

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



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ARTICLE INFO

Article history:

Received 16 July 2015

Received in revised form

9 November 2015

Accepted 12 November 2015

Available online 19 November 2015

Keywords:

Arsenic

Ice core

Antarctica

ICP-SFMS

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

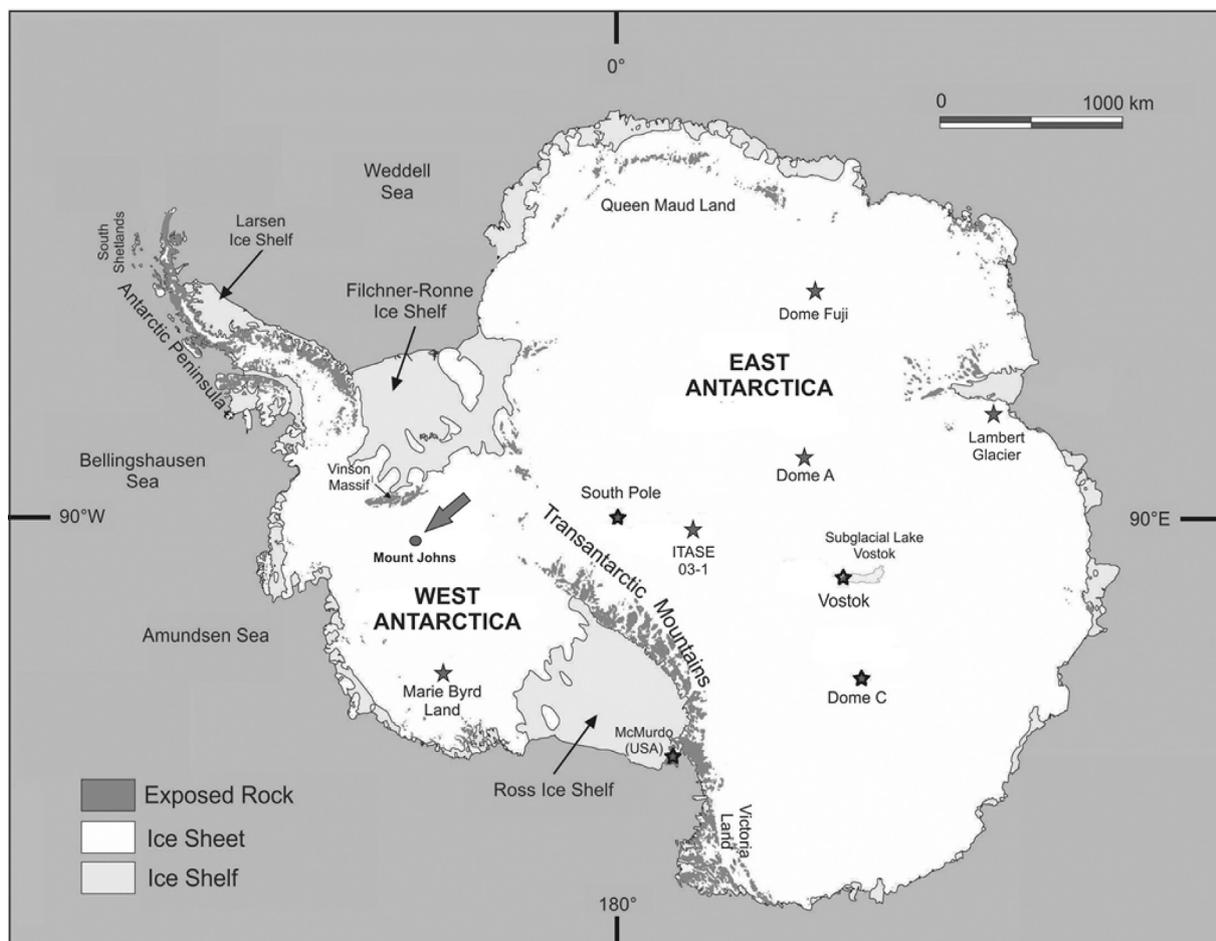


Fig. 1. Map of Antarctica showing the site of the Mount Johns ice core (arrow) and other places discussed in the text (figure adapted from the U.S. Geological Survey, <http://lima.usgs.gov/>).

according Tao et al., 2001). The ends of each section were removed because they are the parts most susceptible to contamination. The core was melted using a Continuous Ice Core Melter System developed by CCI researchers from the model proposed by Röthlisberger et al. (2000). This system uses fraction collectors to gather discrete, high resolution, continuous and co-registered meltwater samples. According to Osterberg et al. (2006), this system can simultaneously and continuously sample the ice core for three different glaciochemical analyses: major elements by ion chromatography (IC), trace elements by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and stable isotopes by isotope ratio mass spectrometry (IRMS). Our samples were collected into acid-cleaned (Optima HNO₃) LDPE vials and acidified to 1% with double-distilled HNO₃ before analysis.

2.3. Determination of arsenic by ICP-MS

Trace element concentrations in 2137 samples (corresponding to the upper 45 m of the MJ ice core) were determined using the CCI Thermo Electron Element2 ICP-SFMS coupled to an ESI model SC-4 autosampler. Working conditions and measurement parameters are described in Table S1 (Supporting Information). The use of an ESI Apex high-sensitivity inlet system increases instrument sensitivity and reduces oxide formation in the plasma, lowering the detection limits and allowing less abundant isotopes to be measured. The ICP-SFMS is calibrated daily with five standards that bracket the expected sample concentration range.

Arsenic has only one isotope ⁷⁵As, which has several potential isobaric interferences. Among them are, ³⁵Cl⁴⁰Ar, ³⁹K³⁶Ar, and ⁵⁹Co¹⁶O, the most significant of these is ³⁵Cl⁴⁰Ar. These interferences can be eliminated by analyzing As in high resolution, however using HR lowers sensitivity and As is present at very low concentrations. In our method we analyze As in both low resolution and high resolution and the data are evaluated to see if there is a bias in the low resolution data. If the data from the two resolutions agree then the low resolution is used because the higher sensitivity in low resolution gives more precise data.

Although there is no certified reference material for trace elements in polar snow and ice, the analyzed samples were certified with water reference material (SLRS-4, National Research Council Canada, Ottawa, Canada) to ensure the concentrations within the certification range, confirming the accuracy of this method (details in Osterberg et al., 2006).

As this study is focused on the arsenic concentration variations, the detection limit for As was defined as three times the standard deviation of blanks samples (10 samples were used), which was 0.32 pg g⁻¹.

3. Results and discussion

3.1. Ice core dating

The MJ ice core record (upper 45 m) was dated by annual layer counting based on seasonal variations of Na and S concentrations (measured by ICP-SMS), as illustrated in Fig. 2; seasonal peaks were identified and dated sequentially. Most of the Na in Antarctic snow precipitation originates from open ocean sources. Peaks in Na concentrations in the continental Antarctic occur primarily in winter/spring due to more intense atmospheric circulation and transport at this time of the year (Legrand and Mayewski, 1997). Layer dating by this type of counting is reliable in polar ice cores, as the original deposited snow sequence is preserved because melting, percolation and refreezing processes are rare in the Antarctic and Greenland ice sheets (Cuffey and Paterson, 2010).

Major historical volcanic eruptions, such as Pinatubo (1991),

Agung (1963), Santa Maria (1902), and Krakatoa (1883), were identified by large sulfur concentration peaks and were used as absolute time horizons during the timescale elaboration. Based on these data, the upper 45 m of the MJ ice core cover the period from 1883 to 2008 A.D.

3.2. Elemental concentration variations for the period 1883–2008 A.D.

Fig. 3 shows As concentrations from 1883 to 2008 A.D., as determined in the MJ ice core. The mean concentration is 4.32 pg g⁻¹, ranging from 0.20 to 20.28 pg g⁻¹. The pre-1900 period was chosen as the reference background because anthropogenic inputs were considered to be potentially smaller. Furthermore, the concentration variability is more pronounced in the following decades.

Three well-defined periods are found when comparing the MJ arsenic concentrations with ice core data from other regions (Table 1): (1) pre-1900, showing the lowest levels that are considered to be a natural reference (background) in which the anthropogenic influence was not pronounced; (2) a second period (1901–1998) with the greatest amplitude variability, with alternating periods of high concentrations of arsenic, followed by low concentration intervals; (3) post-1999, marked by a strong concentration decrease.

3.3. Crustal and oceanic enrichment factors

Arsenic contributions from primary natural sources in each sample were estimated using the following indicators: non-sea-salt-sulfate (nss-SO₄²⁻) for volcanic emissions, aluminum (Al) for rock and soil dust, and sea-salt-sodium (ss-Na) for sea-salt spray. The soil and rock dust contribution for As concentrations are given by the crustal Enrichment Factor (EF_c) using the following equation (Osterberg, 2007):

$$EF_c = \frac{As_{ice}/Al_{ice}}{As_{ref}/Al_{ref}}$$

where As_{ice} is the arsenic concentration in the sample, Al_{ice} is the aluminum concentration in the sample, and As_{ref} and Al_{ref} are the arsenic and the aluminum concentrations in the reference material, respectively. Aluminum is used as the reference element in this work because it is one of the major constituents of the earth's crust (Planchon et al., 2002). The mean elemental concentration used for reference is the average composition of the upper continental crust taken from the literature (Wedepohl, 1995).

Fig. 4 shows the arsenic EF_c values for the MJ ice core. Usually, elements with EF_c lower than 10 are considered to be non-enriched and predominantly have a crustal dust origin (Duce and Zoller, 1975). A high EF_c (average 104.58) during the study period indicates considerable As contributions from other sources in the MJ core. Possible As contributions from marine aerosols were estimated using the ocean enrichment factor (EF_o) from the following equation (Osterberg, 2007):

$$EF_o = \frac{As_{ice}/Na_{ice}}{As_{ref}/Na_{ref}}$$

where As_{ice} is the As concentration in the sample, Na_{ice} is the Na concentration in the sample, and As_{ref} and Na_{ref} are the As and Na concentration in the reference material. Sodium is used as the reference element because it is the main sea salt constituent (Weller et al., 2008; Dixon et al., 2013). We used the average

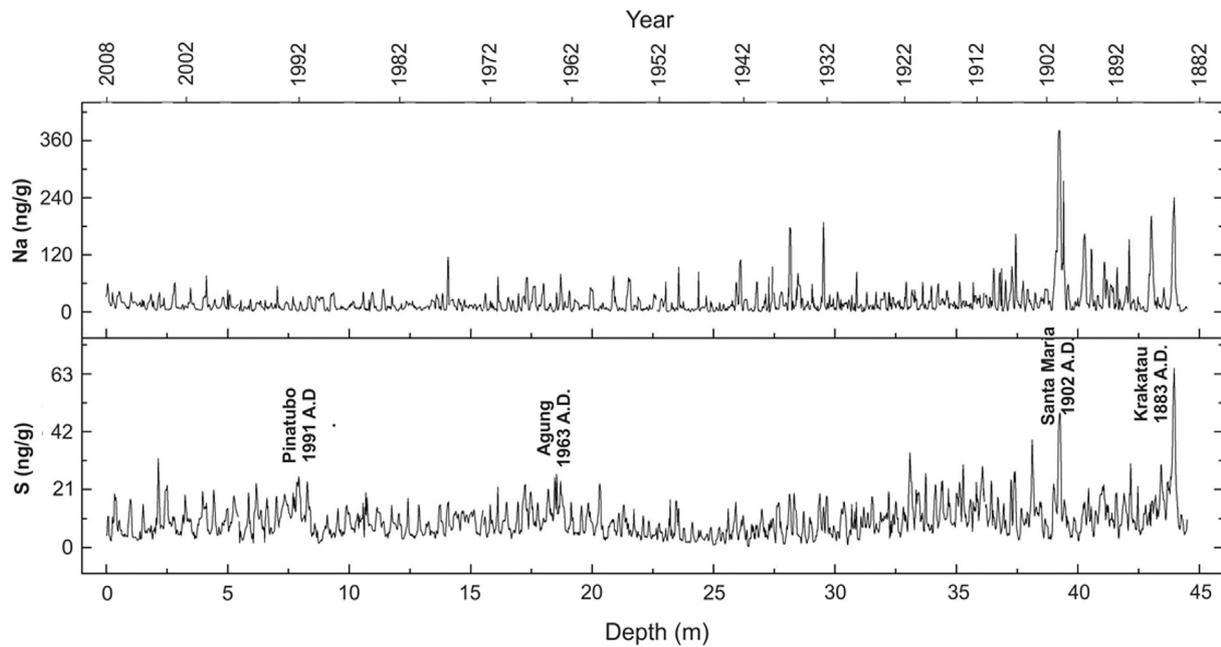


Fig. 2. Mount Johns ice core timescale based on the Na and S concentration variations and major volcanic events in the period.

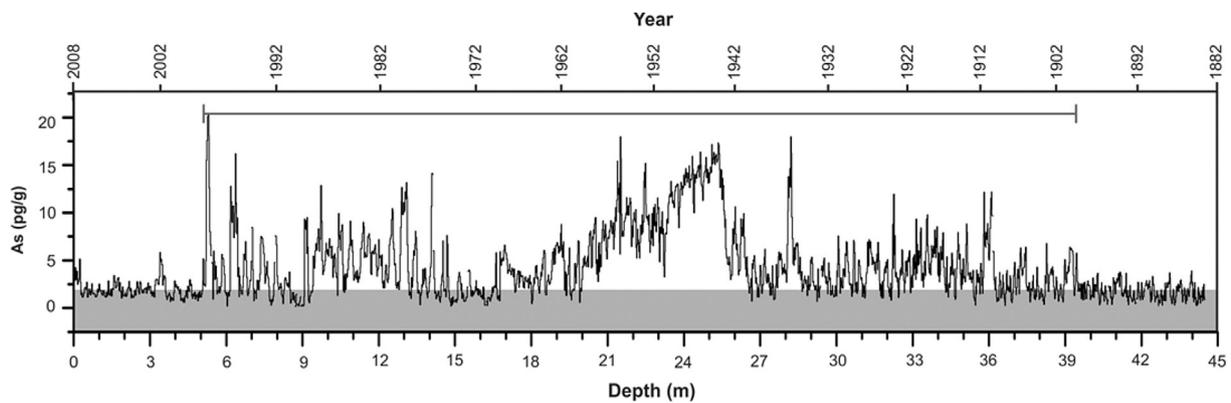


Fig. 3. Arsenic concentration (pg g^{-1}) profile. In gray, the concentration levels less than 1.9 pg g^{-1} are considered to be natural emissions (background). The line above the graph marks the period with increased concentrations of arsenic.

Table 1
Mount Johns arsenic concentrations (mean values) compared with other sites.

| Location | Time period covered | Mean concentration As (pg g^{-1}) | | | Reference |
|---|---------------------|--|--------------|---------------|------------------------|
| | | Before 1900 AD | 1901–1998 AD | After 1999 AD | |
| Mount Johns, Antarctica ($79^{\circ}55'28''\text{S}$; $94^{\circ}23'18''\text{W}$) | 1883–2008 | 1.92 | 4.99 | 1.94 | This work |
| Fuji Dome, Antarctica ($77^{\circ}18'\text{S}$; $39^{\circ}47'\text{E}$) | 1956–2008 | – | 12.9 | 3.5 | Hong et al., 2012 |
| Glacier Lambert, Antarctica ($70^{\circ}50'07''\text{S}$; $77^{\circ}04'29''\text{E}$) | 1998–2002 | – | 10 | – | Hur et al., 2007 |
| ITASE – 03/1 ($86^{\circ}50'24''\text{S}$; $95^{\circ}18'36''\text{E}$) | 1955–1975 | – | 3.25 | – | Dixon et al., 2013 |
| Mount Everest, Himalaya ($28^{\circ}03'\text{N}$; $86^{\circ}96'\text{E}$) | 1200–2002 | 36 | 39 | 45 | Hong et al., 2009 |
| Kilimanjaro, Africa ($3^{\circ}04.6'\text{S}$; $37^{\circ}21.2'\text{E}$) | 1750–1950 | 15.75 | 52.75 | – | Gabrielli et al., 2014 |
| Colle Gnifetti, Alps ($45^{\circ}55'50.4''\text{N}$, $07^{\circ}52'33.5''\text{E}$) | 1700–1992 | 19 | 94 | – | Gabrielli, 2008 |
| Sajama, Andes ($18^{\circ}06'\text{S}$; $68^{\circ}53'\text{W}$) | 1700–1988 | 900 | 1418 | – | Hong et al., 2004 |

composition of ocean water (Lide, 2005) as a reference for the ocean elemental abundances. Fig. 4 shows a highly enriched As content relative to ocean water over the entire record, also indicating a low marine contribution. The mean EFO value for As is 2057.63.

Even without significant natural contributions to arsenic

concentrations, we calculated the marine and crustal fraction according to the following formula (Dixon et al., 2013):

$$X_o = \text{Na}_{\text{ice}} \left(\text{As}_{\text{ref}} / \text{Na}_{\text{ref}} \right)$$

where X_o is the fraction of the oceanic origin of the element, Na_{ice} is

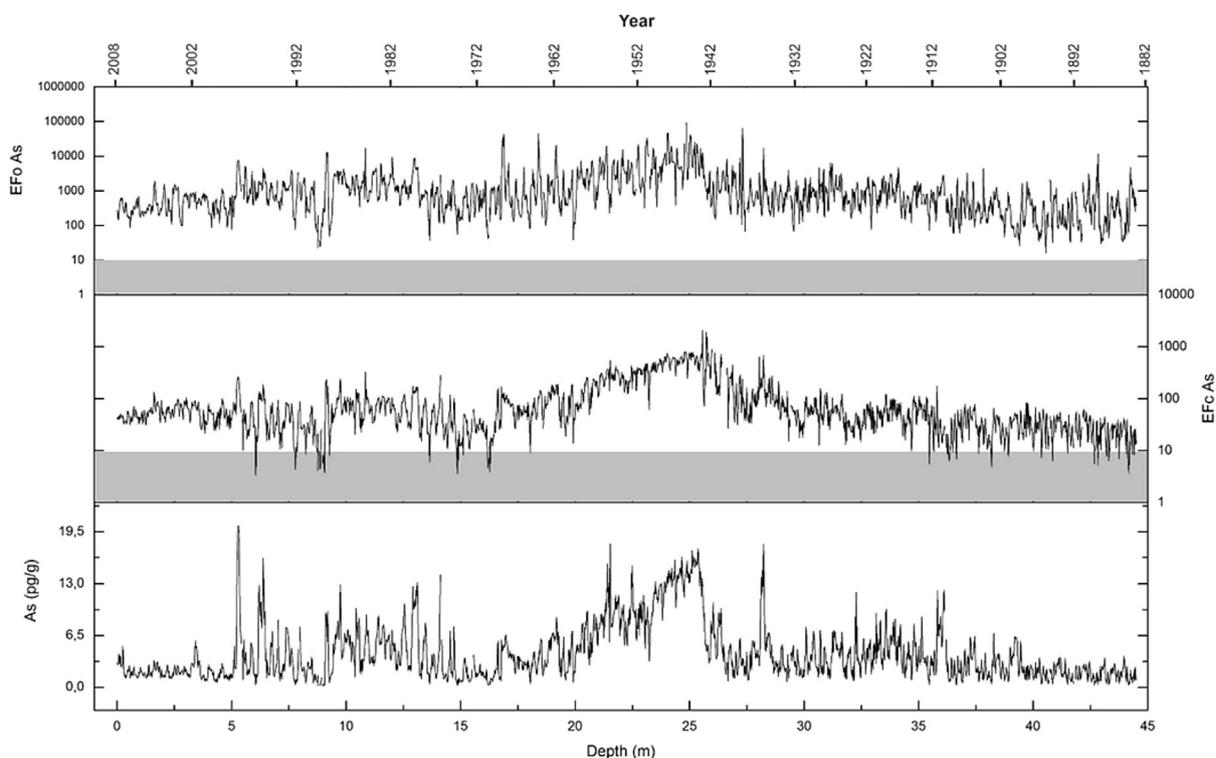


Fig. 4. Arsenic concentration profile compared with crustal enrichment (EFc) and ocean enrichment (EFo) factors. Enrichment values below 10 (rectangle in gray) are considered to be of natural origin.

the Na concentration in the sample, and As_{ref} and Na_{ref} are, respectively, the As and Na concentrations in the reference material. The oceanic fraction was subtracted from each sample, and then, the crustal fraction was calculated using the same formula, but substituting sodium for aluminum as the reference material.

The contribution from volcanic emissions was estimated from the non-sea-salt-sulfate ($nss-SO_4^{2-}$). Approximately 10–15% of the sulfate concentration in the Antarctica atmosphere originates from volcanic activity (Hur et al., 2007). By combining these numbers with estimates of metal/S ratios of volcanic emissions (Hinkley et al., 1999), it is possible to calculate the volcanic arsenic contribution. We also used the metal/S ratios in the Mount Erebus ($77^{\circ}32'S$, $167^{\circ}10'E$) plume (Zreda-Gostynska et al., 1997) to represent regional contributions. Only 1% of the As concentration originates from global volcanic emissions; however, approximately 11% of the concentration originates from regional volcanic sources (e.g., Mount Erebus – $77^{\circ}31'47''S$; $167^{\circ}09'12''E$ and Deception Island – $62^{\circ}58'37''S$; $60^{\circ}39'00''W$).

3.4. Transport and distribution

Arsenic is emitted to the atmosphere from natural and anthropogenic sources. Approximately one-third of global emissions are natural, with volcanism as the main source. Anthropogenic sources release approximately 24,000 tons of arsenic per year. Approximately 60% of these emissions originate from Cu-smelting and coal combustion (Matschullat, 2000; WHO, 2001). Arsenic is released into the atmosphere primarily as As_2O_3 or, less frequently, as one of several volatile organic compounds. These particles are dispersed by the wind to a varying extent depending on their size, and they return to the Earth's surface by wet or dry deposition (WHO, 2001).

Fine and coarse particulates have different residence times in the atmosphere. Arsenic associated with the fine fraction may

remain in the atmosphere for 7 (Pacyna, 1987) to 10 days (Matschullat, 2000) and can travel thousands of kilometers (ATSDR, 2007). Coarse particulates have a much shorter atmospheric residence time, which is typically minutes to hours due to a larger settling velocity (Csavina et al., 2012). Mine waste particle segregation can occur during airborne transport, thereby reducing the size of the individual particles deposited (Castillo et al., 2013). In addition, the atmospheric contaminant concentrations are also influenced by the type of mining operations, the distance and position of a sampling site in relation to the source, the height of the source (e.g., chimney or tailings pile), the exit velocity of the flue gas, and the prevailing wind speed (Lee et al., 1994), as well as changes in industrial technologies (García-Alexis et al., 2013).

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HySPLIT) model, developed by the National Oceanic and Atmospheric Administration's Resources Laboratory, has been configured to simulate a wide range of trajectories related to regional or long-range transport and dispersion of airborne particles (Draxler et al., 2010). In this work, we used the HySPLIT to get backward/forward trajectories between Chile (Chuquicamata Mine – $22^{\circ}17'S$ / $68^{\circ}54'W$) and Mount Johns site (Fig. 5). To calculate these trajectories, we used climate reanalysis data (NCEP/NCAR), it is a robust data set for the South Hemisphere from the beginning of the satellite era, 1979–present (Bromwich et al., 2007). We used 10 day backward/forward daily simulations from January 1992 to December 2002. Ten days is an appropriate length of time when considering transport of smaller size fractions of dust (as well as other aerosols), while transport of larger particles is likely restricted to the first several days (Albani et al., 2012).

3.5. Arsenic emission and copper mining

Non-ferrous metal production, especially Cu-smelting

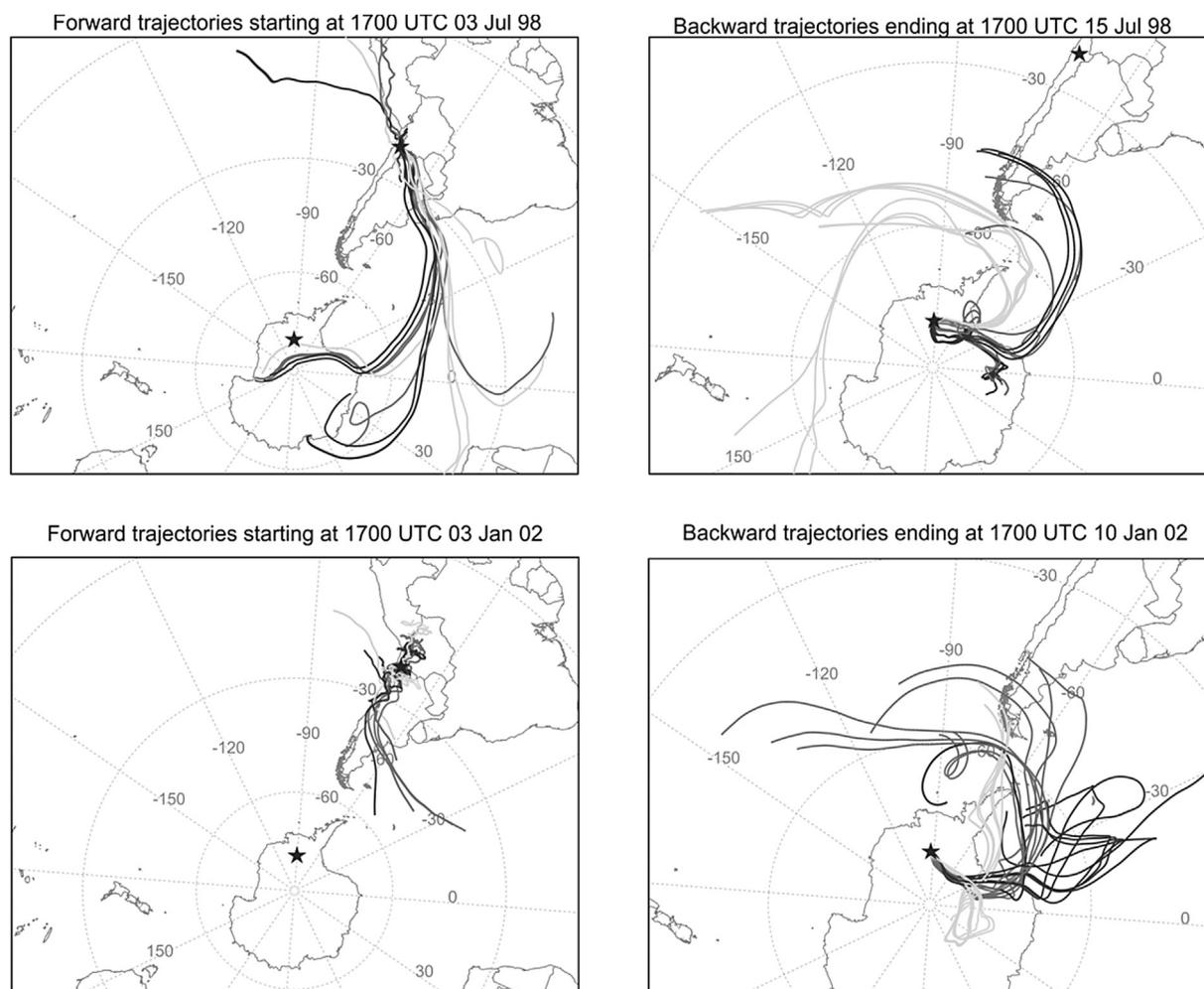


Fig. 5. Ten day HYSPLIT forward/backward trajectories between Chile (Chuquicamata Mine – 22°17'S; 68°54'W) and Mount Johns site (79°55'S; 94°23'W).

processes, is the most important anthropogenic contributor to As emissions (Pacyna and Pacyna, 2001). To determine the relationship between arsenic concentrations in Antarctica and copper mining, we compared the MJ data with the historical records of Chilean copper production (Fig. 6). Chile was used for this comparison because it is currently the world's largest copper producer, accounting for approximately one-third of the total production of this ore (COCHILCO, 2015), and because of the proximity to the Antarctic continent compared to other copper-producing countries (see map S1 of the supporting information with locations of copper mines in Chile).

Arsenic variability in the MJ ice core has several similarities with the historical copper production record in Chile. Before the 20th century, mining production consisted mainly of small and medium companies controlled by Chilean businessmen with some British capital (Collier and Sater, 2004); it accounted for only 5% of the world production in 1900. The arsenic levels in the MJ core were not significant before 1900, so the concentration in this period is considered to be the natural background concentration.

The First World War accelerated the growth of the Chilean copper industry. Production almost tripled and exports more than doubled from 1914 to 1918. In 1917, copper accounted for approximately 19% of the country's exports (Collier and Sater, 2004).

Chilean copper production fell in the early postwar years, but increased foreign investments, mainly from the USA, and the creation of the *Caja de Crédito Minero* sparked an increase in mining

operations between 1922 and the 1930s. However, because of the Great Depression (1929), the US capital input ceased completely in 1931, and as a result, there was a large drop in production. From 1929 to 1933, copper production decreased from 317,000 to 163,000 tons per year (Collier and Sater, 2004). A similar trend is observed in the MJ core arsenic concentration, showing a small fall post-1920, followed by a new decrease in the early 1930s.

Between 1940 and 1960, copper exploration became the main Chilean mining activity. Investment returns and the demand for metals after the Second World War generated a receptive market, culminating in increased production (Collier and Sater, 2004). Arsenic concentrations in the MJ core show a significant increase from 1.92 pg g^{-1} (before 1900) to 7.94 pg g^{-1} (1950).

Since the nationalization of copper mines and the creation of the *Corporación Nacional del Cobre de Chile* (Codelco Chile) in the mid-1970s, copper production has shown a rapid rise accompanied by a substantial increase in production rates (Collier and Sater, 2004). These changes are consistent with the arsenic concentration temporal trend in our ice core samples. However, there is a clear difference between the trend in copper production and the ice core arsenic concentration after the mid-1990s, as a continuous increase in the copper production coincides with a substantial reduction of mining emissions (approximately 60%). Such disagreement is closely linked to the introduction of environmental regulations in Chile, such as the law 19,300 (General Bases of the Environment) in 1994, which set emission limits and air quality standards and led to

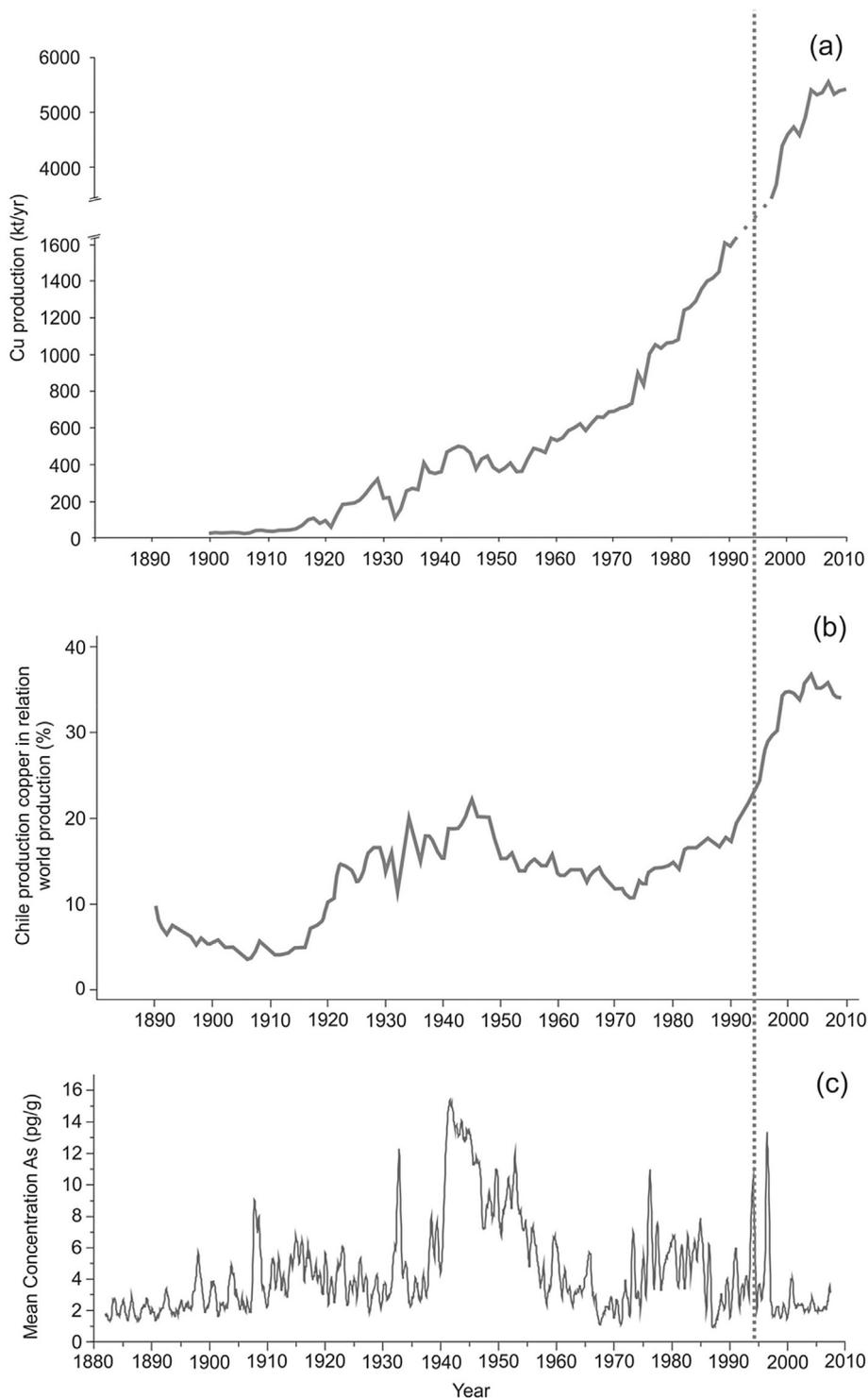


Fig. 6. Historical copper production in Chile compared with variations in the arsenic concentration as measured in the Mount Johns ice core: (a) Chilean production in kilotons from 1900 to 2008 (Source: USGS, 2014; COCHILCO, 2015); (b) Chilean copper production (%) in the world market from 1890 to 2008 (Source: Díaz et al., 2007; COCHILCO, 2015); and (c) the mean arsenic concentration measured in the Mount Johns ice core (Antarctica) from 1883 to 2008. The dotted line marks the introduction of environmental regulations in Chile for arsenic emissions.

the formation of decontamination plants for mining and smelting, and the DS-165 (from 1999), which regulated arsenic emissions into the atmosphere.

After 1999, the arsenic concentrations in our samples decreased to levels comparable to the period before 1900, indicating a reduced anthropogenic influence in the studied region,

concomitant with the implementation of environmental regulations for mining in Chile.

4. Conclusions

This work presents the first detailed record of arsenic

concentration variability in the Antarctic continent for a period of more than 100 years (from 1883 to 2008), indicating an average concentration of 4.32 pg g^{-1} at the Mount Johns ice core site. Our results show significant enrichment in arsenic concentrations due to anthropogenic activities. This enrichment is directly related to emissions from the mining and smelting of non-ferrous metals in South America, especially in Chile (the world's largest copper producer). The arsenic concentration observed since 1999 is interpreted as a response to the introduction of environmental regulations (in 1994) to reduce emissions of arsenic during mining processes and copper smelting in Chile. This observed decrease suggests that government regulations of air pollution have been effective both on regional and hemispheric scales.

Acknowledgments

This research is part of the Brazilian Antarctic Program (PROANTAR) and was financed with funds from the National Council for Scientific and Technological Development (CNPq), project 407888/2013-6 to JC Simões. F Schwanck thanks CNPq for a studentship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.11.027>.

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