Analysis of meteorites and meteorite-like materials (terrestrial forsterite) doped with small organic molecules by LDI-MS using three different analysers and SIMS

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Abstract.

Investigating the composition of meteorites, especially carbonaceous chondrites has been of considerable interest for the scientific world because they could deliver the key to opening the box containing the information of origin of life. Different mass spectrometric methods have been used till now (e.g. ESI-FTICR and SIMS-RTOF) but in this work we want to concentrate on laser desorption ionisation mass spectrometry (LDI-MS) performed on (MA)LDI instruments manufactured by different vendors implying their different performance characteristics [1-2]. Therefore, we developed a target system, which enables the use of only one target for different instruments for a serious comparison of one and the same potential precious sample preparation [3]. The target system consists of modified Bruker target adapter, a standard Waters (MA)LDI imaging target plate and a gold target plate (for fixing meteorite splinters onto the gold surface).

Prior to meteorite splinter examination we investigated the behaviour of three low-molecular weight organic molecules (tryptophan, 2-deoxy-D-ribose and triphenylene) selected due to their different desorption/ionization behaviour and their potential presence in carbonaceous chondrites. To simulate the simplified meteoritic composition we used forsterite (mineral of the olivine group) as our inorganic matrix in which we embedded the three organic test substances. All measurements (LDI and SIMS) were performed using a gold target plate in which the mixture containing the inorganic matrix and the reference substances has been pressed using our in-house built micro press. First attempts at incorporating the splinters of the carbonaceous chondrites into the gold target were performed and the obtained MS data were compared to those obtained from our reference substances.

References:

[1] P. Schmitt-Kopplin et al., PNAS **2010, 107 (7), 2763-2768**. [2] O. J. Stenzel et al., MNRAS **2017, 469, 492-505.** [3] E. Rados et al., Rapid Commun Mass Spectrom **2018, 32 (8), 649-656**.

Introduction

Investigating the composition of meteorites, especially carbonaceous chondrites (stony, primitive, undifferentiated meteorites) has been of considerable interest for the scientific world because they could deliver the key to opening the box containing the information of origin of life.

In this work we want to concentrate on laser desorption ionisation mass spectrometry (LDI-MS) of meteorites and meteorite-like material using (MA)LDI instruments manufactured by different vendors implying their different performance characteristics[1-2].

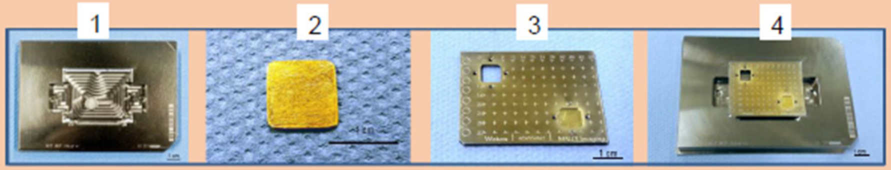
In order to do that, we developed a target system, which enables the use of only one target for different instruments for a serious comparison of one and the same precious sample preparation.

Materials

For the experiments we selected three organic substances (i.e. tryptophan, 2-deoxy-D-ribose and triphenylene) which were mixed with an inorganic substance (forsterite) creating a meteorite-like material. We selected these molecules because they belong to the group of molecules already detected in the carbonaceous chondrites[3] and because of their different desorption/ionization behavior (proton or cation attachment, radical cation formation).

We also performed first experiments using a carbonaceous chondrite CM2 type (Jbilet Winselwan) which was found in 2013 in Western Sahara.

The developed target system (4) used for the measurements consists of modified Bruker target adapter (1), an Au target plate (2) and a standard stainless steel Waters target plate (3).



Instruments

The measurements were performed on three (MA)LDI instruments namely an Axima TOF^2, an ultrafleXtreme and a Synapt G2 using the laser desorption ionisation (LDI) mode. The samples were also analysed on a TOF-SIMS 5 mass spectrometer equipped with Bi-cluster ion gun with a gridless RTOF using only the Au target plate.

Instrument	m/z range	Acquisition mode	Laser fluence a.u.
Axima TOF^2	20-500	RP (+)/LN (-)	130-145 (max. 180)
UltrafleXtreme	20-500	RP (+)/RN (-)	85 (max. 100)
Synapt G2	20-500	RP (+)/RN (-)	350 (max. 500)

Shimadzu Axima TOF^2

Bruker ultrafleXtreme

Waters Synapt G2

Shimadzu Axima TOF^2:
- High vacuum
- Nitrogen laser
- Wavelength 337 nm
- Repetition rate 20 Hz
- Curved field reflectron

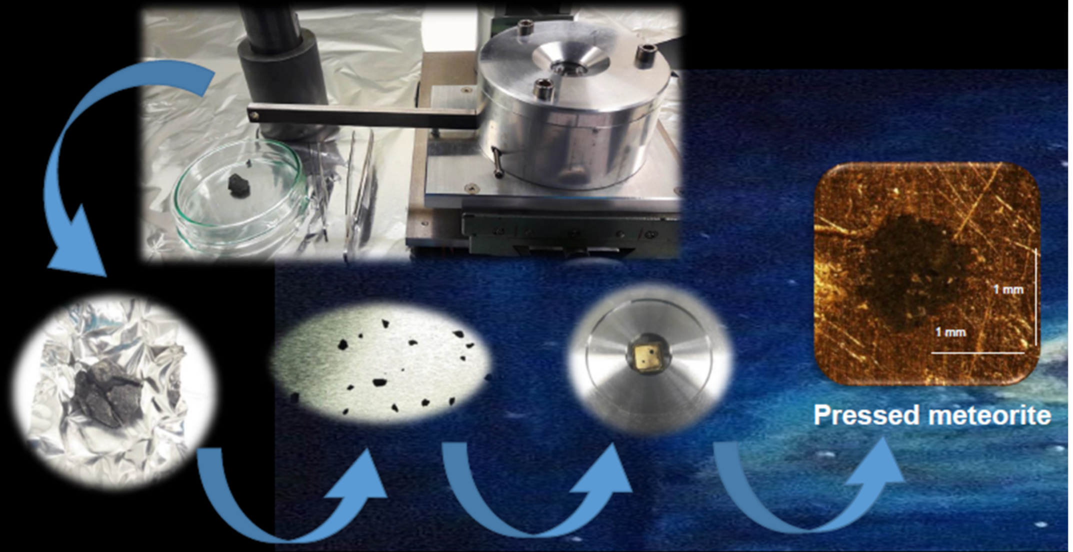
Bruker ultrafleXtreme:
- High vacuum
- Frequency-tripled Nd:YAG laser
- Wavelength 355 nm
- Repetition rate 2 kHz
- Near rectangular beam shape
- Dual stage reflectron

Waters Synapt G2:
- Intermediate pressure
- Frequency-tripled Nd:YAG laser
- Wavelength 355 nm
- Repetition rate 1 kHz
- Orthogonal dual stage RTOF

Sample preparation

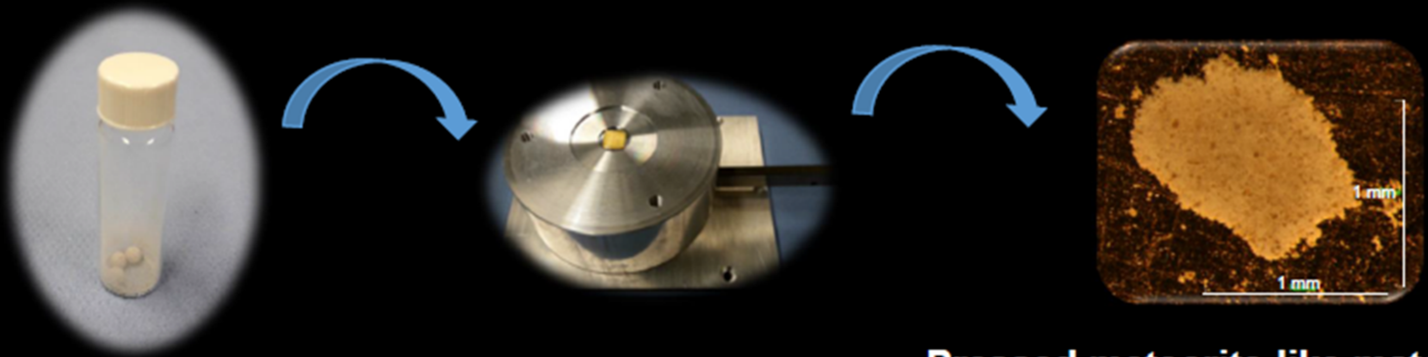
For the formation of the meteorite-like material all substances (inorganic and organic) including sodium chloride (all present in powder form with particle size ranging from 10-100µm) were mixed together in a glass vial using cemented carbide beads without any solvents. The mixture was then pressed into the gold target using the in-house built micropress.

The Jbilet Winselwan meteorite was washed using solvents of different polarity (water, methanol, ethanol, acetonitrile, toluene and chloroform) prior to the crushing procedure, which is shown in the following pictures. Small meteorite splinters were taken from the broken parts and pressed into the Au Target.

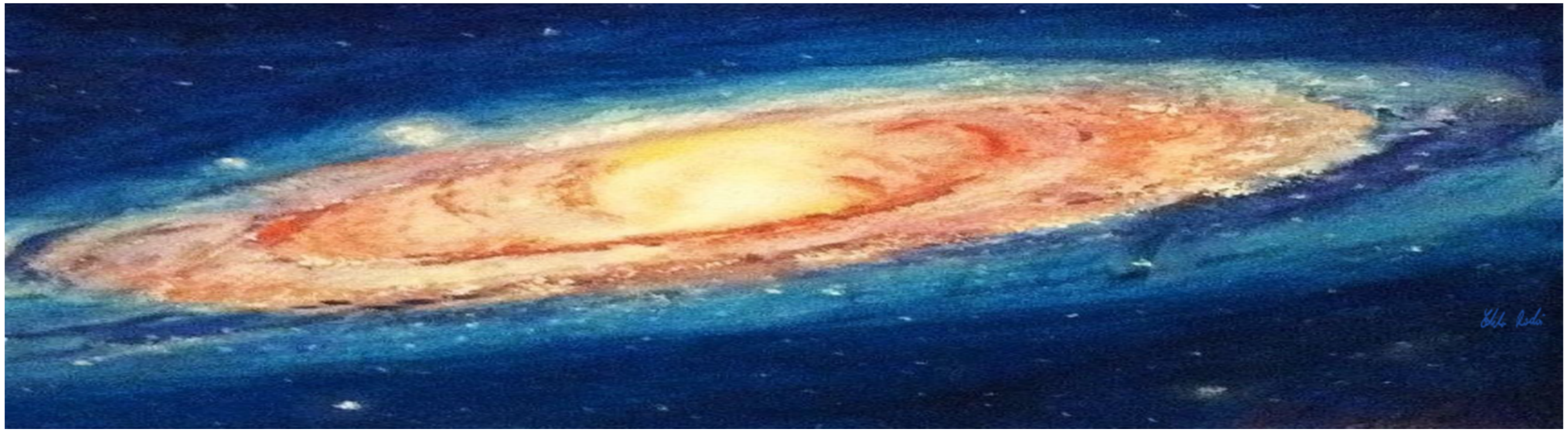


Sample preparation

Substance	Amount
Tryptophan	1mg
2-Deoxy-D-ribose	1mg
Triphenylene	1mg
NaCl	1mg
Forsterite	10mg

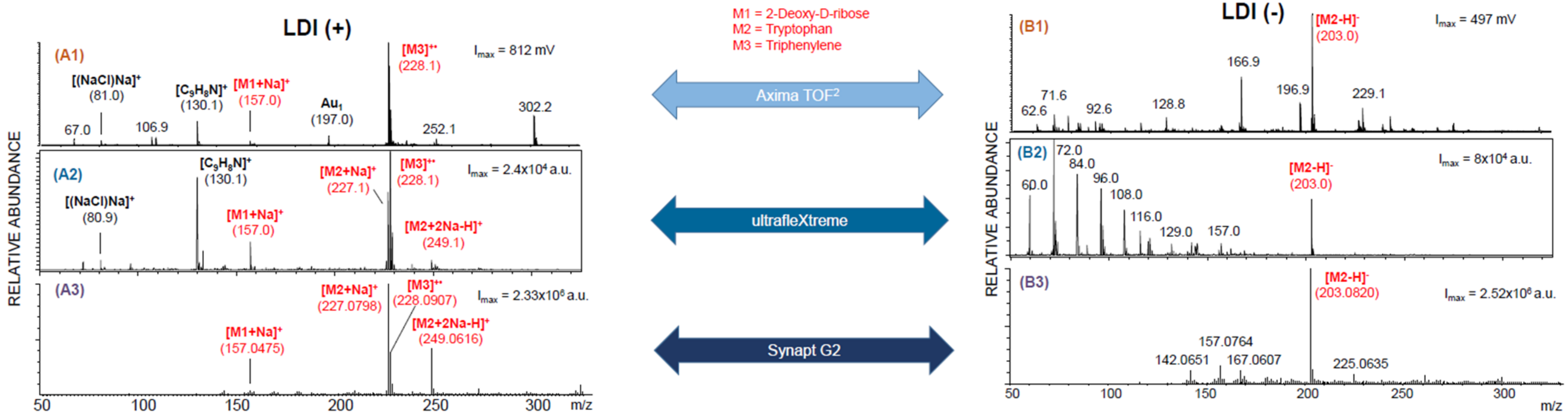


Pressed meteorite-like material



Results and discussion

LDI-MS of meteorite-like material

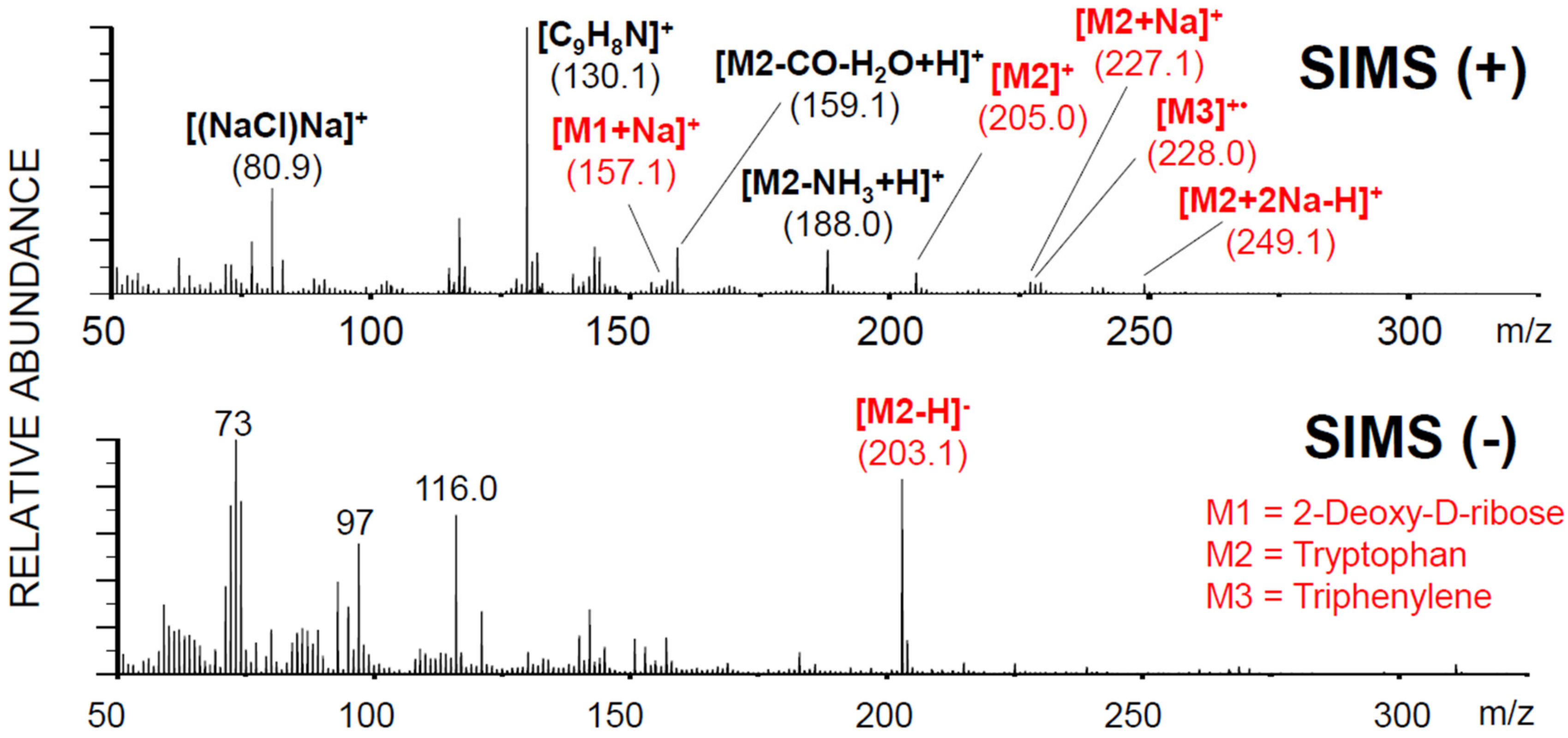


The meteorite-like material was measured on all (MA)LDI-MS instruments in positive and negative ion mode. The three substances were detectable in positive ion mode on all instruments except TOF² where tryptophan could not be detected. 2-deoxy-D-ribose was present as sodium adduct ion at m/z 157, tryptophan was also present as sodium adduct ions present at m/z 227 and m/z 249 while triphenylene was present only as a radical cation visible at m/z 228. In negative ion mode only tryptophan was detected as $[M-H]^-$ at m/z 203.

Some *in-source* generated fragment ions, sodium related cluster ions and the gold cluster are also visible[4]. Other fragment ions probably arise from the background or are the result of the photochemical reactions.

Results and discussion

SIMS-MS of meteorite-like material



Results and discussion

SIMS-MS of meteorite-like material

Because classical SIMS is used in the analysis of carbonaceous chondrites and cometary dust[5], we investigated the behavior of our meteorite-like material pressed into the gold target. As seen on the mass spectra on the left, except for $[M+H]^+$ of tryptophan all other molecular species correspond to those obtained by 337/355 nm UV LDI MS.

Results and discussion

LDI-MS of Jbilet Winselwan meteorite

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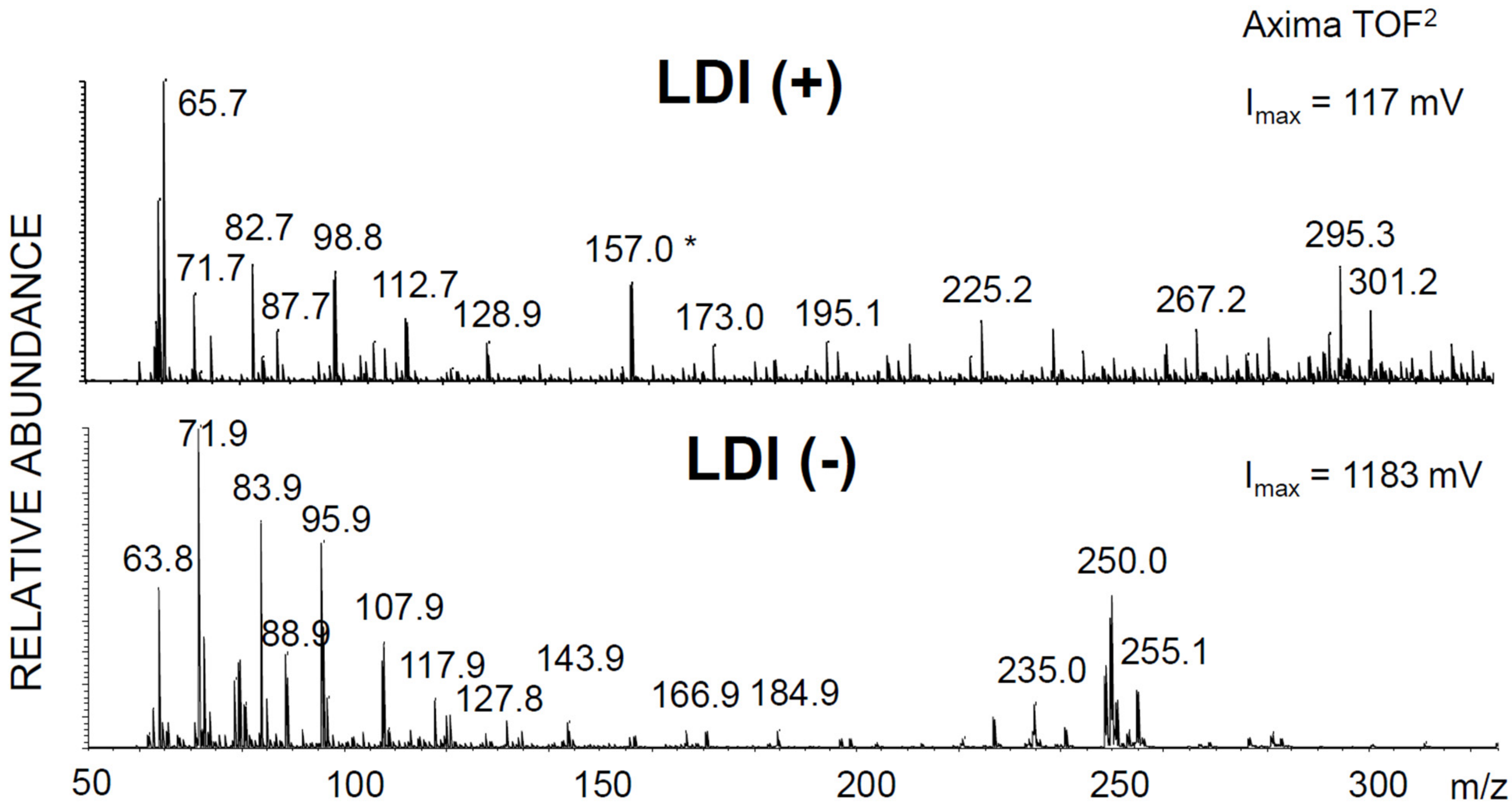
The mass spectra on the right side represent the first results obtained using LDI-MS of the Jbiler Winselwan meteorite. Detailed interpretation of the obtained data and further measurements using ultrafleXtreme, Synapt G2 and SIMS instrument will be the focus of the future investigations. Especially of great interest will be the molecular masses which could represent organic substances (*m/z 157.0).

Results and discussion

LDI-MS of Jbilet Winselwan meteorite



Conclusion and outlook

- The target system for multiple (MA)LDI instruments from different vendors was successfully developed.
- 337/355 nm LDI of small organic molecules is feasible.
- The three selected compounds, related to those found in meteoritic samples, were successfully analyzed even though they were mixed with inorganic substance and no solvent was used.
- Breaking down meteorite grains into small pieces – splinters was successfully performed.
- First LDI-MS measurement of the of the whole meteoritic splinters using the Au target was done.

Future work:

- LDI-MS measurements of the meteoritc extract and meteorite splinters on all instruments
- Accurate molecular mass determination - elemental composition with the use of the Synapt G2 instrument.
- MS/MS (HE-CID) of the meteorite splinters for structural elucidation.

References:

[1] P. Schmitt-Kopplin et al. High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40 years after its fall, PNAS 2010, 107 (7), 2763-2768.

[2] O. J. Stenzel et al. Similarities in element content between comet 67P/Churyumov–Gerasimenko coma dust and selected meteorite samples, MNRAS 2017, 469, 492-505.

[3] Sephton AM. Organic compounds in carbonaceous meteorites. *Nat Prod Rep* 2002;19(3):292-311.

[4] Rados E, Pittenauer E, Frank J, Varmuza K and Allmaier G. A laser desorption ionization/matrix-assisted laser desorption ionization target system applicable for three distinct types of instruments (LinTOF/curved field RTOF, LinTOF/RTOF and QqRTOF) with different performance characteristics from three vendors. *Rapid Commun Mass Spectrom* 2018;32(8);649-656.

[5] Bardyn A, Baklouti D, et al. Carbon-rich dust in comet 67P/Churyumov-Gerasimenko measured by COSIMA/Rosetta. Mon Not R Astron Soc 2017;469(2):712-722.

End.