



Prospects for reconstructing paleoenvironmental conditions from organic compounds in polar snow and ice

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ABSTRACT

Polar ice cores provide information about past climate and environmental changes over periods ranging from a few years up to 800,000 years. The majority of chemical studies have focused on determining inorganic components, such as major ions and trace elements as well as on their isotopic fingerprint. In this paper, we review the different classes of organic compounds that might yield environmental information, discussing existing research and what is needed to improve knowledge. We also discuss the problems of sampling, analysis and interpretation of organic molecules in ice. This review highlights the great potential for organic compounds to be used as proxies for anthropogenic activities, past fire events from different types of biomass, terrestrial biogenic emissions and marine biological activity, along with the possibility of inferring past temperature fluctuations and even large-scale climate variability. In parallel, comprehensive research needs to be done to assess the atmospheric stability of these compounds, their ability to be transported long distances in the atmosphere, and their stability in the archive in order to better interpret their fluxes in ice cores. In addition, specific decontamination procedures, analytical methods with low detection limits (ng/L or lower), fast analysis time and low sample requests need to be developed in order to ensure a good time resolution in the archive.

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1. Introduction

Over the last half century, ice cores have provided a wealth of information about past climate and environmental changes (Jouzel, 2013) over periods ranging from a few years up to 800,000 years. For example, ice core results demonstrate the pattern of glacial-interglacial cycles (EPICA community members, 2004), the existence of abrupt climate changes (Johnsen et al., 1992), and quantify

how greenhouse gas concentrations increased above their pre-industrial values over the last two centuries (MacFarling Meure et al., 2006). The findings are based on three types of information recorded in ice cores: the isotopic content of the water molecules themselves, the gaseous content of air bubbles trapped in the ice (e.g. CH₄, CO₂), and the impurities that are trapped in or on snowflakes. This last component consists both of aerosol particles and of gaseous compounds that are absorbed onto snow surfaces. Multiple studies quantify many different analytes, and discuss, for example, atmospheric transport of dust, past variations of sea ice, and changes in concentrations of pollutants. The overwhelming majority of studies concentrate on the inorganic impurity – major cations and anions, trace elements, and simple components such as hydrogen peroxide. However, a very large proportion, often half or more, of atmospheric aerosols are organic (Jimenez et al., 2009),

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and such material is certainly present in polar ice.

Very few studies investigate the organic component in polar ice, either as a whole (Legrand et al., 2013), or for individual compounds. There are probably a number of reasons for this shortage: analytical issues, a lack of expertise in the ice core community, and difficulties in interpreting changing concentrations of reactive chemicals which may have relatively short lifetimes and limited stability in the atmosphere. Many of the studies that do exist concern: (a) very small molecules such as formaldehyde and low molecular weight organic acids (e.g. Legrand and De Angelis, 1995), (b) methanesulfonic acid (MSA) as a specific marker for marine biological activity and/or therefore sea ice extent (e.g. Curran et al., 2003), and (c) organic markers for biomass burning (Gambaro et al., 2008; Rubino et al., 2016). Studies in ice and snow of persistent organic pollutants (POPs) (Fuoco et al., 2012; Hermanson et al., 2005; Ruggirello et al., 2010) and of other molecules such as long chain fatty acids that are potential terrestrial biomarkers as they are produced by land-dwelling plants (Hopmans et al., 2004 and references therein; Kawamura et al., 1996; Pokhrel, 2015; Pokhrel et al., 2015) have been carried out but are not well developed in ice from the polar ice sheets.

Recent advances in analytical capability and in atmospheric chemistry modelling make it the right time to survey the field of organic geochemistry in ice cores and to discuss potential fields of study. Here, we consider only material in the solid ice phase. Air bubbles in ice do contain trace organic gases (such as methane), but these gases pose a different set of issues and are not discussed here. We also do not consider the use of the ^{14}C content of water-insoluble organic compounds to date glacier ice, which was recently reviewed by Uglietti et al. (2016). In this paper, we first review the problems of sampling, quantifying and interpreting the environmental relevance of organic molecules in ice. We then undertake a broad discussion of the different classes of organic compounds that might yield environmental information. Finally, we consider each class in more detail, discussing what has already been done, and what is needed to advance the study of each class.

2. Challenges with sampling and analysis of organic molecules

2.1. General issues during sampling, storage and analysis of organics in ice and snow

The issues that determine our ability to accurately estimate the concentrations of organic molecules in ice and snow differ with each class of compounds but some general considerations are worth discussing. Challenges result from three main issues: (1) individual compounds are expected to be present at low concentrations (typically ng/L or lower), posing problems for analytical detection and interferences caused by contamination; (2) the range of physical-chemical properties of organic compounds, especially their polarity, requires a variety of extraction and analytical techniques to quantify the range of organic compounds with optimal sensitivity; (3) some of the compounds may not be stable against chemical reactivity, biodegradation, and volatile loss back to the atmosphere. Concentrations of inorganic compounds also occur at very low levels, and ice core scientists are no strangers to the need to adopt contamination-free protocols (e.g. Boutron and Batifol, 1985). Nonetheless, organic compounds require different protocols, not least because the procedures adopted to avoid contamination for inorganics (e.g. involving clean rooms constructed from clean plastic materials, and the use of plastic sample containers) may be unsuitable for organics.

Field sampling of solid ice cores is challenged by the ubiquitous presence of a host of organic contaminants from both the sampling

process and the environment. The most obvious of these impurities is the drilling fluid which keeps the borehole open during deeper ice core drilling projects. Fluid typically consists of a poorly characterised and variable hydrocarbon mixture, but some compounds present in drilling fluid might also be of interest for paleo-environmental markers. The main examples used in recent years are dearomatised kerosenes (D30, D40, D60, with or without added densifier) (Talalay and Gundestrup, 2002), butyl acetate, and the aliphatic ester Estisol series, with or without Coasol (Sheldon et al., 2014). Any such fluid freely coats the outside of all deep cores and remains on the surface throughout transport and storage. However, the advantage of solid ice is that it is impermeable if no cracks penetrate from the outside to the inner core. Therefore, it is possible to shave the outer layer of ice that was coated in fluid, or that has been in contact with plastic bags or organic materials, to obtain clean inner material. A faster way to obtain uncontaminated ice samples for analysis of organic impurity contents is to melt the ice in a way so only the clean inner part is used for the analysis. In this case only the inner section which was never in contact with ambient air and drilling fluid is used and is pumped into a warm lab where it is aliquoted, whereas the possibly contaminated water from the outer part is rejected.

Firn (permeable material that has not yet consolidated into ice, mostly found in the upper 60–100 m of a core depending on the site) and near-surface snow are often more challenging to sample in the field than the deeper, solid ice. Although drilling fluid is not present in the borehole when firn cores are drilled, the cores are vulnerable to contamination from a wide range of other sources: lubricants that may have been used on drill components, spilled liquid and organic vapours in the air (e.g. from fuel used in generators and vehicles and in the laboratories), plastics (bags and bottles) used to contain the ice, and contamination from gloves and other materials used by drillers and core processors. Because of the permeable nature of firn, these materials can penetrate deep into the core (including the entire ~5 cm radius) through liquid ingress and vapour diffusion. The same issues arise with sampling of surface snow, though collecting large blocks from which more material can be discarded may mitigate the problem. Some molecules may be partly volatile (a process that has been suggested to cause loss from surface snow *in situ* (Gregor, 1991)) and so sample preservation should include preventing exposure to temperature gradients (i.e. warmer temperatures during transport and storage compared to sampling conditions).

It is difficult to determine what precautions are necessary when sampling snow and firn for individual organic compounds, without first testing to discover whether those individual target molecules, or related interferences, are present in possibly contaminating media such as plastic bags or the atmosphere. However, general studies of organic material in firn and snow argue for the necessity of storing snow samples in airtight and recently pre-cleaned glass bottles (Legrand et al., 2013) or stainless-steel containers (Domine et al., 2007; Giannarelli et al., 2017; Gustafsson et al., 2005) and avoiding plastics, except perhaps for a low permeability grade of Teflon such as PFAs (i.e. perfluoroalkoxy alkanes). Wrapping firn cores in aluminium foil instead of, or as well as, plastic is also a precautionary measure, which also limits the possibilities for photochemical degradation of some molecules. Maintaining samples in the solid phase rather than as melted samples is preferable for long term storage. However, melted samples can be spiked with HgCl_2 to prevent microbial degradation (Kawamura et al., 2012). For some organic molecules, such as MSA, it has been shown that diffusional loss through solid ice can be prevented if samples are refrozen as discrete samples (Abram et al., 2008).

In the laboratory, similar precautions are necessary in order to avoid additional contamination from ambient air and possible loss

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