Significance of variables for discrimination - - applied to the search of organic ions in mass spectra measured on cometary particles

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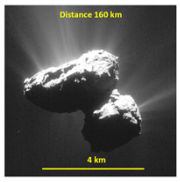
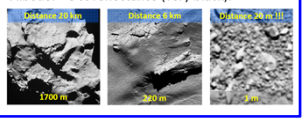
AIM. **Recognition of mass spectral signals from CHNO (organic) compounds present at the surface of particles that have been collected near a comet (ESA mission Rosetta, TOF-SIMS instrument).**

STRATEGY. **Multivariate discrimination of spectra measured on a particle and on the background. Significance of variables indicates potentially relevant CHNO ions originating from the particle.**

The Comet [1]





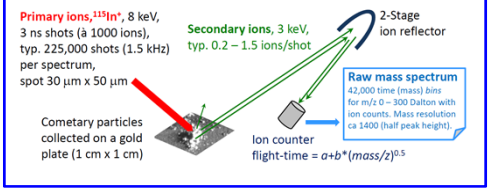
Name: 67P/Churyumov-Gerasimenko
Orbit: 1.2 – 5.7 AU from sun, 6.4 years.
Rotation: 12.76 h. Density: 0.4-0.5 g/cm³.
Albedo: 5 % reflectance (very black).

The Mission (Rosetta) [2]

This mission of the European Space Agency (ESA) is named after the *Rosetta Stone* (196 BC), bearing an inscription that was the key to the decipherment of Egyptian hieroglyphs.

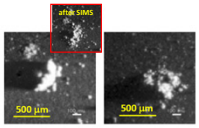
2 Mar 2004 Launch.
6 Aug 2014 Arrival (100 km).
Escorting the comet; typ. distance 10 – 200 km; 1.2 – 3.8 AU from sun.
12 Nov 2014 *Philae* landing.
30 Sep 2016 Controlled landing of Rosetta on comet (2 m/s), switch-off.

The Instrument (COSIMA) [3]



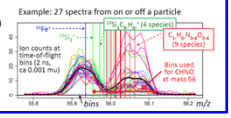
Samples

On metal targets (mostly Au) 1 cm x 1 cm more than 35,000 cometary particles were collected and imaged. Size 10 - 1000 µm. Fluffy material; some particles compact, others disrupted before collection [4].



Spectral Data

For about 200 particles more than 30,000 SIMS spectra were measured [5].
Preprocessing: Mass recalibration and rebinning; selection of mass bins (variables) for the considered CHNO ions.



Chemical Formulae of Ions

Considered mass range: 12 – 72 *
No. of formulae C_{0-}. H_{0-}. N_{0-4} O_{0-4}: 322
No. of mass bins (variables): 665 **

* Avoiding ions $Si(CH_3)_3^+$, mass 73.047, from contamination PDMS (polydimethylsiloxane).
** Mass resolution 1000, ± 1.5 *sd* (Gaussian peaks).

Formulae	*No.*
C H	50
C H N	112
C H O	75
C H N O	85
Total	322

Methods

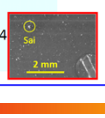
Following methods have been used to characterize the importance of variables for a discrimination between comet particle spectra (class 1) and background spectra (class 2).
A high variable importance indicates (via the mass corresponding to the variable) one or several ion species that may be prominent for the particle or for the background.

- **t-test** for comparing the class means (univariate; u-test gives almost identical results)
  Data preprocessing: Normalization to constant sum of variables
  Criterion: ***LOGp*** = *sgn* [-log(*p*)] *p*, probability of H_0; *sgn* = +1 if $mean_{CLASS1} > mean_{CLASS2}$, else *sgn* = -1
- **D-PLS**
  Data preprocessing: Normalization to constant sum of variables
  D-PLS: Optimum no. of PLS components estimated by repeated double cross validation (rdCV) [6]
  Criterion: ***bPLS*** = standardized regression coefficients of discriminant variable (>0 indicates class 1)
- **Random Forest (RF)** classification
  Data preprocessing: Normalization to constant sum of variables
  RF: R library *randomForest*, function *randomForest*
  Criterion: ***MDA*** (Mean Decreasing Accuracy, mean of 50 repetitions); a variable is important for class discrimination if the classification accuracy decreases considerably when the variable is eliminated.
- **Robust Pair-wise Log-Ratios (rPLR)**
  Data preprocessing: Values $x_{ij} = 0$ are replaced by uniformly distributed noise between 0.1 and 0.2 (median of all *x* is 33.4, maximum is 1907).
  rPLR: R library *robCompositions*, function *biomarker* [7]
  Criterion: ***V**** is a newly developed statistics [7], derived from three variation matrices (for all objects, and for objects of the classes separately) containing robust estimations of the variances of all variable pairs (log-ratio transformed). The distribution of *V** is approximately standard normal, and quantile 0.975 is used to indicate the importance of the variables (biomarkers). The variable importance of a variable considers all other variables, and is not affected by the size effect, as ratios of variables are used.

Data

Positive second. ion spectra; measured at rectangular grid pos., Δx = 15 µm, Δy = 10 – 30 µm. Mass range 12 – 72 Da
***m* = 665 variables** (mass bins)

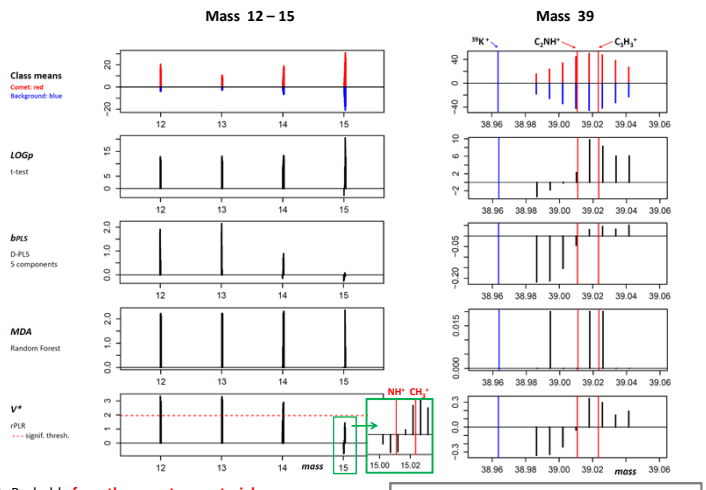
Spectra on particle: class 1
Particle *Sai*, target *3D1*
Size ca 80 µm
Collected 2016-04-13/14
n_1 = 29 spectra



Spectra backgr: class 2
Area *Nick*, target *3D0*
Collected 2016-03-25/26
n_2 = 59 spectra

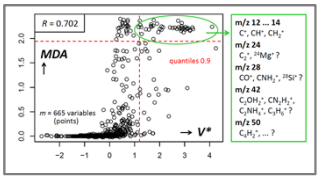
Selected Results

Variable importance measure versus ion mass



☞ Probably **from the cometary material**:
{ } not separable by mass; coded as **obvious** or as *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^+, $C_3H_4^+$}; $C_3H_3^+$; C_4^+; ...

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



Summary

- 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.
- The results are consistent with the previously claimed presence of high molecular weight structures [8].

- ❑ The applied methods for characterizing the variable importance are complementary.
- ❑ Results from the univariate t-test are directly interpretable in terms of ion formulae. Results from the multivariate methods (D-PLS, RF, rPLR) characterize the variable importance within the potential influence of the other variables.

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