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

Varmuza K.*[1], Filzmoser P.[1], Ortner I.[1], Hilchenbach M.[2], Kissel J.[2], Merouane S.[2], Paquette J.[2], Stenzel O.[2], Engrand C.[3], Cottin H.[4], Fray N.[4], Isnard R.[4], Briois C.[5], Thirkell L.[5], Baklouti D.[6], Bardyn A.[7], Siljeström S.[8], Schulz R.[9], Silen J.[10], Brandstätter F.[11], Ferrière L.[11], Koeberl C.[11,12]

[1] TU Wien - Vienna University of Technology (Austria)
Institute of Statistics and Mathematical Methods in Economics, Computational Statistics

kurt.varmuza@tuwien.ac.at | http://www.lcm.tuwien.ac.at/vk/ | https://institute.tuwien.ac.at/cstat/home/EN/

[2]Max Planck Inst. for Solar System Res., Göttingen (Germany); [3]CSNSM, CNRS/Univ. Paris Sud, Univ. Paris Saclay, Orsay (France); [4]Lab. Interuniversitaire des Systèmes Atmosphériques, Univ. Paris Est, Créteil (France); [5]Lab. de Physique et Chimie de l'Environnement et de l'Espace, Univ. d'Orléans (France); [6]IAS, CNRS/Univ. Paris Sud, Univ. Paris Saclay, Orsay (France); [7]Carnegie Institution of Washington, DC (USA); [8]Bioscience and Materials / Chemistry and Materials, Res. Inst. of Sweden, Stockholm (Sweden); [9]European Space Agency, Noordwijk (The Netherlands); [10]Finnish Meteorological Inst., Helsinki (Finland); [11]Natural History Museum (NHM), Vienna (Austria); [12]Dept. of Lithospheric Res., University of Vienna (Austria)

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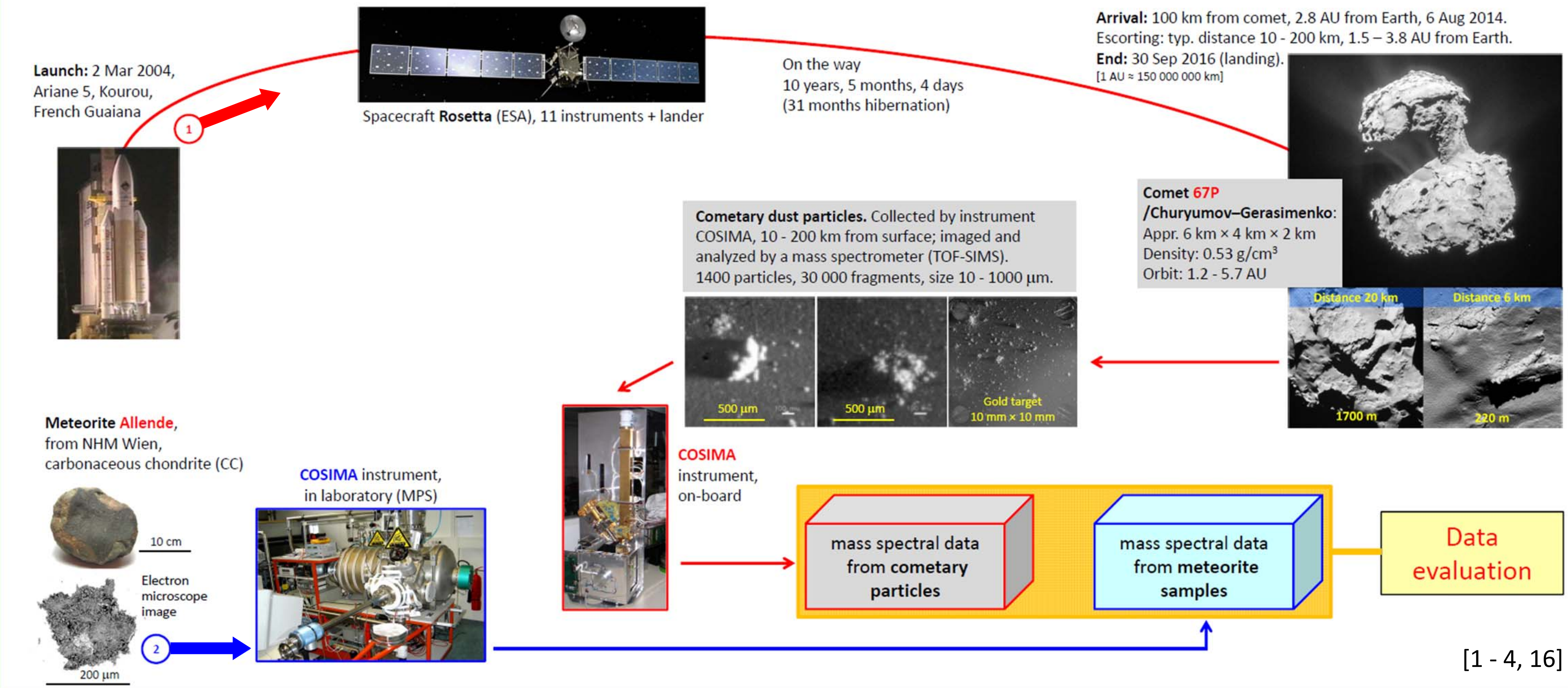
title

(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

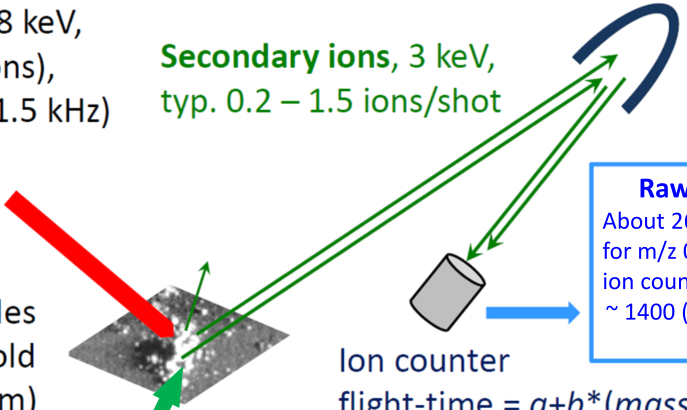
measured on cometary particles or meteorite grains

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

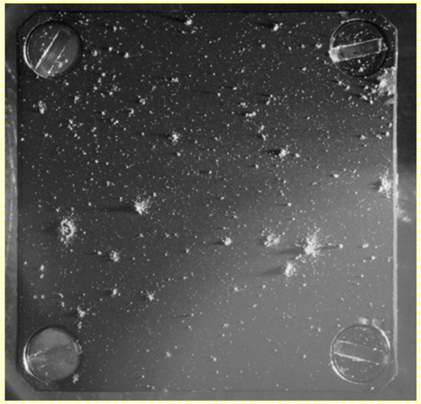
2-Stage
ion reflector



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**

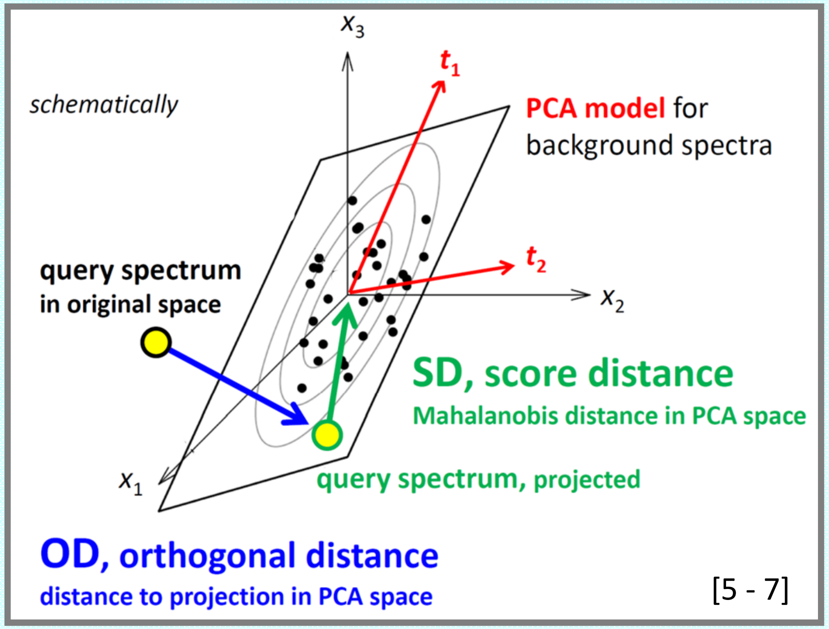
One-class classification

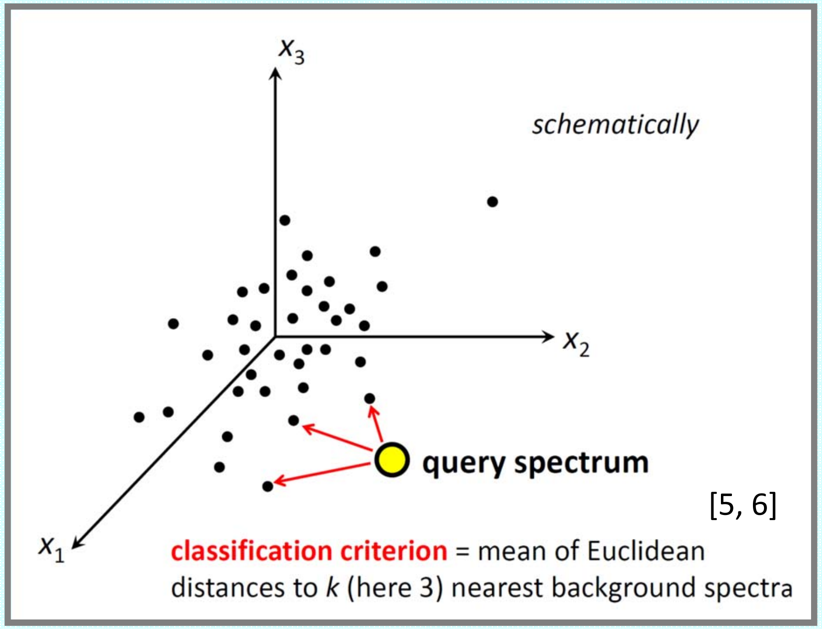
- Target class = background spectra
- Combination of
  - PCA approach (distances of query spectrum to PCA model)
  - KNN approach (mean distance of query spectrum to *k* background spectra)

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].

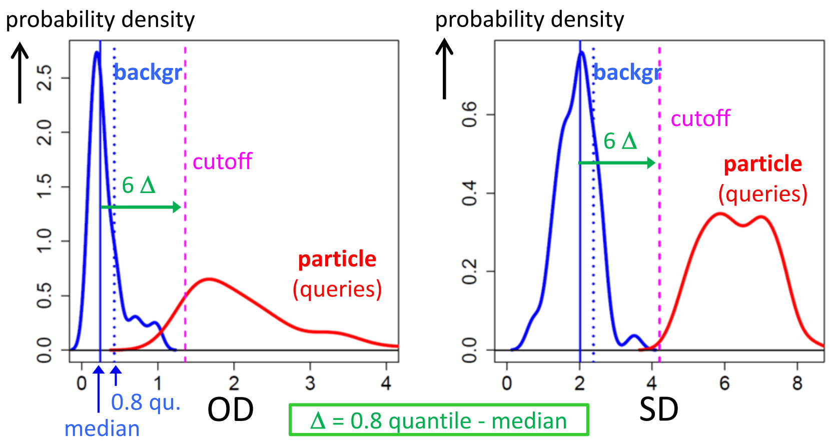
$$_{\text{CLR}}x_j = \ln[x_j / G(\boldsymbol{x})]$$

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

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

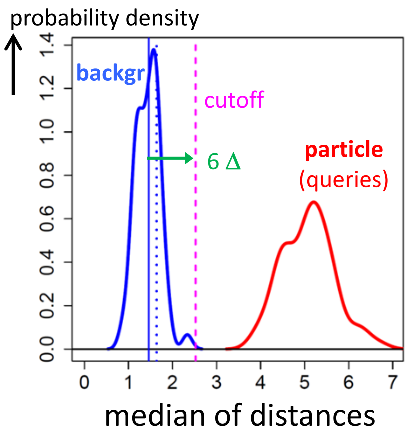
PCA approach (Example)

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.

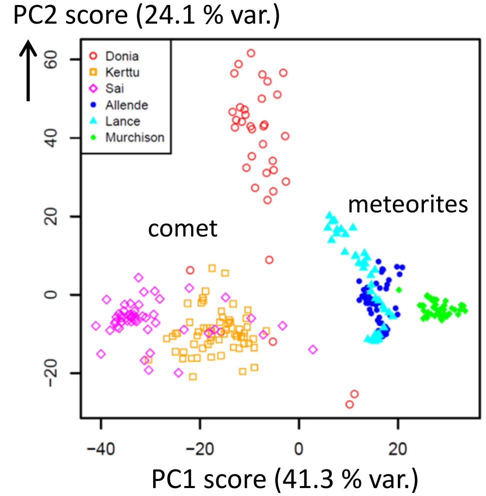
(5) Results

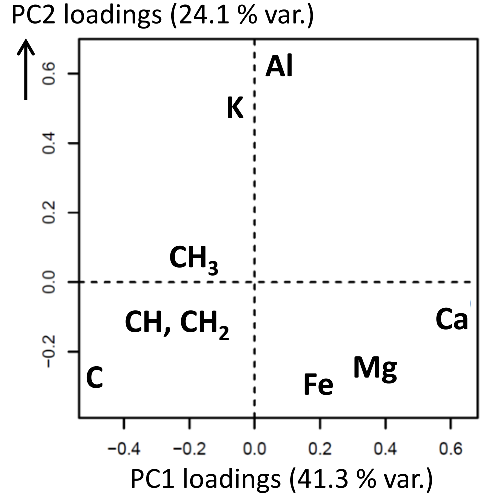
Selection of potentially relevant spectra

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



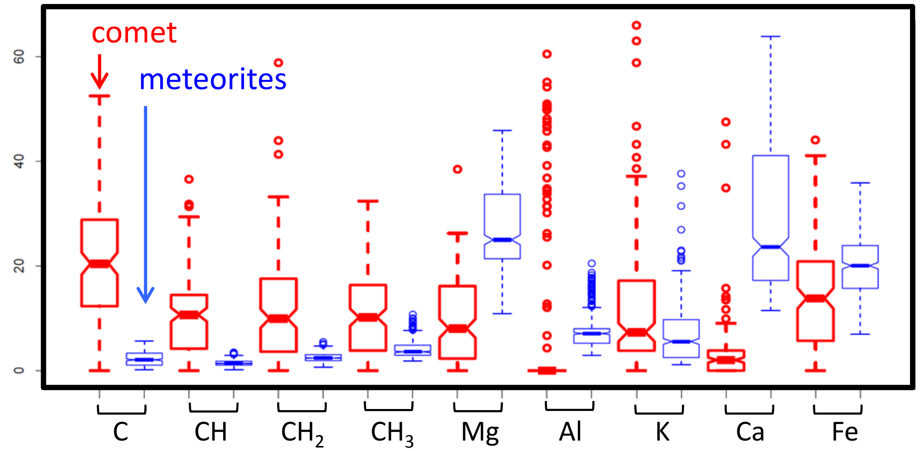


n = 301 spectra (50 randomly selected from each meteorite, 151 comet spectra) for better balanced data set.
m = 9 variables, sum 100 normalized for better interpretation; PDMS subtracted.

- **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]

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