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Data-Driven UPLC-Orbitrap MS Analysis in Astrochemistry

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Abstract

Meteorites have been found to be rich and highly diverse in organic compounds. Next to previous direct infusion high resolution mass spectrometry experiments (DI-HR-MS), we present here data-driven strategies to evaluate UPLC-Orbitrap MS analyses. This allows a comprehensive mining of structural isomers extending the level of information on the molecular diversity in astrochemical materials. As a proof-of-concept study, Murchison and Allende meteorites were analyzed. Both, global organic fingerprint and specific isomer analyses are discussed. Up to 31 different isomers per molecular composition are present in Murchison suggesting the presence of ≈ 440,000 different compounds detected therein. By means of this time-resolving high resolution mass spectrometric method, we go one step further toward the characterization of chemical structures within complex extraterrestrial mixtures, enabling a better understanding of organic chemical evolution, from interstellar ices toward small bodies in the Solar System.

1. Introduction

Organic chemistry is known to be rich and almost universal in astronomical objects, as observed from a huge molecular diversity in the interstellar medium (ISM) [1], in interstellar/precometary ices of laboratory analogs [2,3], or in meteorites [4,5]. The description of astrochemical organic matter as seeds for life and their interactions within various astrophysical environments may thus appear essential to further study problems regarding the emergence of life, in a given telluric planetary environment [1].

Data-driven analytical methods including ultrahigh-resolving instruments and their interplay with quantum chemical computations enable deep insights into the complex and highly diverse chemical spaces that exist in meteorites [4,5]. To date, most high-resolving chemical analytical studies on astrochemical organic matter base on direct infusion electrospray (DI-ESI) analysis [1-5]. By means of this technique, no information on structural isomers can be obtained. The implementation of analytical separation techniques, e.g., chromatography, would increase the level of information on astrochemical complex mixtures. Thus, we will go one step further within the analysis of chemical structures therein [6].

2. Results

Classifying Chemical Families—Bringing Order into the Chemical Diversity. The 2D chromatogram of Murchison soluble organic matter (m/z over retention time, Figure 1C), is rich in signals between m/z = 150–350 amu and from retention time = 5–20 min. Dealing with such a high degree of molecular diversity, it is important to systematically group chemical spaces. Here, chemical families were classified into CHO, CHNO, CHOS and CHNOS within LC-HR-MS data of Murchison. CHO, CHNO, CHOS and CHNOS compounds show different characteristics, both in m/z and in retention time (Figure 1C). This gives hints on chemical characteristics for each chemical class. In general, information on chemical polarity, structural isomers and homologous series can be obtained from this raw data representation. CHNO compounds represent the largest chemical subspace, distributed along the whole mass and retention time range. Detailed chemical characteristics are discussed by the help of van Krevelen diagrams.

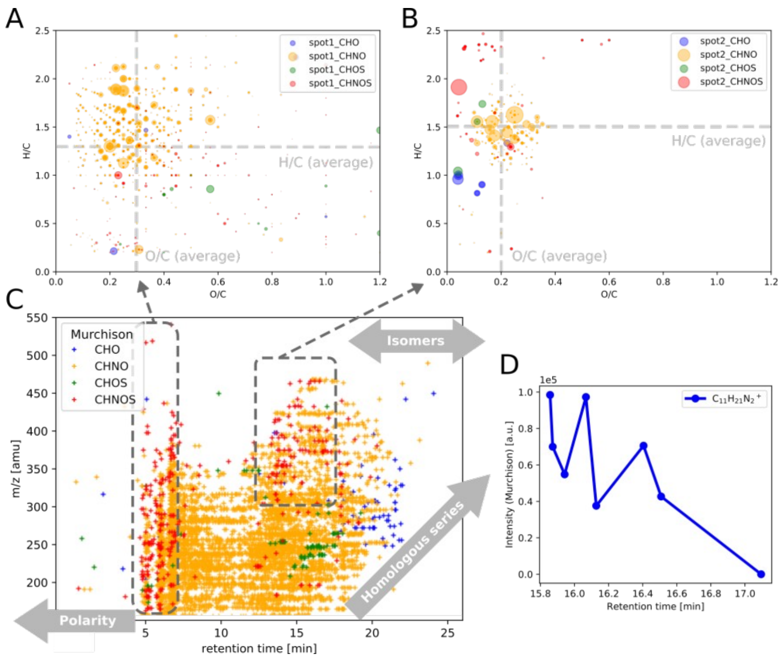

Figure 1: (A) van Krevelen diagrams of spot 1 (RT = 4–7 min, m/z = 150–700 amu); (B) van Krevelen diagrams of spot 2 (RT = 12.5–17.5 min, m/z = 300–500 amu); (C) 2D chromatogram (m/z over retention time) of Murchison soluble organic matter depicts its chemical diversity in these two dimensions but also shows the grouping of distinct chemical subspaces CHO, CHNO, CHOS and CHNOS; (D) the resolved detection of eight $C_{11}H_{21}N_2^+$ isomers in Murchison gives first insights on the different chemical polarity of these compounds.

Comparison of Murchison with Allende—A Difference in Isomeric Diversity. To illustrate the power of comprehensive UPLC-Orbitrap MS analyses in complex extraterrestrial mixtures, we compared Murchison with Allende meteorite in a coarse, first-order manner. The molecular diversity of Murchison soluble organic matter rules the overall chemical space of the two samples. Allende soluble organic matter seems to be more diverse in m/z range. Whereas Murchison organic matter shows a continuum in chemical polarity, Allende is characterized by more distinct properties. Allende bears either fairly polar molecules or apolar compounds, widespread over a large mass range (m/z 150–600 amu).

3. Conclusions

In summary, (i) LC-HR-MS extends the level of information of astrochemical molecular diversity, (ii) a relative polarity scale of compounds out of complex mixtures can be determined, (iii) structural isomers can be resolved by chromatography and separately detected; (iv) the combination of UPLC and HR-MS merges both accurate isomer and isobar detection. By means of this time-resolving high resolution mass spectrometric method, we go one step further toward the characterization of chemical structures within complex extraterrestrial mixtures, enabling a better understanding of organic chemical evolution.

Acknowledgements

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