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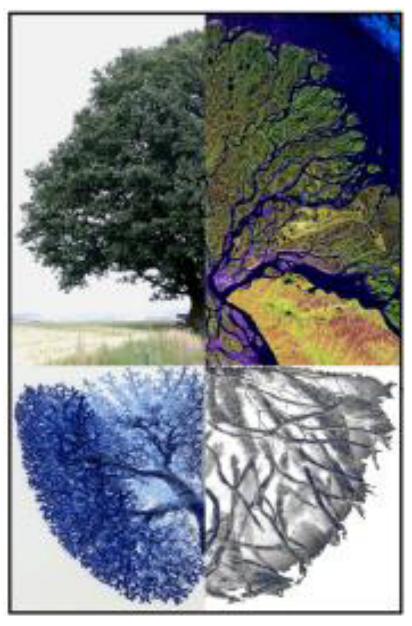
**Analytical BioGeoChemistry**



# HIGH-RESOLVING ANALYTICS REVEALS MOLECULAR DIVERSITY IN METEORITIC SOLUBLE ORGANIC MATTER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## INTRODUCTION/MOTIVATION

Understanding the **origin and evolution of organic matter**, formed in interstellar clouds, is linked to observationally-derived astrochemistry (ground- and satellite-based observations) and analytically-derived astrochemistry (meteorites). The **molecular diversity** of extraterrestrial organic matter in carbonaceous chondrites was studied by means of both, targeted [1] and non-targeted [2,3] chemical analytical methodologies, which are complementary to each other.

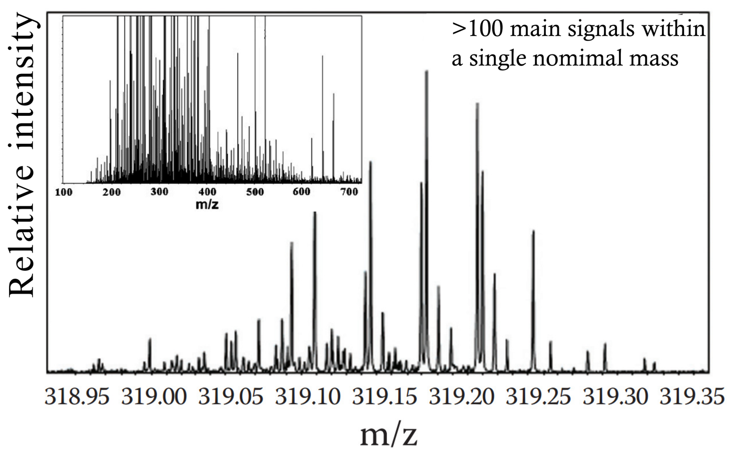
**High-resolving analytics**, like FT-ICR mass spectrometry, NMR spectroscopy or high-resolution separation techniques, represents a powerful tool to allow insights into the holistic complex compositional space to tens of thousands of different molecular compositions and likely millions of diverse structures. This vast diversity could be observed in solvent extracts of pristine carbonaceous meteorites [2,3], and suggests that **interstellar chemistry is extremely active, rich and diverse**. In-depth molecular characterization allows a clear distinction of the complex extraterrestrial chemical spaces.

## DATA-DRIVEN ASTROCHEMISTRY

Meteoritic extracts of >100 meteorites

**MURCHISON (CM2) SOLUBLE ORGANIC MATTER**

12 T FT-ICR mass spectrometry



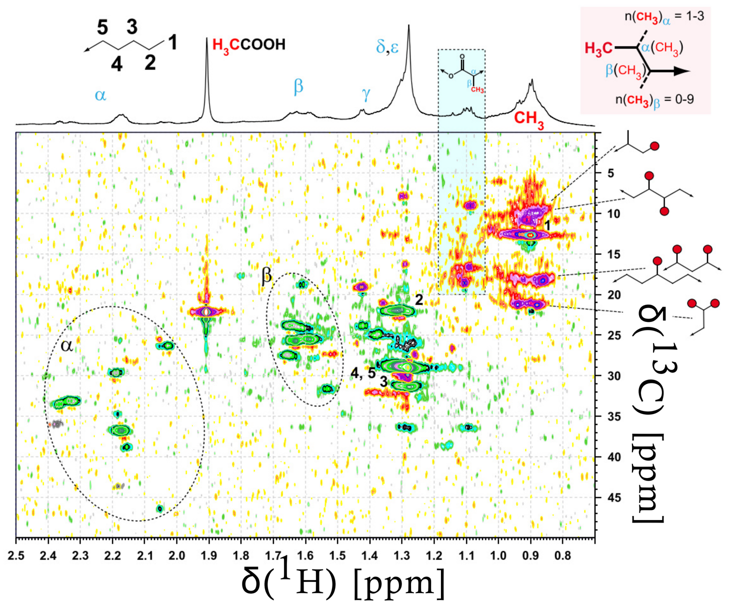

**Compositional information**

High-resolving power ($R > 10^6$ at $m/z < 250$), high mass accuracy (<200 ppb)

→ High peak capacity

→ 15,000 compositions [2]

800 MHz 1D and 2D NMR spectroscopy

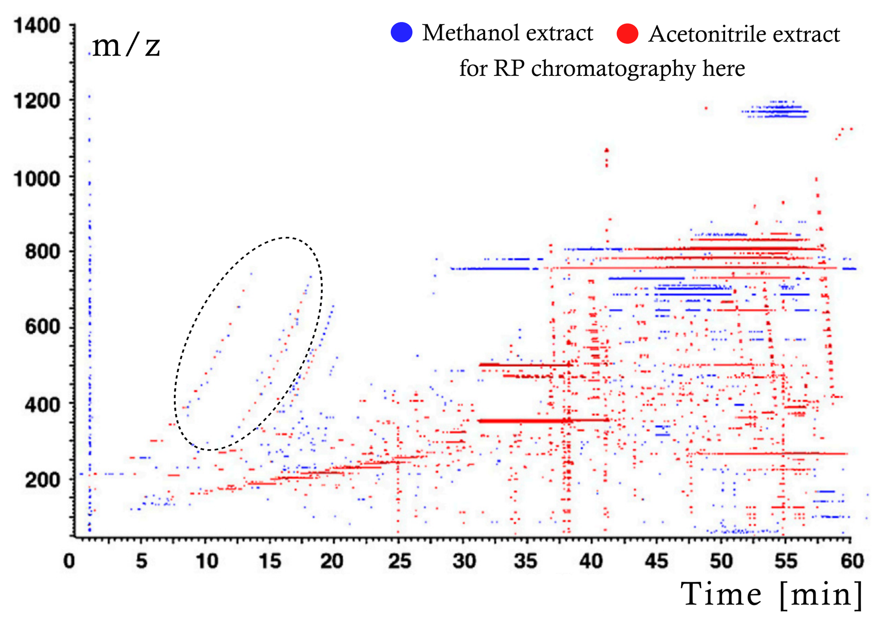



**Functional information**

Carbon and proton chemical environments including organic functional groups [3]

→ structural insights

UPLC-QToF-MS




**Differentiation of isomers** [2]

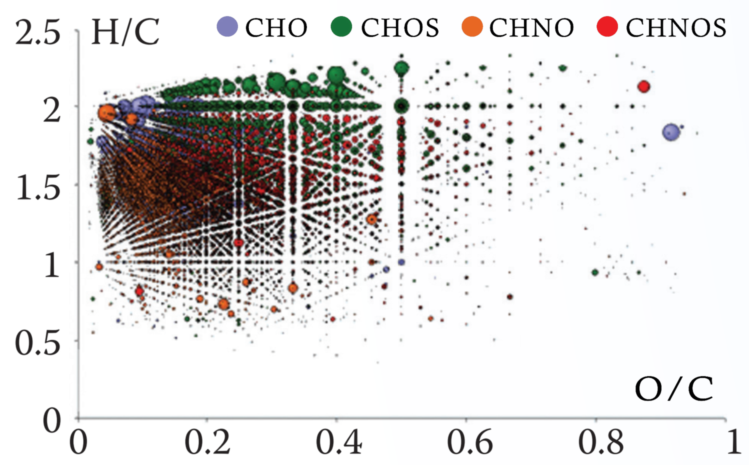
High-resolution analytics both, in the chromatographic and mass spectrometric dimension, distincts isomeric molecular formulas.

**INFORMATION ON COMPLEX MOLECULES (high molecular masses within 100-1,000 amu)**

## VISUALIZATION OF BIG DATA

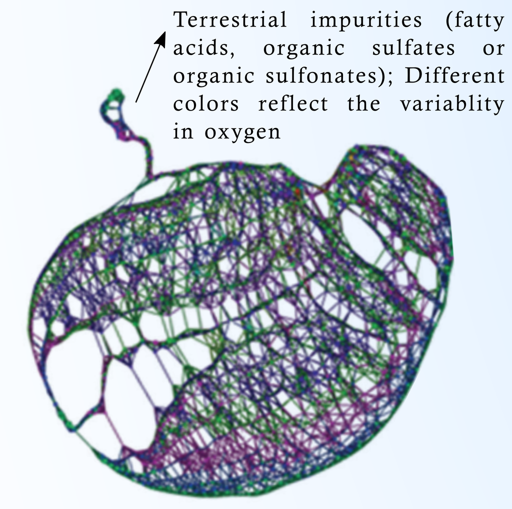
FT-ICR mass spectra depict the complex high-dimensional CHNOS compositional space (~15,000 molecular formulas)

→ Advanced visualization tools are needed for extracting meaningful information




**van Krevelen diagram-type representations** [4]

Information on homologous series can be revealed from experimental FT-ICR-MS data, here from Murchison. The bubble size represents the relative intensity of the mass peaks. Additionally, **properties of chemical spaces** (CHO, CHOS, CHNO and CHNOS) regarding the degree of unsaturation (H/C ratio) and oxygenation (O/C) can be deciphered.




**Mass difference network analysis** [5,6]

Mass difference network analysis visualizes **holistic chemical diversity**. In this data-driven analytical approach, nodes represent experimental $m/z$ values (here, FT-ICR-MS data of Murchison CHO soluble organic matter) and edges represent exact mass differences, which are equivalent to a net molecular formula of a chemical reaction.

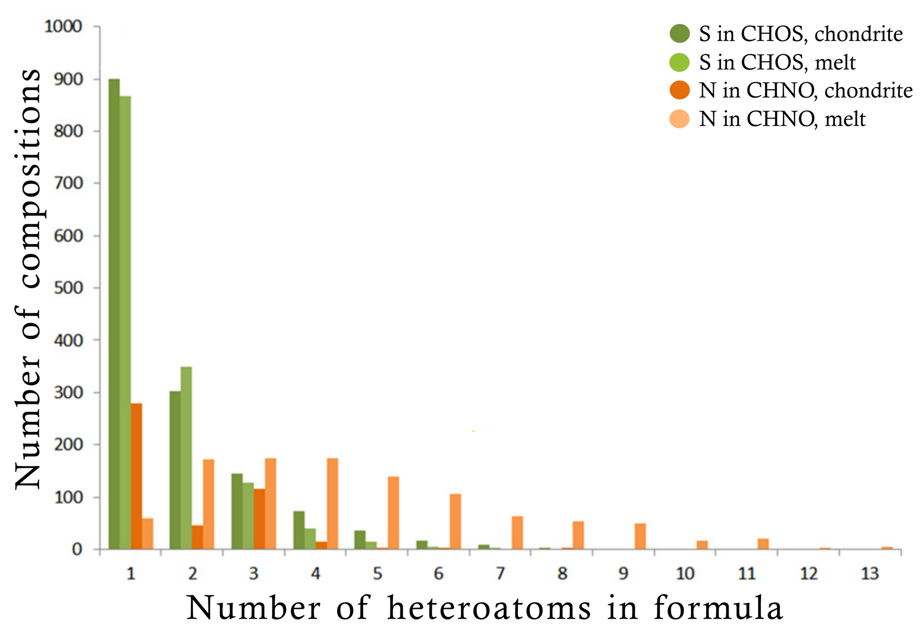
## CHEMICAL ENVIRONMENTS AND THEIR CONNECTION TO HETEROATOMIC ORGANIC MOLECULES

**Heteroatomic organic molecules** play an important role in the description of extraterrestrial chemical evolution.

The **thermally and shock-stressed** Chelyabinsk (LL5) [7] showed high number of nitrogen atoms within CHNO molecular formulas, relative to other L-type meteorites with lower shock grades, especially in the melt region. Analogous concordance of the organic molecular profile with the petrologic character could be also observed for Novato (L6) [8] or Braunschweig (L6).

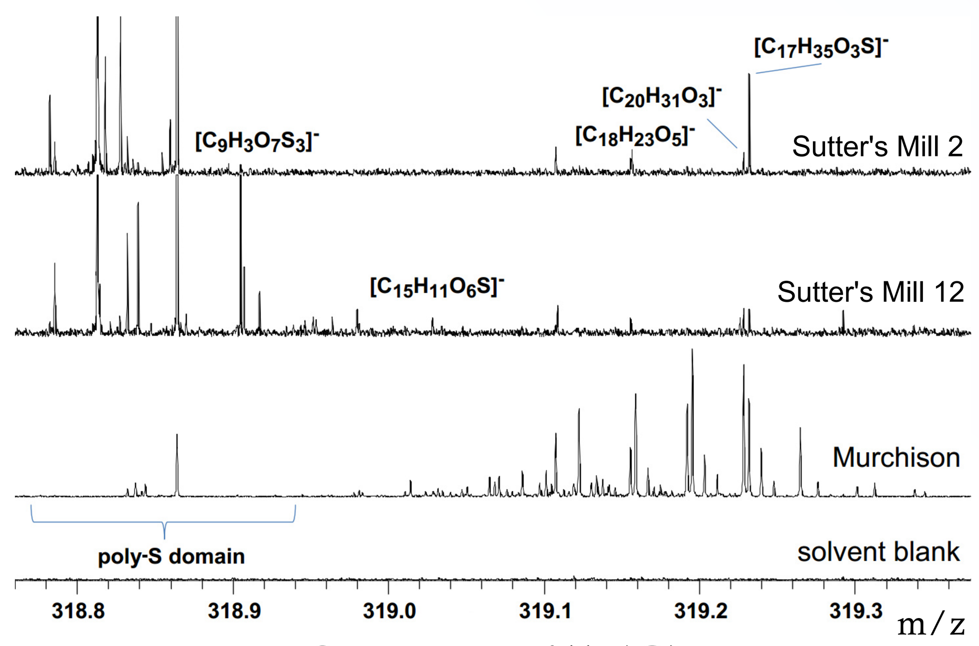
Remarkably, the extremely **thermally altered** Sutter's mill (C-type) [9] reflects a loss in the organic diversity, but an increase in the polysulphur domain, as compared to other CM2-analyzed falls.

**INFORMATION ON METEORITE'S HISTORY**




**Chelyabinsk (LL5)**

Increase of compounds with several nitrogen atoms in melt crust [7]




**Sutter's mill (C)**

High number of poly-S molecules in thermally altered C-type Sutter's mill [9]

## CONCLUSION

The extreme **richness in chemical diversity** of meteoritic soluble organic matter offers information on the meteoritic **parent body history**. Hints on **heteroatom** incorporation and it's chronological assemblies, **shock and thermal events** can be extracted by advanced data-analytical methods of these correlated high-dimensional data sets. Heteroatomic organic molecules (i. e. N- and S- bearing compounds) play an important role in the description of **extraterrestrial chemical evolution**. High-resolving analytics helps in expanding our knowledge in astrochemistry towards higher molecular masses and **complex molecular structures**.

## REFERENCES


[1] Pizzarello, S., et al. (2013). *Proceedings of the National Academy of Sciences*, 110(39), 15614-15619.
[2] Schmitt-Kopplin, et al. (2010). *Proceedings of the National Academy of Sciences*, 107(7), 2763-2768.
[3] Hertkorn, N., et al (2015). Magnetic Resonance in Chemistry, 53(9), 754-768.
[4] van Krevelen, D. W. (1950). *Fuel*, 29(12), 269-284.
[5] Tziotis, D., et al. (2011). *European Journal of Mass Spectrometry*,17(4), 415-421.
[6] Schmitt-Kopplin, et al. (2014). Astrobiology: an evolutionary approach. CRC Press, Florida, 63-80.
[7] Popova, O. P., et al. (2013). *Science*, 342(6162), 1069-1073.
[8] Jenniskens, et al. (2014). *Meteoritics & Planetary Science*, 49(8), 1388-1425.
[9] Jenniskens, P., et al. (2012). *Science*, 338(6114), 1583-1587.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