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Orbitrap mass spectrometry of synthetic exoplanetary particles

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1. Introduction

Organic aerosols are present in every substantial planetary atmosphere in the solar system, but so far the studies of aerosols in exoplanet atmospheres are still largely in their infancy for two reasons: (1) efforts to characterize the atmospheres of exoplanets have focused on the best current targets for exoplanets, which are mainly hot Jupiter-like planets where hydrocarbon destruction rates greatly inhibit the formation of complex molecules [1] and (2) aerosol formation is a complicated process that is still difficult to replicate in the models.

Aerosols affect the chemistry, dynamics and flux of radiation in planetary atmospheres. They can therefore provide organic material to the surface and/or modify the atmospheric temperature and consequently have an impact on the habitability of the planet. Decades of analogous studies of planetary aerosols (notably those of Titan, satellite of Saturn or the primitive Earth) have shown that they can contain complex molecules that serve as bricks for the construction of organized systems [2]. However, little is known about the size distribution, optical properties, and particle composition that can form in the super-Earth and mini-Neptune atmospheres. Thus, laboratory studies on atmospheric particles of exoplanets are essential for the interpretation of future spectroscopic observations and the characterization of the atmospheres of these worlds.

2. Exoplanet particle production by the PHAZER setup

Laboratory analogues were synthesized at Johns Hopkins University by exposing to an AC glow discharge nine different gas mixtures with various compositions varying from 100x to 10000x solar metallicity calculated at thermodynamic equilibrium at 300, 400 and 600 K, that flow continuously through a stainless-steel reaction chamber. The produced particles are retrieved from the chamber's inside wall and wrapped in foil [3]. More details about sample production and compositions can be found in [4].

3. Unveiling the molecular diversity with Orbitrap™ mass spectrometry

A Thermo Scientific LTQ Orbitrap XL (resolving power FWHM m/Δm∼100,000 at m/z=400u) available in Univ. Grenoble Alpes coupled with an electrospray ionisation source (ESI) was used to acquire very high-resolution mass spectra of exoplanets particle soluble organic matter. About 1 mg of particles is dissolved in 1 mL of methanol to generate a primary solution that is vortexed during several minutes and then centrifugated at 10,000 rpm for 10 minutes. 500 μl of the soluble fraction is mixed with 500 μl of methanol to obtain the final solution that is injected in the Orbitrap. Mass spectra were acquired in both positive and negative mode with mass range from m/z=50-300 u and m/z=150-450 u. Only three samples out of the nine analysed show prominent features in their mass spectra and about 3000 stoichiometric formulas are obtained in each spectrum using the Attributor software developed at IPAG [5]. The starting gas mixture composition for the three samples are shown in Table 1.

SAMPLE NAME	GAS MIXTURE COMPOSITION
1000X – 300 K	66%H_2O, 6.6%CH_4, 6.4%N_2,4.9%CO_2, 16%He
1000X – 400 K	56%H_2O, 11%CH_4, 10%CO_2, 6.4%N_2, 1.9%H_2, 14.7%He
1000X – 600 K	42%H_2, 20%CO_2, 16%H_2O, 5.1%N_2, 1.9%CO, 1.7%CH_4, 13.3%He

Table 1: Composition of the starting gas mixture composition for the three samples.

4. Results and Conclusions

From the stoichiometries, some different approaches can be performed: (1) extract the elemental composition of the attributed molecules and link the differences to the gas mix variation, (2) display some proxy representations to understand the evolution of the incorporation of nitrogen and oxygen with the gas mix variation and even (3) compare the stoichiometric formulas to known molecules and select the proper chromatographic methods to confirm or not their presence. Here we will focus on finding the proper proxy to see the differences between samples and link them to the gas mix composition.

We propose in Figure 1 a representation based on ESI negative mode analysis on the higher mass range (m/z ranging between 150 and 450 u) that compares the incorporation of nitrogen and hydrogen compared to the oxygen one. For all the three gas mix compositions, N and H contents are equivalent between samples, roughly at 9 and 10% respectively. The "1000x – 600 K" sample shows a higher amount of incorporated oxygen, corresponding to the lowest O and highest C content, at 63 and 19% respectively. On the other hand, the "1000x – 300 K" shows a higher N+H content, corresponding to the lowest C and highest O content, at 8 and 72% respectively.

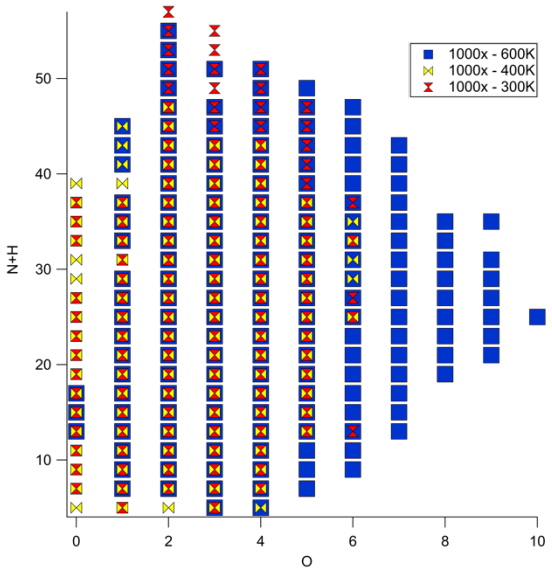

Figure 1: Comparison of incorporation of nitrogen and hydrogen compared to oxygen in ESI negative analysis on the second mass range.

The difference in heteroatom composition seems to correlate to the carbon content and anticorrelate to the oxygen content of the gas mixture. As the gas mixture composition is complex, correlate the variation to one compound only seems difficult to achieve.

Other proxies can be used to check for other sample features, such as the unsaturation with the Double Bound Equivalent (DBE) or Aromaticity Index (Xc) representations [6].

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