



## Free amino acids in the Arctic snow and ice core samples: Potential markers for paleoclimatic studies



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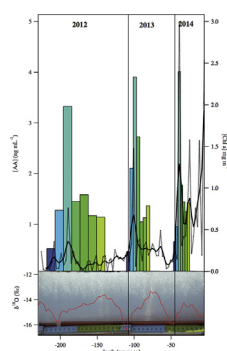
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### HIGHLIGHTS

- Free L- and D-amino acids in Arctic snow and firn samples were determined.
- Marine chlorophyll-a with amino acids in the ice core have a positive correlation.
- Amino acids in the ice samples could represent the oceanic phytoplankton abundance.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The role of oceanic primary production on climate variability has long been debated. Defining changes in past oceanic primary production can help understanding of the important role that marine algae have in climate variability. In ice core research methanesulfonic acid is the chemical marker commonly used for assessing changes in past primary production. However, other organic compounds such as amino acids, can be produced and emitted into the atmosphere during a phytoplankton bloom. These species can be transported and deposited onto the ice cap in polar regions. Here we investigate the correlation between the concentration of chlorophyll-a, marker of marine primary production, and amino acids present in an ice core.

For the first time, free L- and D-amino acids in Arctic snow and firn samples were determined by a sensitive and selective analytical method based on liquid chromatography coupled with tandem mass spectrometry. The new method for the determination of free amino acids concentrations was applied to firn core samples collected on April 2015 from the summit of the Holtedahlfonna glacier, Svalbard (N 79°08.424, E 13°23.639, 1120 m a.s.l.). The main results of this work are summarized as follows: (1) glycine, alanine and proline, were detected and quantified in the firn core samples; (2) their concentration profiles, compared with that of the stable isotope

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$\delta^{18}\text{O}$  ratio, show a seasonal cycling with the highest concentrations during the spring and summer time; (3) back-trajectories and Greenland Sea chlorophyll-*a* concentrations obtained by satellite measurements were compared with the amino acids profile obtained from ice core samples, this provided further insights into the present results. This study suggests that the amino acid concentrations in the ice samples collected from the Høltedahlfonna glaciers could reflect changes in oceanic phytoplankton abundance.

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## 1. Introduction

Amino acids are a fraction of organic matter in marine and freshwater ecosystems that can be used as nitrogen sources by bacteria and by numerous phytoplankton species (Berman and Bronk, 2003). They are released from living phytoplankton or by cellular lysis of senescent algae (Bronk et al., 1994). Amino acids can also be produced and released by terrestrial plants, and from the organic matter present in the soil (Jonsson et al., 2007). Some research has also focussed on the characterization of free amino acids in atmospheric aerosols (Matos et al., 2016). Amino acids are an active component of organic nitrogen in atmospheric aerosol due to their important role in radiative forcing at the Earth's surface and hence in climate (Chan et al., 2005). Some amino acids have been shown to enhance the ice nucleating ability of atmospheric particles (Szyrmer and Zawadzki, 1997) or to act as cloud condensation nuclei (Kristensson et al., 2010). Several amino acids have been found in continental aerosol and are mainly produced by plants, pollen and algae, as well as fungi and bacterial spores (Mace et al., 2003; Milne and Zika, 1993; Scheller, 2001; Zhang and Anastasio, 2003). The concentration of these compounds in the atmosphere could be influenced by additional abiotic sources, such as volcanic emissions (Scalabrin et al., 2012) or biomass burning (Chan et al., 2005; Mace et al., 2003). However, one of the most important sources of free amino acids in the atmosphere, particularly in polar areas, is marine emission through bubble bursting and wave breaking. Polar regions are extraordinary laboratories for investigating the natural sources of aerosol, and their connected processes, due to their distance from anthropogenic and continental emission. The presence of pollutants after long range atmospheric transport is limited to compounds with a great atmospheric stability, such as black carbon (Eleftheriadis et al., 2009; Hegg et al., 2009), persistent organic pollutants (Barbaro et al., 2016; Kallenborn et al., 2012; Vecchiato et al., 2015) and heavy metals (Bazzano et al., 2016).

In a previous study on Antarctic aerosol, amino acids were investigated to characterize their presence in the water soluble organic fraction of marine aerosol and in the particles emitted from the ocean (Barbaro et al., 2015). Particle size distributions obtained from the Antarctic aerosol suggested that the main source these compounds could be marine emissions. Additionally, thanks of the greater stability of amino acids, such as glycine and alanine, and their presence over the Antarctic plateau (Barbaro et al., 2015), these compounds could be used as biogenic markers to describe marine aerosol aged during atmospheric long range transport. Similar studies by Scalabrin et al. (2012) on Arctic aerosol samples reinforce this hypothesis. Their results are in agreements with Antarctic studies, suggesting that amino acids in the polar regions may be mainly emitted from marine sources, particularly during the spring.

Generally, snow deposition reflects the average atmospheric composition and, in absence of snow melting during the summer periods, the snow preserves information on atmospheric conditions around the ice cap. In polar areas, glacier ice is considered to be an archive of past atmospheric composition and ice cores are frequently utilised to extract the paleoclimatic information. Advances in analytical techniques are essential to discover and to investigate the use of new compounds as atmospheric markers for specific environmental processes such as oceanic primary production. In ice cores studies methanesulfonic acid (MSA) has been used as a tracer to evaluate past changes in marine

productivity (Isaksson et al., 2005; O'Dwyer et al., 2000). MSA is an atmospheric oxidation product of dimethyl sulphide produced by marine biota, and thus may indirectly reflect larger-scale changes in primary production. MSA is produced by the marine biota but its concentration could be influenced by other environmental parameters such as changes in sea ice extension (Curran et al., 2003; Isaksson et al., 2005). Additionally Abram et al. (2008) demonstrated that although MSA concentrations were preserved in cold storage conditions for up to 15 years, MSA is able to diffuse through solid ice cores. The determination of other compounds, able to give an indication of past marine productivity, is crucial. As changes in primary production could have influenced  $\text{CO}_2$  sequestration into the ocean and hence affect the radiative forcing of the Earth's atmosphere. Amino acids are such a class of compounds, they are linked to oceanic primary production and their presence in the Antarctic and Arctic aerosol suggests that they can be preserved in the ice archive and be used to investigate changes in the past marine productivity.

The aim of this work was to develop an analytical method based on a coupled method between liquid chromatography with tandem mass spectrometry for the determination of amino acids in snow and ice core samples from Svalbard. Amino acid determination in polar snow and ice samples is challenging since their concentrations are in the range of nanograms per gram of ice, therefore the potential for contamination during sample manipulation is higher than for other species.

The method developed was applied to a shallow firn core of 5 m depth recovered in April 2015 from Høltedahlfonna (HDF) glacier (Svalbard Archipelago) and to snow surface samples collected close to the Ny-Ålesund research facility, to evaluate their behaviour after deposition onto the snow surface. The shallow core has been dated using a  $\delta^{18}\text{O}$  profile and the glacier mass balance data suggests it covers a time period from spring 2015 to the early winter of 2012, covering 3 full years of accumulation. The amino acid shallow core results have been compared with the oceanic phytoplankton abundance of the Greenland Sea, Barents Sea and the sum of the ocean area surrounding the Svalbard archipelago (72°N–84°N, 25°W–50°E) and the results have been discussed in the context of a back trajectory of air masses analysis.

## 2. Experimental section

### 2.1. Study site

HDF glacier is the largest ice field (c.a. 300 km<sup>2</sup>) on the north-western Spitsbergen island, Svalbard, Norway, about 40 km from the Ny-Ålesund station. It is distributed over an elevation range of 0–1241 m a.s.l. (Fig. 1). Despite their location at high latitudes, the Svalbard Islands have a relatively mild climate due to the intrusion of the North Atlantic Current along their western coast and their location on the pathway of both Arctic and North Atlantic cyclones. About 60% of the Svalbard archipelago is covered by glaciers and it is surrounding by oceans (Nuth et al., 2010).

### 2.2. Sampling and samples processing

In April 2015, a 5 m deep firn core was recovered from the summit of the HDF glacier (N 79°08.424', E 13°23.639', 1120 m a.s.l., Fig. 1) using a

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