Cometary Particle Surfaces Characterized by Chemometric Evaluations of Secondary Ion Mass Spectra

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Comet 67P

Name: 67P / Churyumov-Gerasimenko (Chury)
Size: 6 km x 4 km x 2 km; Density: 0.53 g/cm³
Orbit: 6.44 years; 1.24 AU (perihel) – 5.7 AU (aphel)
1 AU (Astronomical Unit) = 150,000,000 km,
* mean distance Earth – Sun
Rotation: 12.76 h
Albedo: ca 5% (“black like charcoal”) [14]

Spacecraft Rosetta (ESA)
Launch: 2 March 2004 (Kourou), Ariane 5. More than 10 years journey.
Arrival at comet (ca 100 km): 6 Aug 2014, 2.8 AU from Earth.
First mission to rendezvous with a comet. Escorting the comet at typical distances of 10 – 200 km [2].
Nov 2014: lander Philae reached the surface of the comet.
Aug 2015: nearest to Sun (perihel, 186. 10⁶ km).
30 Sep 2016: end of mission by controlled touch down at comet & shut down.

Instrument COSIMA on board of the ESA mission Rosetta collected cometary particles with 20 - 1000 μm diameter at distances of 10 - 1500 km from comet Churyumov-Gerasimenko (67P) between August 2014 and September 2016.
More than 30,000 particles were documented by images. About 33,900 secondary ion mass spectra were measured (time-of-flight mass analyzer) by COSIMA and sent to Earth.

Sets of selected positive SIMS spectra were evaluated by univariate and multivariate statistical techniques.

Aims of the data analyses and result shown here are:
- characterization of carbon-containing substances on the surface of cometary particles,
- determination of atomic ratios,
- search for different chemical compositions of the particles collected at various distances from the sun.

Cometary dust particles
About 1400 dust particles (30 000 fragments) of 10 – 1000 μm size have been collected on metal targets [4] (1 cm x 1 cm, see picture) by the COSIMA instrument.
Distances to the comet typically between 10 – 150 km.
Distance to Sun: 1.24 – 3.83 AU.

Mass spectrometer COSIMA onboard of Rosetta
- Collected dust particles on metal targets (Au, Ag).
- Analyzed them by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The mass resolution of ca 1400 (half peak) at m/z 100 separated several inorganic and organic ions with the same mass number. About 30,000 full spectra have been sent to ground [1,5].
- Primary ions: 115In, 3 ns shots, 8 keV, 1.5 kHz.
- Typical 225,000 shots per spectrum.
- Measurement spot: 30 μm x 50 μm.
- Secondary ions (positive & negative): 3 keV, 2-stage ion reflector.
- 26,300 time bins (4 ns) for m/z 0 - 300.
- COSISCOPE camera: 1024 x 1024 pixel (14 μm diameter) [3].
Organics
- Organic material on the surface of cometary particles is macromolecular [6].
- No specific organic compounds could be identified on cometary particles.
- Cometary particles appear different from the meteorite type carbonaceous chondrites (CC meteorites) [9].
- Cometary material contains more (organic) carbon than CC meteorites.

The mineralic composition of the cometary material is similar to that of chondritic meteorites, however, with the more volatile rock-building elements C, S, Na, K, Cu, Li enriched in the comet [9].

Distance between collection area and Sun may affect the composition of particle surfaces
Collection of cometary particles occurred at various distances between comet and Sun. Is the composition of the particles dependent on the distance to the Sun – and may this be reflected in the mass spectral data? A first approach:

Data: n = 3095 mass spectra, m = 11 peak heights (C*, CH*, CH4, CH5+, Mg+, Al*, C2H5+, K+, C3H7+, Ca*, Fe*).

Distance to Sun (mean in the sampling interval): 2.16 – 3.6 AU
3 classes: <2.5 AU (n=579); 2.5 – 3.1 AU (n=1023); >3.1 AU (n=1493)

Methods
- Robust PCA [14] with data transformed by the centered log-ratio method (compositional data) [13].
- KNN classification with repeated double cross validation (rdCV) [16].

Unsaturated CH-ions
have been found to be characteristic in the mass spectra of cometary material. The presence of C6H10O5+, C7O5+, etc. indicates unsaturated organic compounds [10].

Methods used to characterize the importance of variables for a discrimination between the two classes (1) comet particle spectra and (2) background spectra are [17]:
- t-test: comparing class means, criterion LOGPr = sgn [-log(p)]
- D-PLS: standardized regression coefficients of discriminant variable
- Random Forest: criterion MDA (Mean Decreasing Accuracy)
- Robust Pair-wise Log-Ratios (rPLR): criterion V*, developed for the identification of biomarkers, based on all ratios of all variables [12].

PC indicates some separation of the classes.
KNN gives 67 – 78% correct assignments to the classes.

References
Cometary particle surfaces - characterized by chemometric evaluation of secondary ion mass spectra


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The instrument COSIMA on board of the ESA mission Rosetta collected at distances of 10 - 1500 km from comet Churyumov-Gerasimenko solid cometary particles with 20 - 1000 µm diameter. More than 30,000 particles were documented by images, and about 17,000 positive secondary ion mass spectra were measured (time-of-flight mass analyzer, mass resolution 500 - 1200, measuring spot 35 µm x 50 µm). Sets of selected data with some dozen to some thousand mass spectra were evaluated by univariate and multivariate statistical techniques. Aims of the data analyses were a characterization of carbon-containing substances on the comet, determination of elemental ratios and estimation of the chemical homogeneity of the particles collected at different distances to the sun. Supported by Austrian Science Fund (FWF), P 26871-N20.
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