Recognition of relevant spectra in TOF-SIMS measurements on meteorite and comet grain samples by a chemometric approach

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Poster at Conference on Solid State Analytics, 6 – 8 July 2015, Vienna, Austria
"*18. Tagung Festkörperanalytik* (FKA18)"

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Aims

- The surfaces of comet dust particles, and of meteorite samples, are characterized by TOF-SIMS.
- Experiments are performed near a comet (instrument **COSIMA** on ESA spacecraft **Rosetta**), and in laboratory.
- Multivariate data analysis supports evaluation of the obtained mass spectra.

1 Comet

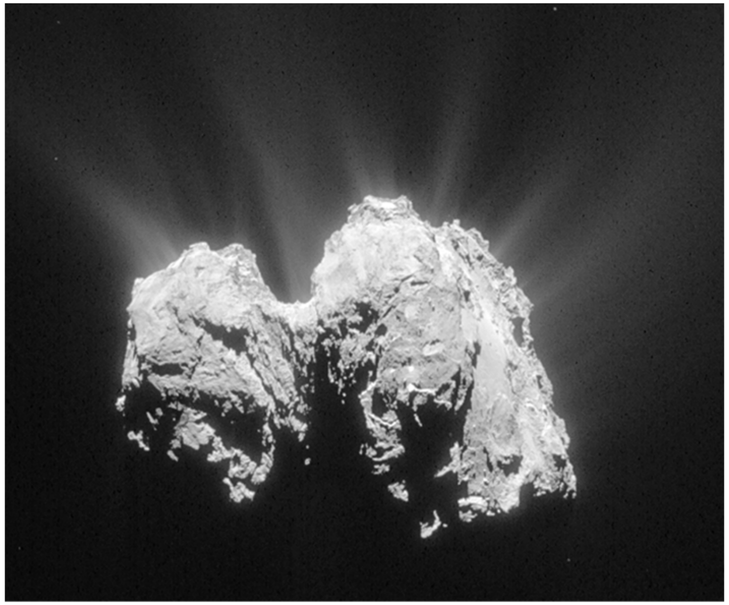
Name: 67P/Churyumov-Gerasimenko (Chury, C-G)

Size: 4 km x 3.5 km x 3.5 km; *Density:* 0.4 g/cm^3

Orbit: 6.44 y; 1.2 – 5.7 Astronomical Units distance from Sun

Rotation: 12.76 h; *Albedo:* ca 5% ("black like charcoal")

6 July 2015: *Distances;* Earth, 283.10^6 km; Sun, 199.10^6 km



Comet 67P/C-G [ESA/Rosetta/NAVCAM] [1]; 3 May 2015,
Distance 135 km; rotation axis is roughly vertical through the comet's "neck"; resolution: 11.5 m/pixel (original picture).

2 Rosetta (ESA)

Launch: 2 March 2004 (Kourou, French Guyana), Ariane 5.

Arrival at comet (ca 100 km): 6 Aug 2014 (>10 years travel).

First mission to rendezvous with a comet.

Escorts the comet as it orbits the Sun (perihel in Aug 2015,
186 .10^6 km from the Sun).

Sent lander “Philae” to the comet’s surface (12 Nov 2014).

3 COSIMA instrument

COSIMA is one of eleven instruments on Rosetta *orbiter*.

A time-of-flight secondary ion mass spectrometer (**TOF-SIMS**) **CO**metary **S**econdary **I**on **MA**ss spectrometer [3].

- Collects dust particles on metal targets;
- makes pictures of them;
- analyzes them by TOF-SIMS (mass resolution of ca 1400 at *m/z* 100 separates inorganic and organic ions).

20 kg; 20 W

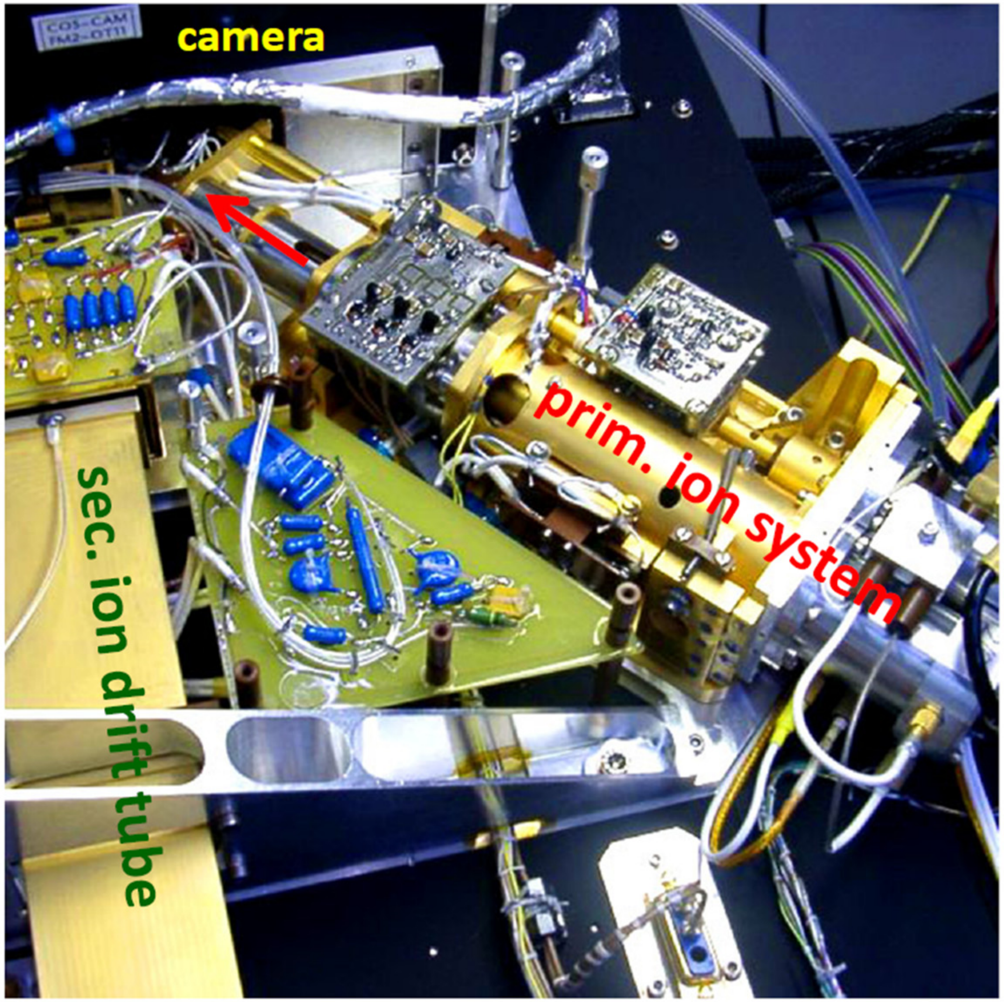
Primary ions: ^{115}In, 6 ns pulses, 8 keV, 2 kHz; measurement spot 50 μm x 70 μm.

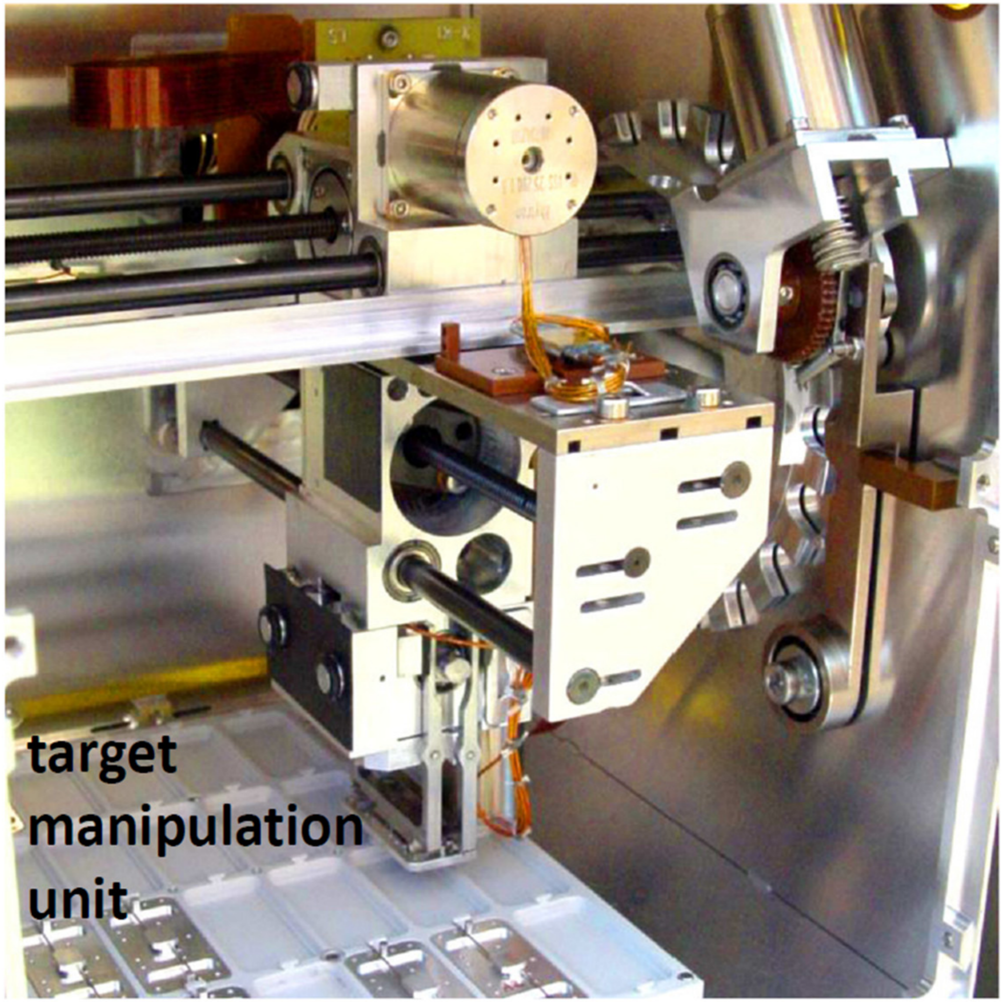
Secondary ions: 3 keV, ion reflector, ion counter (4 ns intervals), *m/z* 0.001 … 3000, positive or negative.

COSISCOPE camera: 1024 x 1024 pixel (14 μm diameter).

Targets: 1 cm x 1 cm, metal (Au, Ag; blank, black).

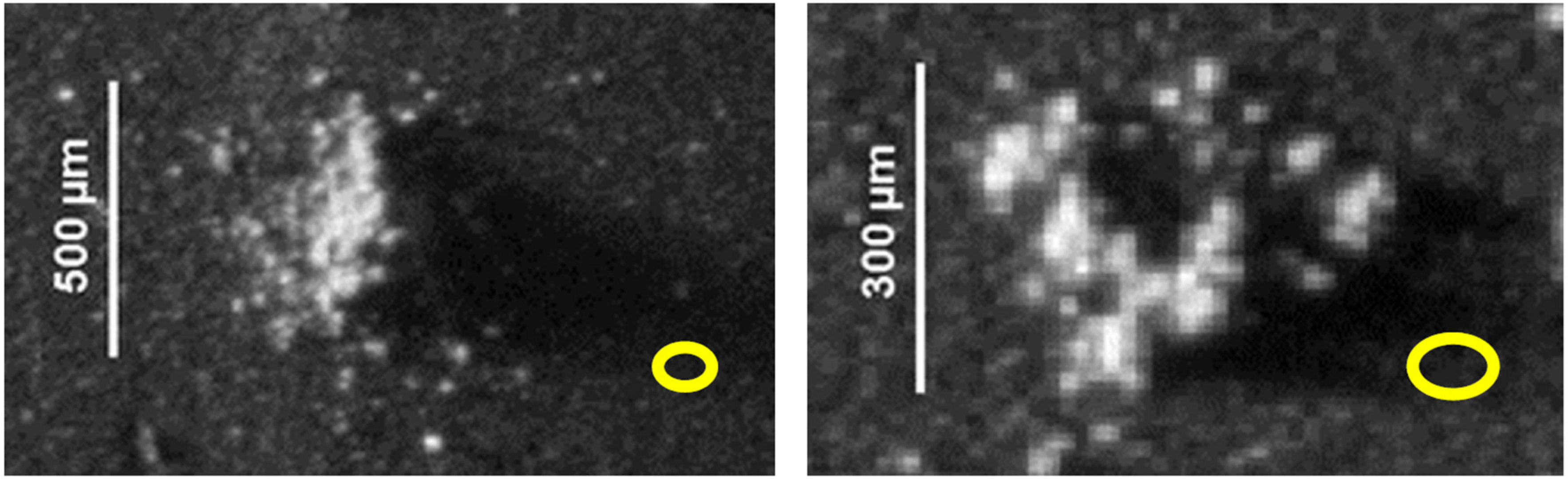
COSIMA instrument





4a Sample: Comet dust particles

More than 12,000 cometary dust particles (15 – 600 µm size) have been collected by COSIMA until June 2015.



Examples of two comet grains [4, 5]. Grazing incidence illumination (from left).

Grain heights of 60-100 µm are derived from the lengths of the shadows. Collected 25–31 Oct 2014 at distances 10–20 km from the comet nucleus (inner coma).

Cometary particles are “fluffy”, “flocculent”, perhaps “fractal-like highly structured”, and obviously may fragment at impact (1 – 10 m/s), sometimes even crumble into a “rubble pile” (Y. Langevin, M. Hilchenbach, J. Paquette).

The yellow ellipses indicate the size of the SIMS measurement spots (areas hit by primary ions).

4b Sample: Meteorite

Meteorite **OCHANSK**; an ordinary chondrite (H4);
fall 30 Aug 1878 (observed), 500 kg total,
near Ochansk (60 km southwest of Perm, Russia).

Sample from the meteorite collection of the Natural History Museum Vienna.

Sample preparation (C. Engrand): Meteorite samples have been fractured, and from the fresh fracture grains were taken by scalpel scraping and transfer with Titanium and/or ceramic tweezers to a gold target (see picture in Results).

Another 4.2 g piece of “Ochansk”: http://www.encyclopedia-ofmeteorites.com/test/17979_16232_223.jpg

5 Mass spectral data

SIMS mass spectrum measured on a comet dust particle.

Not shown here because of copyright reasons.

6 One-class classification (spectrum on/off grain)

SIMS measurements are made at rectangular grid positions or along straight lines at the estimated position of a photographically detected grain.

The precision of the SIMS spot location is only $\pm$ 80 μm. Therefore, some spectra are (accidentally) measured on grains and some on substrate.

We use a one-class classification method [6, 11] for an automatic recognition of potentially relevant spectra.

A PCA model is made from a set of "off grain spectra".

A query spectrum is assigned by the value of its orthogonal distance (OD) and its score distance (SD) to this PCA model [7, 8].

One-class classification (spectrum on/off grain)

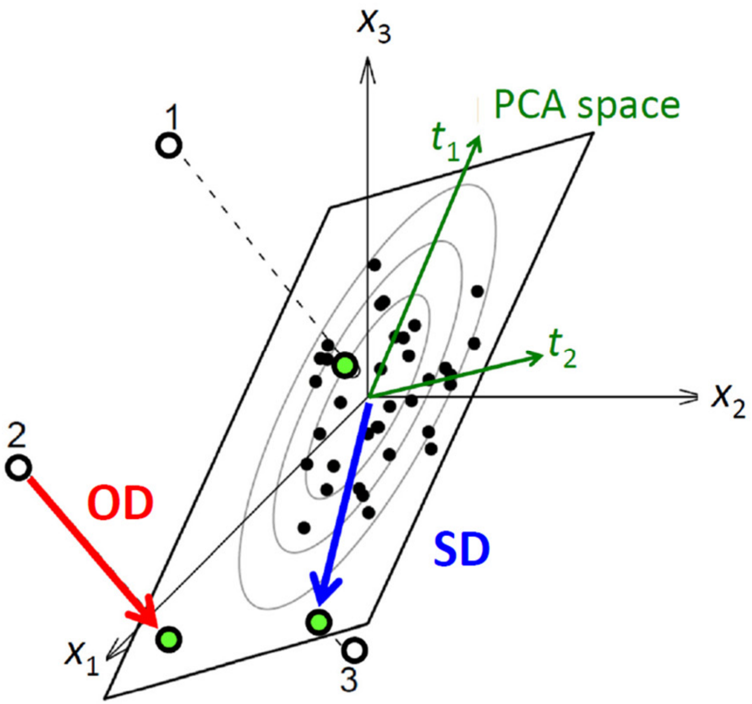
For query spectrum $\boldsymbol{x}_i$

$$\mathrm{OD}_i = \| \boldsymbol{x}_i - \boldsymbol{P} . \boldsymbol{t}_i^{\mathrm{T}} \|$$

$$\mathrm{SD}_i = \Big[\sum_h t_{ih}^2 / v_h \Big]^{0.5}$$

$h = 1, 2, \ldots, A$

v_h variance of scores of PC h



Orthogonal distance (OD)
= Distance in x-space between point and projection onto the PCA space.
Describes information loss by projecting into the *A*-dimensional PCA score space.

Score distance (SD)
= *Mahalanobis* distance from center, measured in the PCA space (plane).
Describes the distance to the center (of the background spectra) in PCA score space, considering the covariance structure of the x-variables.

Demo scheme for OD and SD

$\boldsymbol{X_0}$ with m = 3 variables; PCA model with A = 2 components (scores t_1 and t_2);

$\boldsymbol{P}$ ($m \times A$), PCA loadings; $\boldsymbol{T} = \boldsymbol{X_0} . \boldsymbol{P}$, PCA scores.

- ● Projection of X_0-points into the PCA model (plane, defined by t_1 and t_2)
- ○ Query points 1, 2, 3 in x-space with projections ● into the PCA plane

1: large OD, small SD (outlier not visible in PCA projection, effects classical PCA*);
2: large OD, large SD (clear outlier, *bad leverage point,* may lever PCA model*);
3: small OD, large SD (*good leverage point,* stabilizes PCA model*)

* Influence on PCA if belonging to $\boldsymbol{X_0}$

One-class classification (spectrum on/off grain)

Large OD - AND large SD - indicate an ‘outlier‘
(a spectrum not belonging to the background group).

The described chemometric method – based on orthogonal distances to a PCA model for a given class of samples –
uses a „multivariate view“ instead of the strategy in often applied univariate approaches, requiring a known characteristic variable (mass peak, etc.).

The method is also applicable for multivariate outlier detection; in this case a robust estimation of the PCA model [9] is recommended.

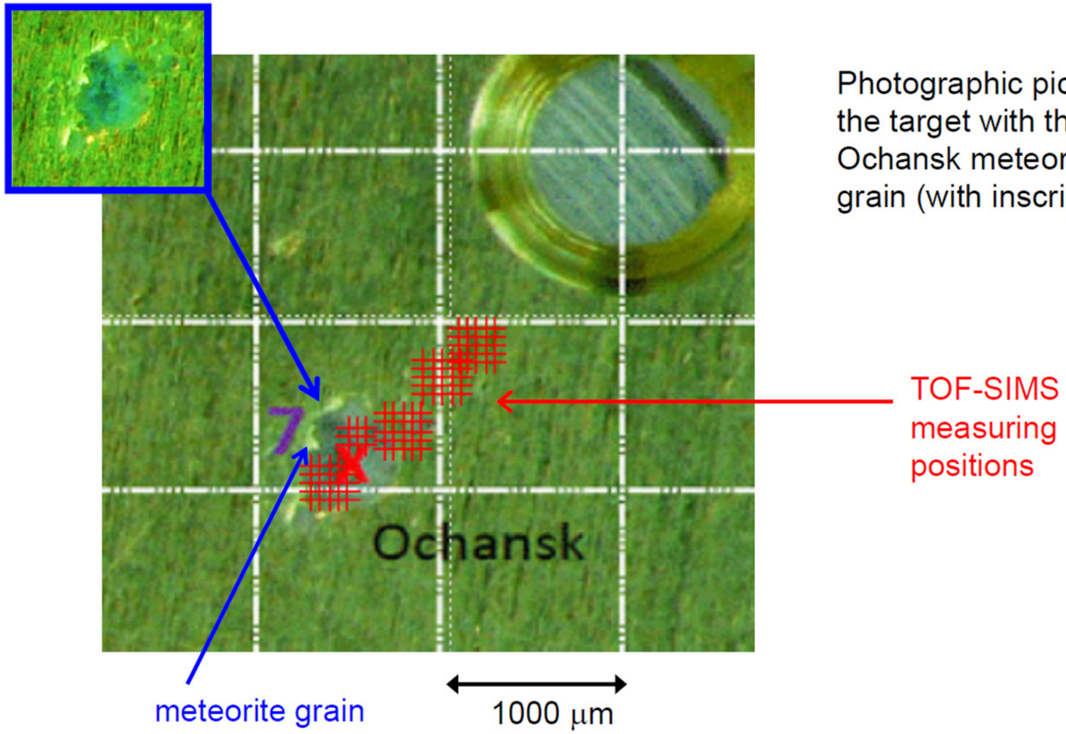
All used software has been developed in the R programming environment [12].

7a Results: Comet particle

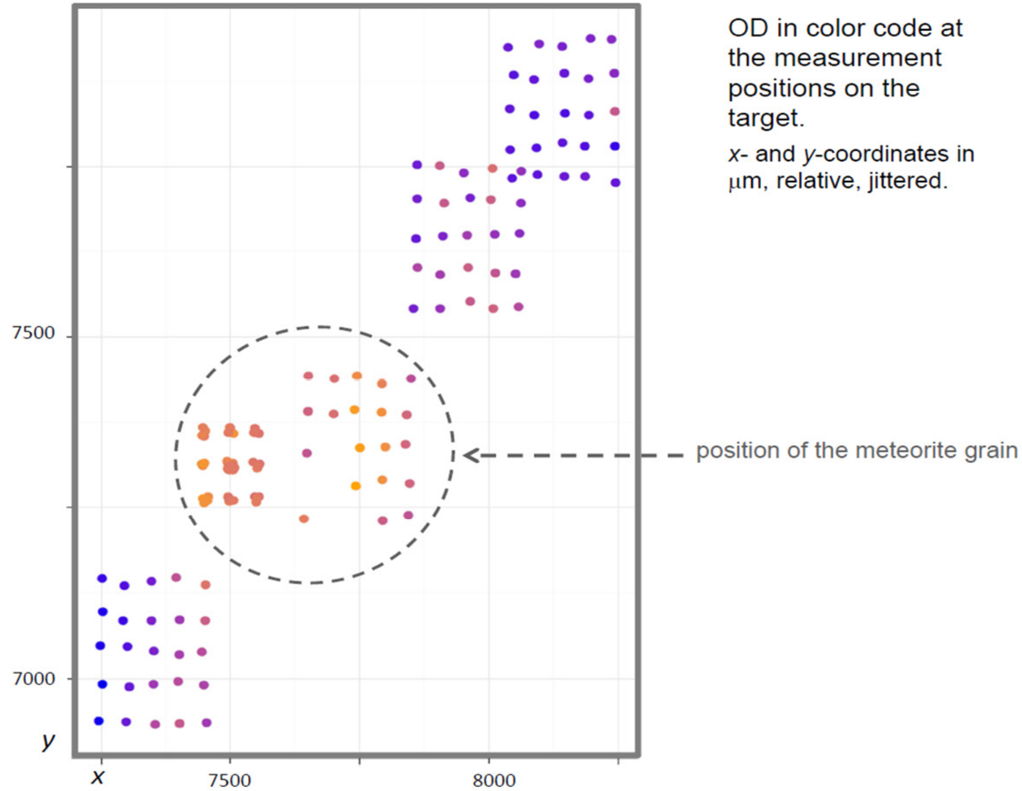
Not shown here because of copyright reasons.

7b Results: Meteorite sample

Data 63 spectra measured „off grain“ (background, substrate)
155 spectra measured „on grain“ or near grain (queries)



Photographic picture of the target with the Ochansk meteorite grain (with inscriptions)



OD in color code at the measurement positions on the target.
x- and *y*-coordinates in μm, relative, jittered.

Spectral data (variables): inorganic ions, m/z 1 … 200
m = 3535 variables, normalized to sum = 100
PCA: 2 components (85 % variance)

8 Conclusion

One-class classification using the orthogonal distance to a PCA model (from background spectra) is an evident and fast method for the recognition of potentially relevant TOF-SIMS spectra measured on unknown, heterogenous surfaces.

Future work will focus on automatic methods for finding the spectroscopic differences between „off grain spectra“ and „on grain spectra“, ranging from t-tests to promising NMF (nonnegative matrix factorization) [10].

This work is supported by the Austrian Science Fund (FWF), project P 26871-N20.

Acknowledgments. COSIMA was built by a consortium led by the Max-Planck-Institut für Extraterrestrische Physik, Garching, Germany, in collaboration with the Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Orléans, France, the Institut d'Astrophysique Spatiale, CNRS/Université Paris Sud, Orsay, France, the Finnish Meteorological Institute, Helsinki, Finland, the Universität Wuppertal, Wuppertal, Germany, von Hoerner und Sulger GmbH, Schwetzingen, Germany, the Universität der Bundeswehr, Neubiberg, Germany, the Institut für Physik, Forschungszentrum Seibersdorf, Seibersdorf, Austria, the Institut für Weltraumforschung, Österreichische Akademie der Wissenschaften, Graz, Austria and is led by the Max-Planck-Institut für Sonnen-systemforschung, Göttingen, Germany. The support of the national funding agencies of Germany (DLR, grant 50QP1302), France (CNES), Austria, Finland and the ESA Technical Directorate is gratefully acknowledged. The authors thank the other members of the **COSIMA team** for their contributions.

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Logos of the COSIMA groups

End of poster.