Classification of silicates - contained in micro meteorites and comet dust particles - using laboratory TOF-SIMS data

C. Engrand	Orsay, France[1]
J. Kissel	Katlenburg-Lindau, Germany[2]
F.R. Krueger	Darmstadt, Germany[3]
P. Martin	Orléans, France[4]
J. Silén	Helsinki, Finland[5]
L. Thirkell	Orléans, France[4]
R. Thomas	Orléans, France[4]
K. Varmuza*	Vienna, Austria

* Presenting author

Laboratory for Chemometrics, Institute of Chemical Engineering
Vienna University of Technology

Getreidemarkt 9/166, A-1060 Vienna, Austria
kvarmuza@email.tuwien.ac.at, www.lcm.tuwien.ac.at

[1] CSNSM, F-91405 Orsay, France. [2] Max-Planck-Institute for Solar System Research, D-37191 Katlenburg-Lindau, Germany. [3] Ingenieurbureau Dr. Krueger, D-64291 Darmstadt, Germany. [4] Laboratoire de Physique et de Chimie de l'Environnement, F-45071 Orléans, France. [5] Finnish Meteorological Institute, FIN-00101 Helsinki, Finland.

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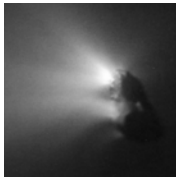
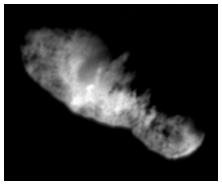
Introduction

Investigation of comets, asteroids, and interstellar dust gains increasing interest.

Comets are considered to consist of pristine material from the begin of the solar system. Impact of comets on earth may have brought water to earth, as well as organic precursor molecules for the development of life.

First in situ mass spectrometric measurements of cometary dust particles were done during a fly-by near comet Halley in year 1986 [1].



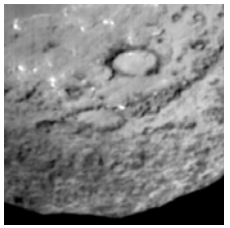


First good pictures from a comet were shot 2001 by the Deep Space mission (comet Borelly, 2200 km distance, comet size ca 10 km).

The Stardust mission with a fly-by at comet Wild-2 gave hints about substance classes [2].

Comet Wild-2 (ca 4.5 km diameter, distance 240 km, 2004).

The ROSETTA mission (ESA) was launched 2004, and will enter into an orbit around a comet in 2014. One of the instruments on board is a TOF-SIMS (COSIMA). This work is related to COSIMA.



Shooting a 370 kg missile into comet Temple-1 on 4 July 2005 resulted in fascinating pictures (Deep Impact, NASA).

[1] Kissel J. et al.: *Nature* 321 (1986) 336.
[2] Krueger F.R. et al: *Rapid Commun. Mass Spectrom.* 18 (2004) 103.

Samples

The investigated minerals are present in micrometeorites and have been found in comets.

Terrestrial samples analyzed are:

Class	Mineral	No.
1	Serpentine	12
2	Enstatite	9
3	Olivine	9
4	Talc	9
	Sum	n = 39

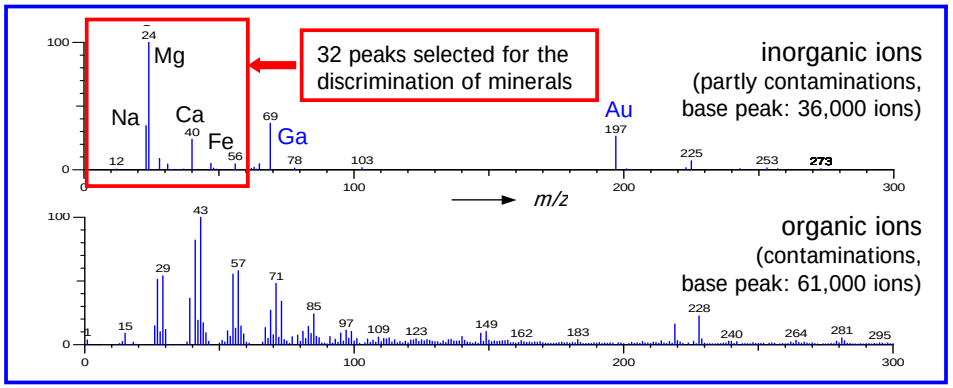
Samples have been prepared and stored under clean nitrogen atmosphere to minimize contaminations.

Experimental

The used time-of-flight secondary ion mass spectrometer (TOF-SIMS) has been built in Orléans. Design parameters are similar to those of the flying COSIMA instrument on board of ROSETTA.

Primary ions: Ga liquid metal ion source; energy 8 keV; 1000 pulses per second, each ca 200 ions; spot with 30 μm diameter.

Secondary ions: Energy 1 keV; two-stage reflectron; mass resolution $m/\Delta M$ is 2000 at half peak height; 1-20 detected secondary ions per pulse; 8-80 min analysis time per spectrum.



TOF-SIMS data of sample olivine, separated into peaks of inorganic and organic origin.

Data

A raw mass spectrum consists of 65,000 time channels (1.6 ns) with numbers of detected ions. A peak recognition algorithm and a time/mass calibration gives a peak list with high mass resolution data.

Inorganic ions can be separated form organic ions because of the typical mass difference (e.g. $^{39}K^+$, 38.964 Dalton; $C_3H_3^+$, 39.023 Dalton; Δm = 0.059 Dalton).

A set of 32 different ions has been selected, appearing typical for mineral origin. The intensities of the corresponding 32 peaks have been normalized to a constant sum of 100. These normalized peak intensities have been used as features for chemometric evaluations.

Examples of selected ions:

H^+, $^7Li^+$, O^+, H_2O^+, $^{23}Na^+$
$^{24}Mg^+$, $^{25}Mg^+$, $^{26}Mg^+$
$^{28}Si^+$, $^{28}SiH^+$, $^{29}Si^+$, $^{29}SiH^+$, $^{30}Si^+$
$^{39}K^+$, $^{40}Ca^+$, $^{41}K^+$, $^{28}SiO^+$, $^{28}SiH_2O^+$
$^{24}Mg_2^+$, $^{24}MgH^+$, $^{54}Fe^+$, $^{56}Fe^+$

Data Analysis

(1) Exploratory Data Analysis

PCA

CORICO

CORICO (CORrelations ICOnography) is a non linear mapping of the feature space onto a sphere. The algorithm is based on correlation coefficients calculated from object vector pairs, and on partial correlation coefficients. The method has been successfully applied in medicine but is rather unknown in chemometrics. CORICO visualizes multivariate data in form of graphical networks. Dots representing similar vectors, are close. 'Remarkable correlations' are indicated by lines connecting dots.

(2) Classification

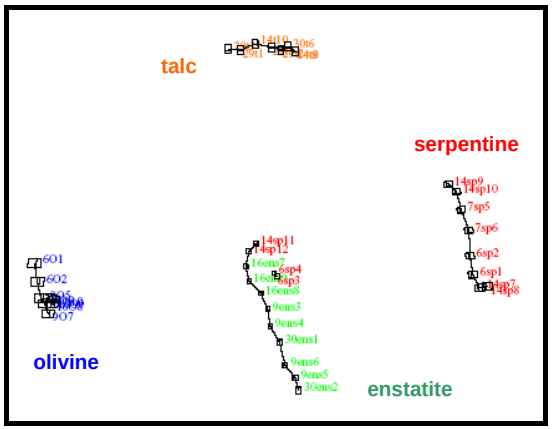
KNN

CART Decision Tree

References to CORICO

Lesty C., Pleau-Varet L., Kujas M.: *J. Appl. Statistics* 32 (2004) 191.
Lesty M: *CORICO* 3.3, Versailles, 2003.
C. Engrand et al.: *Applied Surf. Sci.* 231 (2004) 883.

Exploration



CORICO

p = 32 features

Good separation of mineral classes.
Four serpentine samples are in the enstatite cluster. Olivine and talc samples are very well separated from the other classes.

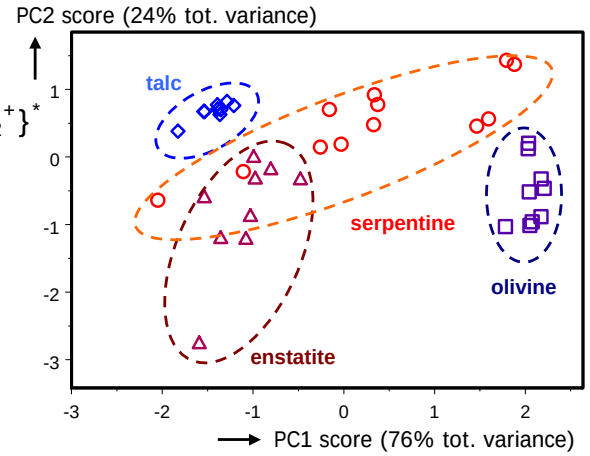
PCA

p = 3 features

$^{24}Mg^+$, $^{28}Si^+$, {$^{56}Fe^+$, $^{28}Si_2{}^+$}*

(sum 100)

Good separation of mineral classes.
Two serpentine samples are in the enstatite cluster. Olivine and talc samples are separated from the other classes.



* Ions $^{56}Fe^+$ (mass 55.935) and $^{28}Si_2{}^+$ (mass 55.954) could not be resolved.

The used data contain information about mineral classes. Reduction to data from $^{24}Mg^+$, $^{28}Si^+$, $^{56}Fe^+$ is reasonable.

Classification

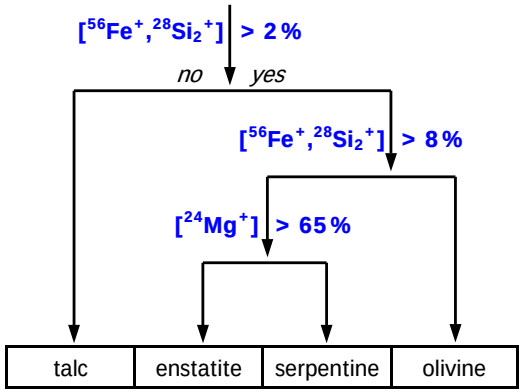
All results obtained by leave-one-out cross validation.

KNN

p = 32 features

Euclidean distance, optimum is one neighbor, 3 wrong classifications (1 serpentine, 1 enstatite, 1 olivine), total predictive ability 92.3 %

True class	Predicted class No. of samples			
	1	2	3	4
1	11	0	1	0
2	0	8	0	1
3	1	0	8	0
4	0	0	0	9



CART Decision Tree

p = 3 features (2 used)

Peak intensities for ions $^{24}Mg^+$, $^{28}Si^+$, {$^{56}Fe^+$,$^{28}Si_2{}^+$} normalized to sum 100.

3 wrong classifications (2 serpentine, 1 enstatite), total predictive ability 92.3 %

Selection of peaks from appropriate inorganic ions allows a successful discrimination of the studied four mineral classes (> 90 % correct classifications in full cross validation).

We conclude that expected data from the COSIMA space instrument will be principally appropriate to characterize mineralogical cometary material.