Molecular characterization of Dissolved Organic Matter in glacial and interglacial Antarctic ice.

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Abstract

Antarctic ice sheets accumulated from past snowfall represent a formidable archive of information on paleoclimatic and paleoenvironmental conditions such as air temperature, atmospheric composition, solar activity and volcanic eruptions.
The dissolved organic material (DOM) is generally investigated in snow and ice in the bulk form through the determination of Dissolved Organic Carbon (DOC). DOM is an example of the complexity and difficulty in the molecular characterization of environmental matrices. Only recently, with the development of high-resolution analytical instruments (FT-ICR-MS and Orbitrap-MS), the DOM study is dealt from a molecular point of view in order to identify the individual chemical species of the organic fraction, obtaining an overall view of chemical composition of ice.
Very few studies in the literature report the molecular characterization of DOM in snow and ice due to the extremely low concentration of substances. Generally, the analytical approach for environmental matrices involves the preconcentration of the aqueous sample (melted snow or ice) using between 100 mL and 15 L. Such volumes are huge considering an ice core where the volume available for analysis is generally of few mL.
This work is a first step in the development of an innovative analytical approach for the characterization of DOM in polar ice. The characterization of DOM in ice has been addressed aiming at improving instrumental sensitivity using the nano-UHPLC-nanoESI-HRMS technique. This analytical technique was applied to some samples of last glacial and interglacial periods from the TALDICE ice core. The melted ice injected was of 4μL.
We evaluated the Van Krevelen diagrams, the average carbon oxidation state (OSc) and the Double Bond Equivalent (DBE), considering the area of the analytic peak as signal strength indicator of species observed. Remarkable differences between samples belonging to different historical periods, glacial and interglacial, were observed. The highest signal intensity was observed for the most oxidized species in glacial periods, while in interglacial samples there were more species characterized by a high intensity with a degree of oxidation variable between the most oxidized and the most reduced species. This suggests that the DOM present in the interglacial period ice is less aged and probably derives from more productive and /or nearer sources to the Talos Dome site. Whereas the DOM in glacial ice is more aged, oxidized and, given the lower intensity, it was produced by weaker or farther sources. These preliminary observations will be carefully evaluated considering previous studies conducted on TALDICE ice core and information concerning sea ice extension and atmospheric circulation in glacial and interglacial periods.

Keywords: Molecular characterization, ice core, TALDICE.