

Insight into the molecular composition of laboratory organic residues produced from interstellar/pre-cometary ice analogues using very high resolution mass spectrometry

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Abstract

Experimental simulations in the laboratory may provide important information about the chemical evolution occurring in various astrophysical objects such as extraterrestrial ices. Interstellar or (pre)cometary ice analogues made of H₂O, CH₃OH, and NH₃ at 77 K, when subjected to an energetic process (VUV photons, electrons or ions) and then warmed-up to room temperature, lead, in the laboratory, to the formation of an organic residue. In this paper we expand our previous analysis of the residues in order to obtain a better insight into their molecular content. Data analyses show that three different chemical groups are present in the residue in the negative electrospray ionization (ESI) mode: CHN, CHO and CHNO— whereas only two groups are detected in the positive ESI mode: CHN and CHNO. In both cases, the CHNO group is the most abundant. The application of specific data treatment shows that residue mainly contains aliphatic linear molecules or cyclic structures connected to unsaturated chemical functions such as esters, carboxylic acids, amides or aldehydes. In lower abundances, some molecules do present aromatic structures. The comparison of our residue with organic compounds detected in the Murchison meteorite gives an interesting match, which suggests that laboratory simulation of interstellar ice chemistry is relevant to understand astrophysical organic matter evolution.

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1. INTRODUCTION

Understanding the origin and evolution of the organic matter present in small bodies of the Solar System is of prime interest in linking observationally-derived astrochemistry to analytically-derived cosmochemistry in pristine

carbonaceous meteorites. Complementary to observations (telescopic) or analytical chemistry of extra-terrestrial materials, a third route is the development in the laboratory of experimental simulations, a scientific field known as experimental astrochemistry. It allows for a thorough investigation of the organic content and evolution toward a very high molecular diversity of a medium mimicking a given astrophysical environment. Such level of complexity cannot be described ab initio by models involving necessarily

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limited chemical networks, unable to reproduce the large diversity of organic species detected in meteorites, for instance.

Our current investigation is focused on the chemical evolution of interstellar/pre-cometary ice analogues. In this perspective, different approaches are developed. Some experiments are focused on the chemical reactivity that lead to the formation of specific molecules detected in a given environment (Danger et al., 2011). Other experiments consider a global approach to study the chemical evolution of such objects, by simulating in the laboratory the whole processing (Greenberg et al., 1995) that ices may undergo in astrophysical environments from molecular clouds, hot cores, to proto-star surroundings and incorporation in small bodies in the nascent Solar System, such as comets or asteroids. Our work deals with the second, global approach.

To this end, an ice analogue is formed in physicochemical conditions that are relevant to the considered environment. The composition of pristine ice analogues is derived from infrared observations that give evidence on the composition of ices observed in molecular clouds (Dartois, 2005; Öberg et al., 2011). The main components of ices are H₂O, CO, CO₂, CH₃OH and NH₃. In the laboratory, they are deposited at low temperature (10 K to 77 K) on an inert substrate under high vacuum (10⁻¹⁰–10⁻⁷ mbar). To simulate the ice evolution, it is submitted to energetic processes (photons from visible up to VUV, electrons or ions impact) and subsequently warmed-up to room temperature. The association of energetic processing together with the warming-up simulates the evolution of an icy grain in the vicinity of a proto-star or cometary matter approaching the Sun. During the energetic processing of the pristine ice, reactive species are formed, diffuse and recombine, leading to new molecules (Öberg et al., 2009). However, due to the low temperature at which this reactivity occurs, the molecular diversity obtained is limited. To produce a higher order of molecular diversity (higher molecular weight compounds), the warming is essential: it increases molecular diffusion (Mispelaer et al., 2013) and reactivity (Theule et al., 2013). It also provides energy to trigger the thermal reactivity (Theule et al., 2013) that increases molecular complexity (Vinogradoff et al., 2013). During heating, an important fraction of the molecules formed, including the initial ones, will desorb from the processed ice (Collings et al., 2004; Abou Mrad et al., 2014, 2016). Water being the main component of the ices, desorption mainly occurs between 150 and 180 K. After the desorption and reaching room temperature, an organic residue made of refractory species is present on the surface of the sample holder (Muñoz-Caro and Schutte, 2003). The molecular diversity of such residues has been highlighted by their analyses using Very High Resolution Mass Spectrometry (VHRMS). It has been shown that from an initial pristine ice composed of only three species, H₂O, CH₃OH and NH₃, submitted to VUV and subsequently warmed-up to 300 K, thousands of molecules are present in the resulting organic residues, with molecular masses up to 4000 Da (Danger et al., 2013). The molecular richness observed and the entire residue solubility in water and methanol suggest that processes leading to these

residues can be considered as analogues to the ones that led to the formation of the soluble organic matter (SOM) in meteorites (Schmitt-Kopplin et al., 2010).

The objective of the present work is to obtain, *in a single step*, a view of the molecular characteristics of the chemical structures present in these residues from VHRMS data. The difficulty in obtaining this information resides in the treatment of VHRMS data. Raw data is not readily usable and data processing using specific representations has to be used. Numerous representations have already been developed. This article focuses on the analysis of VHRMS data of irradiated ice residues using van Krevelen diagrams (van Krevelen, 1950) and the Aromaticity Equivalent (X_c) concept (Yassine et al., 2014).

Van Krevelen diagrams were developed for organic maturation analysis applied to petroleum analyses. To obtain information on the molecular content using van Krevelen diagrams from VHRMS, stoichiometric formulas have to be attributed to each molecular ion as long as the mass spectrometer resolution and accuracy allow an unambiguous attribution. This can be done by means of commercial or in-house programs. Van Krevelen diagrams display the data distribution in two (three) dimensions by taking into account H/C, O/C (N/C) ratios of each molecular ions (Wu et al., 2004). Van Krevelen representations of VHRMS data have been used for various samples containing natural organic matter such as soils and sediments (Sleighter and Hatcher, 2007), meteorites (Schmitt-Kopplin et al., 2010) or planetary science experimental simulations (Imanaka and Smith, 2010; Gautier et al., 2014). Here we use van Krevelen diagrams to derive insight on the molecular compositions (i.e. atomic compositions) present in our residues as well as on the molecular composition of each group (i.e. molecular families). Previous analyses (Sleighter and Hatcher, 2007; Hockaday et al., 2009; Ohno et al., 2010, 2014; Wollrab et al., 2016) provide a benchmark for the 2D van Krevelen diagram in the (H/C;O/C) plane. Specific zones in that plane can be associated to chemical functions and chemical structures that we will describe in the rest of this manuscript as molecular families.

The aromaticity equivalent parameter (X_c) is a parameter that is calculated from the molecular formulae of the compounds. It is based on the Double Bond Equivalent (DBE) information, which is normalized to the number of carbons available for chain elongation. It allows identifying different levels of aromaticity in molecular species of very diverse size and composition.

The association of the van Krevelen diagrams with the aromaticity equivalent parameter (X_c) gives some insight on the carbon backbone of detected molecules.

2. METHODS

2.1. Residue synthesis and VHRMS analyses

The experiments leading to the formation of the organic residue as well as blanks for comparison are fully detailed in Danger et al., 2013 and references therein. The VHRMS data used in the present work are based on a residue resulting from activation of an ice containing H₂O:CH₃OH:NH₃

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