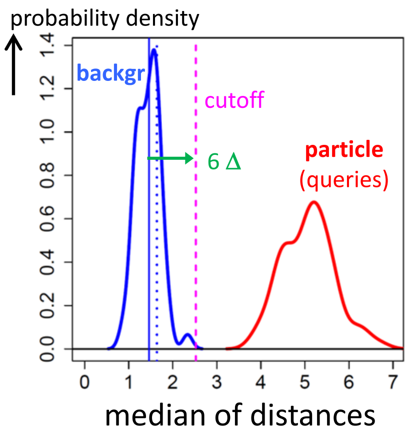
PCA approach (Example)

Distributions of OD (left) and SD (right) for background spectra (**blue**, 55 spectra) and spectra on/near the cometary particle *Kerttu* (**red**, 68 query spectra). Query spectra with distances > cutoff are considered as relevant (63 selected).



KNN approach (Example)

Distributions of median distances from query spectra to $k = 8$ nearest background spectra (for inscriptions and colors see left). Query spectra with median distances > cutoff are considered as relevant (all 68 selected).



Considering $k = 8$ nearest neighbors is a compromise between

- overfitting (instability) with a too small k, and
- underfitting (the bulk of 55 background spectra is taken) with a too big k.

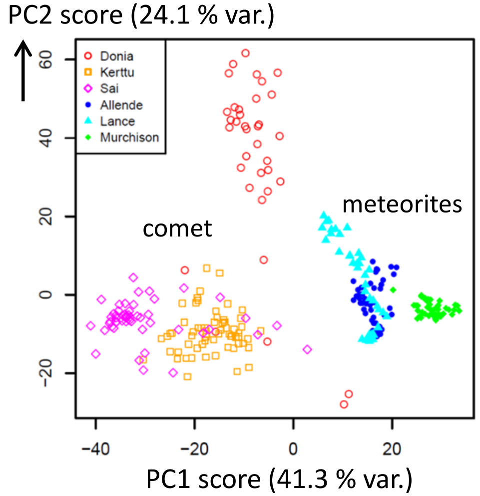
(5) Results

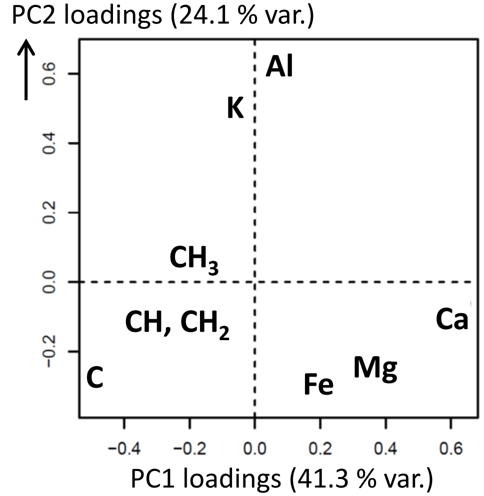
Selection of potentially relevant spectra

by 1-class classification with OD, SD and KNN

Sample particle class		Number of spectra (objects) Used	Selected by OD&SD	KNN	OD&SD & KNN
Comet	*Donia*	147	36	87	36
Comet	*Kerttu*	68	63	68	63
Comet	*Sai*	60	52	60	52
Meteorite	*Allende*	447	212	301	212
Meteorite	*Lancé*	121	105	116	105
Meteorite	*Murchison*	133	123	130	123
Sum		976	591	762	591

PCA of selected spectra



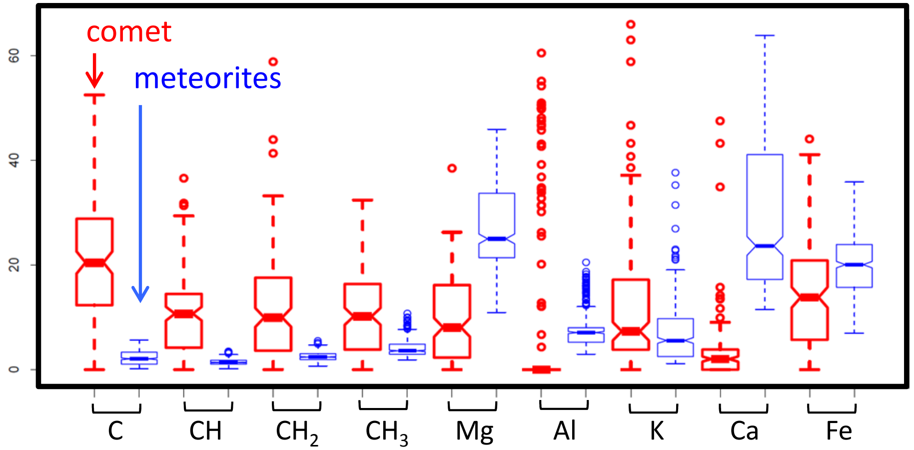


n = 301 spectra (50 randomly selected from each meteorite, 151 comet spectra) for better balanced data set.
m = 9 variables, sum 100 normalized for better interpretation; PDMS subtracted.

- **Carbon-containing ions prominent in comet data.**
- **Comet data more diverse than meteorite data.**

Comparison of comet and meteorite data

Distribution of sum-100 normalized ion counts (univariate)



All *n* = 591 selected spectra used.
Contamination of PDMS (polydimethylsiloxane) subtracted.
Normalized to sum 100 of *m* = 9 variables.

- **Comet material contains more carbon (based on CH_{0-3}^+ ions) than the considered meteorites (which are C-rich meteorites, so called *carbonaceous chondrites*).**
- **Ca^+ and Mg^+ are more prominent in meteorites than in comet.**

(6) Summary

One-class classification

based on orthogonal & score distances and a *k*-nearest neighbor approach

- Data from background (target) define the "one-class".
- Minimum assumptions; concepts from robust statistics and compositional data processing.
- Cutoff criteria solely derived from the "one-class data".
- Stable and reliable results with *difficult* TOF-SIMS data from space and with laboratory data.

Cometary/meteoritic material

TOF-SIMS data from space and lab, including results from the ***COSIMA team***

- Cometary particles appear diverse and different from CC meteorites (carbonaceous chondrites) [10].
- More (organic) carbon in comet than in CC meteorites.
- Organics: macromolecular [11].
- Ions $C_3H_{0\text{-}4}^+$, C_4^+, etc. indicate unsaturated organic compounds in cometary particles [12].
- Atomic ratios from SIMS data:
  C/Si ~ 5 [13] C/N ~ 30 [14]
  C/H ~ 1 [15]

summary

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One-class classification for the recognition of relevant measurements - applied to mass spectra from cometary and meteoritic particles

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Motivation. The mass spectrometer COSIMA on board of the ESA mission Rosetta to comet Churyumov-Gerasimenko (67P) collected particles (20 - 1000 μm diameter) at distances 10 - 1500 km from the comet and measured TOF-SIMS spectra at the particle surfaces. Because of the special conditions for these remote experiments, it is not trivial to assign the spectra either to particles or to the background (target). An objective classification of the spectra's origin (measuring spot 35 μm x 50 μm with position uncertainties up to 70 μm) has been developed by applying multivariate one-class classification strategies.

Method. The single class (target, background) for one-class classification is described by a set of multivariate objects (spectral data) measured on the target (gold). Two methods for modelling the target class are applied: robust PCA, and KNN. Criteria are defined for characterizing the dissimilarity (δ) between a query object and the target class: for robust PCA the orthogonal and the score distances from the median; for KNN the median of the distances to the k nearest neighbors. The cutoff values of δ for assigning a query object to the target class or not (the later indicates a potentially relevant object) are derived from the distributions of δ for the target objects, based on median, 0.8-quantile and an adjustable parameter (controlling the efficiency of classification). Because of the nature of the data, concepts for compositional data and robust methods have been preferred.

Application. The data used consist of 275 spectra measured on three cometary particles, and 701 spectra measured by a laboratory twin instrument of COSIMA on particles from three meteorites (carbonaceous chondrites, often considered having similar composition as comet material). A set of nine variables is derived from the measured ion counts at masses 12-15 (CH_{0-3}^+), 24 (Mg^+), 27 (Al^+), 39 (K^+), 40 (Ca^+), and 56 (Fe^+) characterizing minerals and presumed organics. Results show distinctive differences between the cometary and the meteoritic samples with considerably more carbon containing material in the comet particles.

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SSC16

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The 16th Scandinavian Symposium on Chemometrics

Book of Abstracts

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