



Anomalous high arsenic concentration in a West Antarctic ice core and its relationship to copper mining in Chile



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ABSTRACT

Arsenic variability records are preserved in snow and ice cores and can be utilized to reconstruct air pollution history. The Mount Johns ice core (79°55'S; 94°23'W and 91.2 m depth) was collected from the West Antarctic Ice Sheet in the 2008/09 austral summer. Here, we report the As concentration variability as determined by 2137 samples from the upper 45 m of this core using ICP-SFMS (CCI, University of Maine, USA). The record covers approximately 125 years (1883–2008) showing a mean concentration of 4.32 pg g⁻¹. The arsenic concentration in the core follows global copper mining evolution, particularly in Chile (the largest producer of Cu). From 1940 to 1990, copper-mining production increased along with arsenic concentrations in the MJ core, from 1.92 pg g⁻¹ (before 1900) to 7.94 pg g⁻¹ (1950). In the last two decades, environmental regulations for As emissions have been implemented, forcing smelters to treat their gases to conform to national and international environmental standards. In Chile, decontamination plants required by the government started operating from 1993 to 2000. Thereafter, Chilean copper production more than doubled while As emission levels declined, and the same reduction was observed in the Mount Johns ice core. After 1999, arsenic concentrations in our samples decreased to levels comparable to the period before 1900.

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1. Introduction

Arsenic (As) is a metalloid that is widely distributed in the earth's crust. It occurs primarily in the sulfide form in complex minerals that contain silver, lead, copper, nickel, antimony, cobalt, and iron. Arsenic is present in more than 200 mineral species, the most common of which is arsenopyrite (FeAsS). The terrestrial abundance of arsenic is approximately 5 mg kg⁻¹ (WHO, 2001). Arsenic can be released into the atmosphere as a result of natural processes and human activities (Mandal and Suzuki, 2002). Volcanic emissions are the most important natural source, but biological activity and physical weathering (e.g., erosion and landslides) can also release arsenic. Anthropogenic sources include the use of pesticides, fossil fuel combustion, mining and smelting of non-ferrous metals (Merian, 1984).

Anthropogenic sources are estimated to account for nearly

24,000 tons of arsenic emitted to the global atmosphere per year (IARC, 2012). Approximately 60% of these emissions originate from Cu-smelting and coal combustion (Matschullat, 2000). In some urban and highly industrialized areas, less than 2% of the atmospheric arsenic inputs originate from natural sources.

Contamination of arsenic from mining operations is a serious ongoing issue in many localities throughout the world. In Chile, the high arsenic concentration in copper ore has caused serious environmental problems, forcing the national government to impose arsenic emission limits for mining (Newbold, 2006). Consequently, significant decreases in the amount of waste contaminated with arsenic and in atmospheric emissions have been observed since the 1990s.

Anthropogenic arsenic pollution has significantly altered the natural geochemical cycles in many regions of the earth's surface. These modifications are recorded in snow and ice cores and can be used to study past atmospheric composition changes (Hong et al., 2012). Some studies, especially from the Arctic (Krachler et al., 2009), South America (Hong et al., 2004), and the Himalayas (Hong et al., 2009) have documented arsenic enrichment in recent

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decades. These results reflect the hemispheric scale of human interference in the environmental mobilization of this element.

Detailed long-term arsenic data in Antarctica are rare, largely because of their extremely low concentrations, requiring ultra clean protocols throughout fieldwork sampling and in the laboratory and the use of highly efficient analytical methods for the direct determination of elemental concentrations down to the picogram per gram level ($1 \text{ pg g}^{-1} = 10^{-12} \text{ g g}^{-1}$) (Krachler et al., 2005).

Here, we present the arsenic concentration variability from 1883 to 2008 in the Mount Johns (MJ) ice core collected in the West Antarctic Ice Sheet (WAIS) during summer 2008/2009. Ice core sections were subsampled using a careful decontamination protocol in a cold room ($-20 \text{ }^\circ\text{C}$) and melted in a continuous melting system (class 100 clean room). Subsamples were analyzed by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS).

2. Methodology

2.1. Sampling site

The Mount Johns (MJ) ice core ($79^\circ 55' 28''\text{S}$, $94^\circ 23' 18''\text{W}$, and 91.20 m depth) was recovered in the austral summer of 2008/2009 near the WAIS ice divide (Fig. 1). MJ is approximately 400 km southwest of the Ellsworth Mountains; the ice thickness at the ice core site reaches 2115 m, the average accumulation rate is

$0.21 \text{ m H}_2\text{O equivalent yr}^{-1}$ and the mean surface temperature (measured at a depth of 12 m) is $-33 \text{ }^\circ\text{C}$.

This drilling site was selected considering the following characteristics: (1) it has a relatively high accumulation rate, (2) it is located on a drainage basin divide (separating the Pine Island Glacier drainage basin from the one that flows to the Filchner-Ronne Ice Shelf), (3) it is in an area of air mass confluence (air masses from the Weddell, Amundsen and Bellingshausen seas) and, (4) no ice cores have been drilled nearby.

Drilling was performed using FELICS (Fast Electromechanical Lightweight Ice Coring System) equipment, which can reach a maximum extraction depth of 160 m in ice (Ginot et al., 2002). The MJ core (8.5 cm diameter) was cut into sections of approximately 1 m in length, packed in polyethylene bags and then stored in high-density Styrofoam boxes and transported by air to Punta Arenas (Chile). Then, it was sent to the Climate Change Institute at the University of Maine (USA), where it was sub-sampled and analyzed.

2.2. Laboratory subsampling

Sample preparation and decontamination were performed at the Climate Change Institute (CCI), University of Maine in Orono, USA. Decontamination of the MJ ice core was carried out in a certified cold room ($-20 \text{ }^\circ\text{C}$) of class 100. The outer layer of the snow, firn and ice, was scraped (between 2 and 4 mm) using a clean ceramic knife to prevent contamination (procedure performed

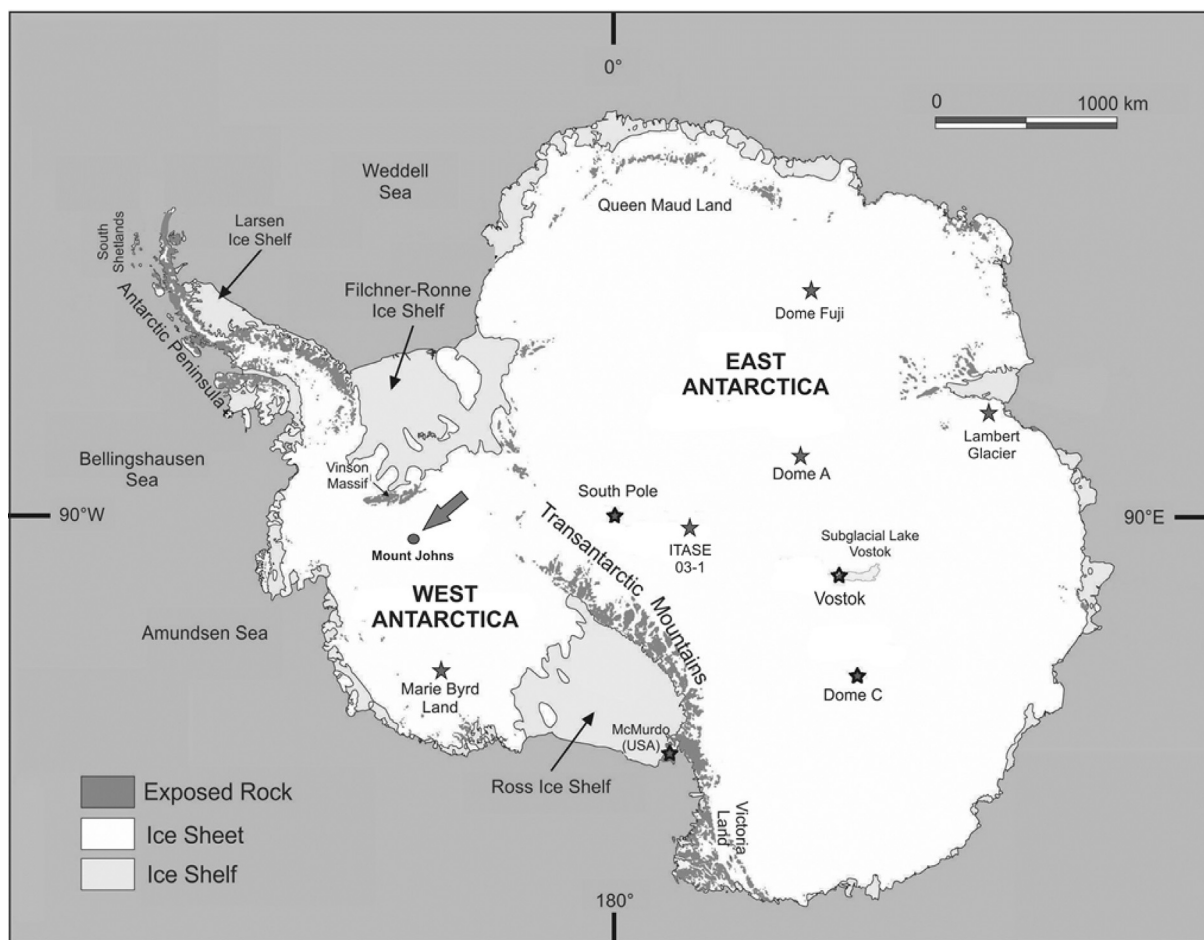


Fig. 1. Map of Antarctica showing the site of the Mount Johns ice core (arrow) and other places discussed in the text (figure adapted from the U.S. Geological Survey, <http://lima.usgs.gov/>).

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