Selected Topics of Project Proposal (FWF)

Meteorite chemistry and comparison with Rosetta comet data

German title: Meteoriten-Chemie und Vergleich mit Kometendaten von Rosetta

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1 Scientific aspects

1.1 Introduction

1.1.1 Background and goals

About 40,000 tons extraterrestrial material in the form of cosmic dust and meteorites fall on the Earth per year. The masses of these objects vary from micrograms (dominant) to several tons (very rare). For the next future, a protection against catastrophic impacts is not realistic; however, a better understanding of the composition of asteroids and extraterrestrial particles is a fundamental goal in science. Small samples, in the form of cosmic dust with sizes around 200 µm, currently dominate the incoming mass flux of extraterrestrial matter. These particles are constituted of minerals embedded in a small fraction of carbonaceous matter. They are related to the relatively rare meteorite family of carbonaceous chondrites and probably, in some cases, also to comets.

This extraterrestrial material has preserved the record of the formation of the solar system, thus it has escaped planetary accretion and still represents the pristine material from which larger bodies, like planets, have been built about 4.5×10^9 years ago. Carbonaceous chondrite-like objects (submillimeter cosmic dust and carbonaceous meteorites) contain hydrous minerals, and their impact could have brought a large proportion of the current water on the early Earth, about 4×10^9 years ago [1-3]. They contain a few weight percent of carbon in form of "organic" matter, which is a very complex mixture of highly diverse organic compounds [4-6]. This organic material was synthesized by abiotic processes on their parent body [7,8]. Carbonaceous chondrite matter delivered organic substances that could have acted as building blocks for the formation of life on Earth (prebiotic matter).

Meteorite research is complementary to comet research. Comets are believed to have best preserved the composition of the initial solar material, as they are stored very far from the Sun and thus escaped planetary accretion and thermal or aqueous alteration. They contain water ice, minerals, and organics. Samples brought back by the STARDUST mission (NASA) in 2006 from comet 81P/Wild 2 showed that the rocky component of this comet has striking similarities with carbonaceous chondrites [9-13]. Some cosmic dust samples collected in the stratosphere or in Antarctic snow have also been proposed as cometary material [14-16].

In 2014, the **Rosetta** space mission by the European Space Agency (ESA) will make a close inspection of comet 67P/Churyumov-Gerasimenko. A lander will be delivered on the comet nucleus, and the cometary environment will be analysed with various instruments on the orbiter. The orbiter includes COSIMA (COmetary Secondary Ion Mass Analyzer), which is a reflectron time-of-flight secondary ion mass spectrometer (TOF-SIMS) that will analyze the composition of solid particles emitted by the comet and will provide ground truth on the possible link between cometary matter and primitive meteorites, such as carbonaceous chondrites.

This project proposes a novel approach to study the chemical composition of meteorites, with the perspective of the analyses of material from comet 67P/Churyumov-Gerasimenko by Rosetta. We will use a COSIMA twin instrument - the so called Reference Model (COSIMA-RM) at the Max Planck Institute for Solar System Research in Katlenburg-Lindau, Germany - to characterize the composition of carbonaceous and ordinary chondrites, combined with multivariate statistical data analysis (chemometrics). The aim is to get more insight into the chemical composition of these meteorites and, especially, to obtain a better understanding for comparing the laboratory analyses of reference samples with the expected analyses of comet dust. Some TOF-SIMS data from organic and inorganic compounds are already available from comet Wild 2 samples, measured by a high-performance laboratory instrument [17-20].

The COSIMA-RM analyses will be complemented by TOF-SIMS analyses at high mass resolution and high spatial resolution, by LDI (laser desorption ionization) mass spectrometry in the imaging mode with MS/MS capability, and by IR and Raman microscopic measurements. A concerted evaluation of these multivariate data from sample surfaces is promising for the characterization of compound classes and the composition of meteorite matter.

1.1.2 Meteorites, comets, and the origin of life on Earth

The Earth accreted about 4.5×10^9 years ago, and was probably left as a dry planet after the Moon-forming impact [21]. Water was brought later by extraterrestrial carbonaceous chondrite-like matter, in the form of small planetesimals and cosmic dust [1,3] and, possibly, comets [2]. Life probably appeared on Earth about 3.5×10^9 years ago [22]. A widely accepted model for the origin of life starts with an abiotic production of organic molecules, followed by chemical evolution in the presence of liquid water [23]. Carbonaceous chondrites and cosmic dust particles - originating from the outer regions of the asteroid belt - are representative of the meteorites that could have brought the building blocks of life on Earth. Comets are considered to be quantitatively richer in organic compounds than carbonaceous chondrites, and could have contributed essentially to the prebiotic matter budget [24]. Some classes of carbonaceous chondrite meteorites could even have cometary origin [25-27]. Results from the STARDUST mission suggest a continuum between asteroids and comets, stressing the need to better characterize meteorites and establish a link with cometary matter - as planned in this project.

1.1.3 TOF-SIMS

Time-of-flight mass spectrometry (TOF-SIMS) has become an increasingly important tool in geo- and cosmochemistry laboratories, as it gives information on the organic as well as inorganic species of a sample [28,29] at lateral resolutions of 70 µm to below 1 µm. Comet material brought back by the NASA STARDUST mission has been investigated by TOF-SIMS [18-20], finding that in general, the cometary particles resemble carbonaceous chondrites and anhydrous chondritic porous interplanetary dust particles (containing e.g., olivine, pyroxene, iron sulfide and carbon containing substances).

TOF- SIMS is sometimes claimed not to be very sensitive to some classes of organics, but on the other hand TOF-SIMS spectra often show spurious organic compounds in a sensitivity range not achieved by IR or RAMAN [30]. One of the aims of this project is the investigation of the capability of TOF-SIMS for characterizing organic compounds present in mixtures with minerals, and a comparison with the related technique LDI-MS (see 1.1.4).

The COSIMA instrument and its twin (to be used in this project) have a spatial resolution of about 70 µm and a mass range up to 3000 Dalton with a mass resolution allowing the separation of inorganic and organic ions up to about 120 Dalton. Mass analyzer is a time-of-flight device in the reflectron mode. Supplementary TOF-SIMS measurements on meteorite samples will be made with a high performance laboratory instrument ION-ToF 4 (mass resolution ca 10,000; spatial resolution ca 1 µm).

1.1.4 LDI-MS in the imaging MS mode and LDI-MS/MS

Laser desorption ionization mass spectrometry (LDI-MS) [31] can be considered as the forerunner of the Nobel-prize-honored technique MALDI (matrix-assisted laser desorption ionization) [32] but has also its own development and impact. It belongs to the large group of SIMS techniques and uses either an UV-laser or a far IR-laser as primary beam for desorption and ionization of organic molecules from the top-layers of solid samples. It allows desorption and ionization of organic molecules as molecular ions up to masses of approximately 2000 Da in underivatized form (intact molecular species). The method is very sensitive down to a few atto-moles for organic, polar compounds; furthermore it can be used for the detection of positive as well as negative molecular ions, and produces highly reproducible isotope patterns. With a UV laser beam diameter between 10 and 60 µm, the lateral distribution of molecular ions of known molecules and even unknown species can be determined (one mass spectrum per 10 µm diameter) and these ion intensity images can be overlaid with light microscopic images. Thus a localization of minerals and organic molecules in meteorite samples at a 10 to 60 µm scale will be possible [33,34].

The combination of LDI with high energy (20 keV) collision activated ion decomposition [35,36] realizes MS/MS via a combination of a linear TOF analyzer (MS 1) and a timed ion selector, followed by a gas (He) collision chamber and a reflectron TOF analyzer (MS 2). This technique allows the generation of characteristic fragment ion patterns (a kind of unique molecular finger print) from selected ions, and thus enhances the identification or characterization of compounds. This method seems to be very useful for a substance class specific analysis of meteorites, and will be explored in this project.

Furthermore, LDI-MS is a complementary technique for meteorite analysis to the already used ESI-FTICR-MS instrument [6]. The later works with very high mass resolution (ca 10^6), however, is restricted to soluble substances and does not allow imaging. LDI-MS is capable to see insoluble, organic compounds with high sensitivity, and can localize certain compounds for correlating their presence with light microscope images and the mineral composition. An essential fact for planning this part of the project is the availability of an LDI-MS machine - and high expertise [37] - in the laboratory of project contributor G. Allmaier. No appropriate FT-ICR-MS instrument (price >10^6 Euro for an ultra-high-field instrument with >10 Tesla) is running in Austria and including this working area would define a very different project - far away from supporting the evaluation/comparison of Rosetta data.

1.1.5 IR micro spectroscopy and imaging spectroscopy

Infrared (IR) micro spectroscopy and imaging spectroscopy have been widely used for the analysis of complex organic and inorganic composite terrestrial matter such as biological based materials [38,39], and minerals [40]. IR spectroscopy is also a very useful technique to characterize the minerals and the organic compounds in micrometeorites, meteorites and comets [41-44], as well as in astronomical observations of distant objects [45,46]. IR intensity images can be prepared and overlaid with light microscopic pictures.

Project contributor M. Schwanninger has broad experience in IR spectroscopy and micro spectroscopy of wood and plant materials together with chemometrics [47-50]. This is beneficial for the project, as these materials are complex mixtures, not unlike meteorite samples. IR band assignments of minerals [51] and of meteorites [52] in particular are available in the literature and vibrational spectroscopy features of olivines have been reviewed recently [53].

1.1.6 Raman spectroscopy

The method is non-destructive (if the laser power is adjusted correctly) and the sample preparation is the same as for TOF-SIMS. Raman identifies qualitatively (and in some cases quantitatively) the spectral features of most minerals of interest such as pyroxene and olivine as well as organic compounds and amorphous carbon [54,55].

IR and Raman imaging data together with corresponding mass spectral data - combined by chemometric methods - are very promising for the development of new strategies to characterize the chemical composition of complex surfaces such as that of meteorites.

1.1.7 Chemometrics

Probably the first application of chemometric methods [56] to TOF-SIMS data from minerals has been published 2006 [57] by members of the COSIMA team and collaborators of this project: see Figure 1. Samples of the minerals serpentine, enstatite, olivine, and talc have been used as proxies for minerals existing in extraterrestrial matter. Mass spectral peaks from inorganic ions could be selected in the spectra due to a sufficient high mass resolution, and their intensities have been used as variables for characterizing mineral classes. Cluster analysis by principal component analysis (PCA) and related methods showed a good separation of these mineral classes.

In a preliminary experiment [58] 149 spectra from 16 mineral classes (relevant for meteoritic and cometary material) have been measured with the COSIMA twin instrument. Table 1 shows classification performances for the mineral classes (olivin, clino- and orthopyroxene could not be separated) between 78 and 100% with a mean of 96.7%, by applying KNN classification with a strict evaluation of the performance by repeated double cross validation [56,59]. These results are promising for application of the same method to meteorite samples.

Recently, Varmuza, et al. [60] applied the method random projection (introduced into chemometrics 2010 by Varmuza, et al. [61]) to TOF-SIMS data from scanning experiments on mineral grains that have been used as calibration samples for cometary dust particles.

Great attention will be paid on a careful and cautious ("conservative") evaluation of the developed empirical models. This will be based on extensive experiences with the development of the strategy "repeated double cross validation" by collaborator P. Filzmoser et al. [59]. Application of various variable selection methods and their strict evaluation (see recent work by K. Varmuza et al. [62]) will support the interpretation of model parameters in terms of the underlying chemistry.

An important fact for mass spectral data has often been overlooked, namely their compositional character. That means that usually only ratios of peak intensities are relevant and adequate mathematical data transformation methods are required [63]. Considering the compositional nature of TOF-SIMS data, and development of appropriate methods will be an important aspect in this project. Extensive experiences in this area by collaborator P. Filzmoser [63,64] is noted.

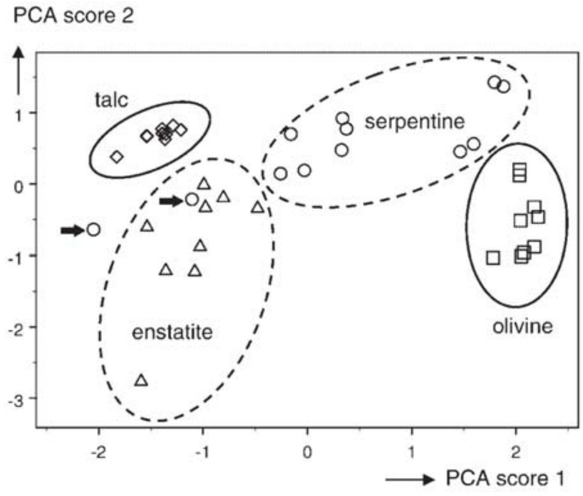

Figure 1. PCA score plot [57] using as variables the intensities of three selected peaks ($^{24}Mg^+$, $^{28}Si^+$, and $^{56}Fe^+ + ^{28}Si_2^+$) from TOF-SIMS spectra. Peak intensities are normalized to a constant sum in each spectrum. First and second principal components preserve 75.7% and 24.3% of the total variance, respectively. The mineral classes are well separated; bold face arrows indicate two serpentine outliers.

Table 1. Classification results for mineral reference samples. Data: *n* = 149 TOF-SIMS spectra from 16 mineral classes; *m* = 39 peaks heights (normalized to sum 100) used as variables; KNN classification with evaluation by repeated double cross validation [59] (*k* = 1 optimal, Euclidean distance). (*) is the mean of the 16 values for % correct classified [58].

Mineral class	No. of spectra	% correct classified
albite	8	96.4
calcite	10	100
corundum	10	99.0
dolomite	8	78.2
fayalite	10	100
hypersthene	9	100
ilmenite	10	100
magnetite	9	95.0
nepheline	8	100
orthoclase	8	98.9
olivine, clino/ortho-pyroxene	24	100
plagioclase	8	100
richterite	6	99.0
smectite	7	90.9
sphalerite	5	99.0
pyrite	9	93.8
sum, mean	149	96.7 (*)

The expected data sets will contain spectra of different types (SIMS, LDI, LDI-MS/MS, IR, Raman) for each measured position (typically, measurements at positions of rectangular grids 5×5 to 10×10 will be made on sample surfaces. Such data are complex and the relevant chemical information could be masked by the analytical method itself but also by mixtures present in the samples. Because the combination of such data sets is rather new, in the first step a "data-driven" strategy will be applied; that means "exploratory data analysis methods" will be used first to detect potential chemistry-relevant information in the data. In a next step, "supervised methods" for the development of classification and calibration models will be tested with reference data from well defined samples. Own extensive experiences with the application of chemometric methods to electron impact (EI) and SIMS mass spectra from organic and mineral matter is a good fundament for successful applications to multi-source data measured on meteorites.

The project leader together with collaborator P. Filzmoser published 2009 a book [56] about chemometrics in which the first time the programming environment R (an open source activity with rapidly increasing importance in science and technology) has been intensively used in chemometrics. In this project, the instrument data will be imported into R and all further software development done in R. For tests and comparisons, as well as for easy transformation of spectral data formats, the widely used commercial software "The Unscrambler" (Camo Software, Norway) will be used.

Figure 2 shows the planned work flow, and Table 2 summarizes the characteristics of the surface analysis methods to be applied.

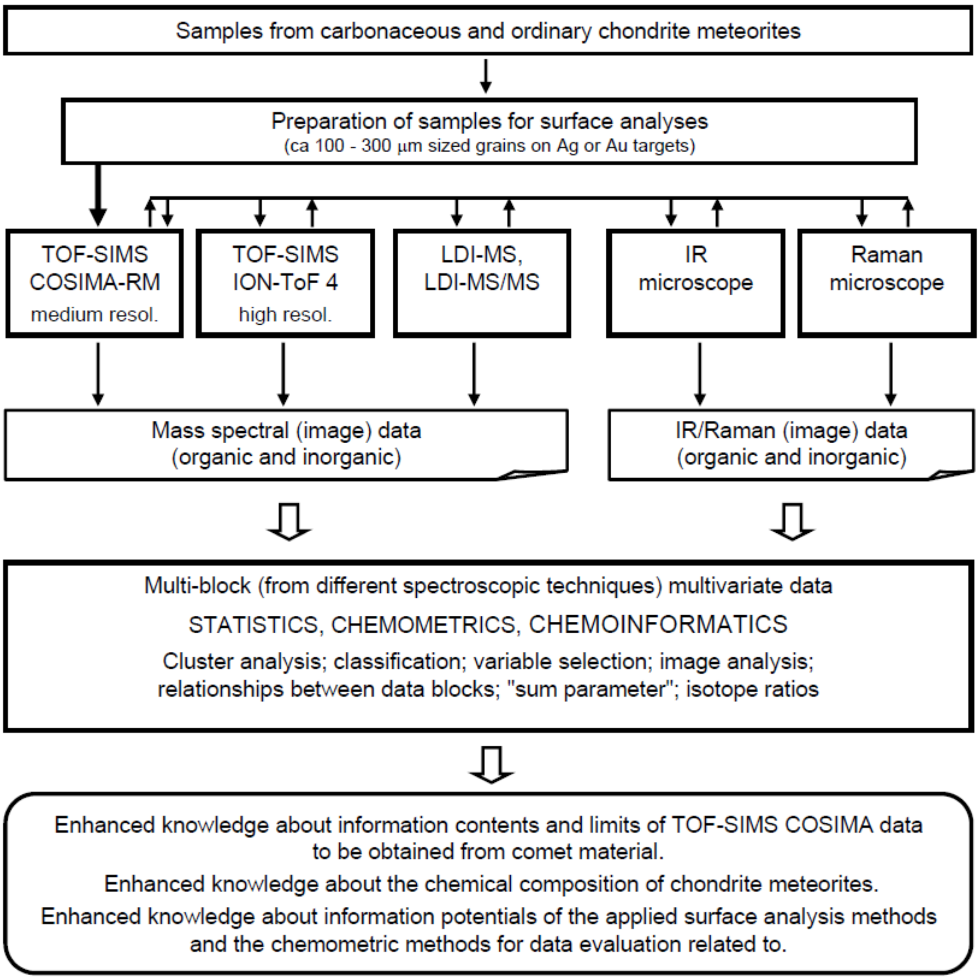

Figure 2. Scheme of the project work flow.

Table 2. Characteristics of the surface analysis methods

Method	Spatial resolution	In vacuum	Inorganics	Organics	Isotope abund.	Selective signals for substance classes
TOF-SIMS COSIMA	70 µm	yes	yes	yes	yes	inorganic/organic ions up to ca 70 Dalton
TOF-SIMS ION-ToF 4	1 µm	yes	yes	yes	yes	molecular formulae
LDI-MS, LDI-MS/MS	10 - 60 µm	yes	yes	yes	yes	ion fragmentation pathways
IR microscope	50 - 100 µm	no	yes	yes	no	functional groups (organics), minerals
Raman microscope	30 µm	no	yes	yes	no	functional groups (organics), minerals

1.5 Summary of project goals

This interdisciplinary and international project (guided by research groups in Austria) will follow a novel approach to study the chemical composition of meteorites, with the perspective of the analyses of dust particles from a comet by the time-of-flight secondary ion mass spectrometer (TOF-SIMS) COSIMA onboard of the ESA mission Rosetta (2014 - 2015).

Carbonaceous and ordinary chondrite meteorite grains will be analyzed by

- a COSIMA twin instrument and a high-performance TOF-SIMS instrument;
- laser desorption ionization (LDI) mass spectrometry (including MS/MS) and imaging mode;
- IR and Raman microscopy.

A concerted chemometric evaluation of the data from these instruments

- will give a better knowledge about the chemical information content of the expected COSIMA comet data;
- will provide insight into relationships between data blocks of the different methods (multivariate multi-source data) applied for surface analyses, and their capabilities - when used together - for characterization of meteorites and other solid surfaces with complex compositions;
- will give new results about the chemical composition of chondritic meteorites (minerals, organics and their relationships) - and together with the expected Rosetta data a better understanding of the links between comets and meteorites.

More specific goals are:

- development of a chemical analytical strategy for characterizing meteorite grains, based on TOF-SIMS, LDI-MS and high energy CID, IR-, and Raman-microscopy;
- development of data evaluation methods (chemometrics) for these data allowing a joint or separate interpretation, based on multivariate data analysis (with software development in R);
- development of methods for mass spectral data considering their compositional character;
- development of multivariate classification methods for the recognition of different classes of chondrite meteorites by mass spectral, IR and Raman data;
- database with mass spectral, IR and Raman data from the measured meteorite samples allowing a comparison with future measurements from other meteorites or from comet samples.

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