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# Methanesulphonic acid (MSA) stratigraphy from a Talos Dome ice core as a tool in depicting sea ice changes and southern atmospheric circulation over the previous 140 years

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## **ABSTRACT**

Firn core methanesulphonic acid (MSA) stratigraphy from Talos Dome (East Antarctica) was compared with anomalies of the satellite-measured sea ice extent (1973–1995) in the Ross Sea and Wilkes Land oceanic sector. In spite of the sparseness of sea ice data, the MSA maxima fit with many positive sea ice anomalies in the Ross Sea. This evidence suggests that marine biogenic activity enhanced by large sea ice cover is an important, but not exclusive, factor in controlling MSA concentration in snow precipitation at Talos Dome. Other than source intensity, differences in regional atmospheric transport mechanisms affect the arrival of MSA-rich aerosol at Talos Dome. To clarify the role of transport processes in bringing biogenic aerosol to Talos Dome, a spectral analysis was applied to the MSA, SOI (South Oscillation Index), and SAM (Southern Annular Mode) record. Synchronicity or phase shift between the chemical signature and atmospheric circulation modes were tested. The variations in the MSA profile have a periodicity of 6.9, 4.9, 3.5, and 2.9 years. The 6.9 and 2.9 year periodicities show a strong positive correlation and are synchronous with corresponding SOI periodicity. This variability could be related to an increase in MSA source intensity (by dimethylsulphide from phytoplanktonic activity) linked to the sea ice extent in the Ross Sea area, but also to an increased strength in transport processes. Both of these factors are correlated with La Niña events (SOI positive values). Furthermore, SAM positive values are related to an increased sea ice extent in the Ross Sea sector and show two main periodicities 3.3 and 3.8 years. These periodicities determine the MSA variability at 3.5 years. However, the effect of intensification of the polar vortex and the consequent reduction in transport process intensity, which reduce the delivery of air masses enriched in MSA from oceanic areas to Talos Dome, make the effect of the SAM on the MSA concentration at Talos Dome less active than the SOI. In this way, snow deposition at the Talos Dome records larger MSA concentration by the combined effects of increased source emissions and more efficient transport processes. The MSA record from Talos Dome can therefore be considered a reliable proxy of sea ice extent when the effect of changes in transport processes in this region of Antarctica is considered. Over the previous 140 years, these conditions occur with a periodicity of 6.9 years.

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### 1. Introduction

The interaction between oceanic biogenic productivity and global climate is one of the most intriguing and controversial aspects in understanding the complex relationship between climate forcing and environmental feedback. Changes in phytoplanktonic activity are influenced by variations in solar irradiance, Sea Surface Temperature (SST), and nutrient availability. Oceanic biota metabolic processes are likely to affect climate through direct and indirect effects ([Charlson et al., 1987; Andreae and Crutzen,](#page--1-0) [1997\)](#page--1-0). These effects are due to biogenic aerosol production and can be influenced by changes in cloud coverage (in turn, affecting albedo and the hydrological cycle), uptake of  $CO<sub>2</sub>$  at the atmosphere–seawater interface,  $CO<sub>2</sub>$  storing via oceanic biological pump, and CH4 emission. In this way, changes in phytoplanktonic productivity caused by external forcing, such as variations in oceanic and atmospheric circulation, sea ice extent and nutrients or oligo-element supply (from changes in up welling areas or

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continental dust deposition on the seawater surface), can exert positive or negative feedback, which can amplify or mitigate climate changes on a regional or global scale.

While the climate–ocean relationship is generally recognised in a qualitative sense, the quantitative estimation of the contribution of oceanic biogenic activity to climate tuning at present and in the past is still under discussion. The sulphur-cycle compounds emitted into the atmosphere by algal metabolic processes are assumed to constitute the most effective source of Cloud Condensation Nuclei (CCN) in remote oceanic regions, although it is now recognised that many other non-sulphuric marine biotic compounds can affect CCN formation in the atmosphere ([Meskhidze and Nenes, 2006\)](#page--1-0). Gaseous dimethylsulphide emitted into the atmosphere is oxidised into  $H<sub>2</sub>SO<sub>4</sub>$  and methanesulphonic acid (MSA) [\(Gondwe et al., 2003](#page--1-0) and references therein). A large Henry constant, which defines the affinity toward atmospheric moisture, results in a highly efficient gas-to-particle conversion processes making these compounds the dominant source of sub-micrometric secondary aerosol in remote marine regions [\(Brimblecombe, 1996\)](#page--1-0).

Antarctica is encircled by a highly biologically productive ocean and is a major site for the production of the cold and deep water that drives ocean circulation. Antarctica is also a major participant in the Earth's albedo dynamics and is an important driving component for atmospheric circulation. For these reasons, ice core stratigraphies of oceanic biogenic markers (mainly sulphate and methanesulphonate) have been used in reconstructing cause and effect relationships between climate forcing and environmental feedback in the past. While a general picture is now widely accepted, specific features of these interactions are still poorly understood. This is mainly due to uncertainties in the reliability of biogenic marker stratigraphies measured along ice cores for recording past changes in phytoplanktonic activity ([Saigne and](#page--1-0) [Legrand, 1987; Wolff et al., 2006\)](#page--1-0). Indeed, sulphate is produced by several other sources, such as sea spray, continental dust, and volcanic emissions. Additionally, MSA, which only arises from the oxidation of biogenic DMS (e.g. [Gondwe et al., 2003](#page--1-0)), is affected by post-depositional processes in the snow layers [\(Curran et al., 2002;](#page--1-0) [Legrand et al., 1996; de Angelis and Legrand, 1995; Wagnon et al.,](#page--1-0) [1999](#page--1-0)). Therefore, changes in the MSA stratigraphies that were previously attributed to variation in oceanic productivity ([Legrand](#page--1-0) [et al., 1991\)](#page--1-0) were really caused by changes in snow accumulation rates, snow acidity, and atmospheric load of dust particles (able to fix MSA as non-volatile salts). More recent evidence from highresolution stratigraphies of sulphate and MSA fluxes along the ice core drilled at Dome C (East Antarctica), in the framework of the European Project for Ice Coring in Antarctica (EPICA), revealed that oceanic productivity was not significantly changed during glacial and interglacial periods ([Wolff et al., 2006\)](#page--1-0). This result weakened the generally accepted consideration that higher phytoplanktonic growth (by atmospheric deposition of oligo-elements) in High-Nutrient Low-Chlorophyll (HNLC) oceanic areas was a common feature in cold climatic stages and could have exerted a powerful feedback on the climate during glacial inceptions or terminations (Röthlisberger et al., 2004 and references therein).

Furthermore, the relationship between DMS production (and, by extension, the MSA concentration in the snow deposition) and regional meteorological conditions (SST, atmospheric circulation modes, and sea ice) is still controversial.

On one side, changes in MSA deposition in Antarctica could be attributed to a higher phytoplanktonic activity (i.e., larger DMS emission into the atmosphere) primed by larger sea ice extent. It is important to note that the capability of reconstructing past sea ice extension from ice core stratigraphy deserves increasing attention due to the relevant and complex role played by sea ice in the climate system. Sea ice affects the salinity through freezing and melting processes and temperature via albedo of superficial seawater, thereby influencing Antarctic bottom water formation and global ocean circulation ([Keeling and Stephens, 2001\)](#page--1-0). The ice cover also limits the atmosphere/seawater exchange of  $CO<sub>2</sub>$ , which affects the positive feedback of this greenhouse gas on the climate, especially during periods of glaciation and deglaciation ([Stephens](#page--1-0) [and Keeling, 2000](#page--1-0)).

On the other hand, changes in the efficiency of transport processes, which transports marine air masses toward the internal areas of the continent (hemispheric and regional circulation modes), could rule MSA deposition on coastal and inner areas of the continent.

To clarify these aspects, MSA stratigraphies from ice cores drilled in Antarctic coastal sites, where the snow accumulation rate is sufficient enough to preserve its annual record, have to be compared with contemporaneous changes in sea ice extent and the atmospheric circulation mode. This knowledge is crucial in order to reliably interpret the MSA stratigraphies from the past.

In this paper, the periodicity in the MSA stratigraphy from Talos Dome (Northern Victoria Land, East Antarctica), Antarctic Circumpolar Wave (ACW) (e.g. [White and Tourre, 2003](#page--1-0) and references therein), SOI (e.g. [Turner, 2004](#page--1-0) and references therein), and Antarctic Oscillation or Southern Annular Mode (AAO or SAM) (e.g. [Hall and Visbeck, 2002; Thompson and Solomon, 2002](#page--1-0)) were compared with the aim of understanding how the most effective atmospheric circulation modes in Antarctica can affect MSA snow deposition at Talos Dome. This information will be used to reconstruct changes in sea ice extent and atmospheric circulation modes from stratigraphies of a deep ice core (about 1600 m depth) now being carried out at the same site by the TALDICE project that is assumed to cover all of the previous glacial–interglacial cycle.

### 2. Data and methods

#### 2.1. Drilling site

Talos Dome (72°48'S, 159°06'E; 2316 m a.s.l.; 290 and 250 km from the Pacific and Ross Sea coasts, respectively) is a coastal dome in Northern Victoria Land on the edge of the East Antarctic ice sheet (Fig. 1). It is located on the ice divide between accumulation basins



Fig. 1. Schematic map of Antarctica with an indication of the drilling site (TD).

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