

Recent increase in Ba concentrations as recorded in a South Pole ice core



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HIGHLIGHTS

- A 450-year record of atmospheric Ba concentrations from a South Pole ice core.
- Ba concentrations and Ba EFC values increased significantly since ~1980 A.D.
- South Pole Ba is 23 times above background as a result of local human activities.

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ABSTRACT

Here we present high-resolution (~9.4 samples/year) records of Ba concentrations for the period from 1541 to 1999 A.D. obtained from an ice core recovered at the South Pole (US ITASE-02-6) site. We note a significant increase in Ba concentration (by a factor of ~23) since 1980 A.D. The Ba crustal enrichment factor (EFC) values rise from ~3 before 1980 A.D. to ~32 after 1980 A.D. None of the other measured major and trace elements reveal such significant increases in concentrations and EFC values. Comparison with previously reported Antarctic Ba records suggests that significant increases in Ba concentrations at South Pole since 1980 A.D. are most likely caused by local source pollution. The core was collected in close proximity to Amundsen–Scott South Pole Station; therefore activities at the station, such as diesel fuel burning and intense aircraft activity, most likely caused the observed increase in Ba concentrations and its EFC values in the South Pole ice core record.

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1. Introduction

Human activities now have a major impact on the global atmospheric cycles of many trace elements. A number of studies show that even the remote Antarctic continent is significantly contaminated by heavy metals due to anthropogenic activities in the Southern Hemisphere. Several Antarctic records show clear evidence of anthropogenic influence on the Pb cycle in the Antarctic atmosphere (Barbante et al., 1997; Vallelonga et al., 2002; Planchon et al., 2002; Hur et al., 2007). Increased concentrations of Cu, Cr, Zn, Ag, Pb, and Bi have been observed during recent decades (Wolff and Cachier, 1998; Wolff et al., 1999; Planchon et al., 2002; Hur et al., 2007) and the elevated values of these metals in

Antarctica are attributed to atmospheric emissions from human activities in South America, Southern Africa and Australia (Planchon et al., 2002).

Activities at research stations, tourist ships and air traffic, are also contributing to contamination over the Antarctic environment. Model simulations by Graf et al. (2010) show that ship emissions, both sulfurous and black carbon, dominate anthropogenic pollution near the Antarctic coast. Another study conducted at Halley Research station links black carbon contamination with emissions from station generators (Wolff and Cachier, 1998). Higher concentrations of carbon particles, Pb and Zn are reported near McMurdo Station likely due to station activities (Mazzera et al., 2001).

Here we present a ~450-year record of atmospheric Ba concentrations as recorded in a South Pole ice core. Several previous studies have reported records of Ba concentrations in Antarctica (Planchon et al., 2002; Van de Velde et al., 2005; Hur et al., 2007; Dixon et al., 2011; Hong et al., 2012). They show that rock and soil dust is a major source for Ba in Antarctica and several studies

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use Ba concentrations in snow and ice samples as a proxy for natural source dust input to evaluate potential anthropogenic contributions for other elements (Van de Velde et al., 2005; Burn-Nunes et al., 2011; Hong et al., 2012). Our records indicate that Ba in Antarctica itself is affected by local source pollution.

2. Methodology

2.1. Ice core collection and chemical analysis

The South Pole SPRESSO (South Pole Remote Earth Science and Seismological Observatory) ice core was drilled during the 2002–2003 Antarctic field season at 89.93°S, 144.39°W at an elevation of 2808 m a.s.l. and to a depth of 291.26 m (Fig. 1). The core was packed and processed by the United States International Trans Antarctic Scientific Expedition team that assigned it the following core ID: US ITASE-02-6.

The section from 0.8 to 59.4 m of the US ITASE-02-6 ice core were melted using the Climate Change Institute continuous melting system (Osterberg et al., 2006) at an average sample resolution of ~1.4 cm. Before melting, the ends of each section of ice were scraped inside a HEPA clean hood using a clean ceramic knife to prevent contamination. Melted co-registered samples were collected from the inner and outer parts of the core. To avoid contamination, only the inner portion of each sample was used for ICP-SFMS (Inductively Coupled Plasma Sector Field Mass Spectrometry) analysis.

Samples were collected into acid-cleaned (Optima HNO₃) LDPE vials and acidified to 1% with double-distilled HNO₃ before being analyzed. All samples were analyzed for major and trace elements (Na, Mg, Ca, Sr, Cd, Cs, Ba, La, Ce, Pr, Pb, Bi, U, As, Al, S, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Li and K) using the Climate Change Institute (CCI) Thermo Electron Element2 ICP-SFMS coupled to a Cetac Model ASX-260 autosampler.

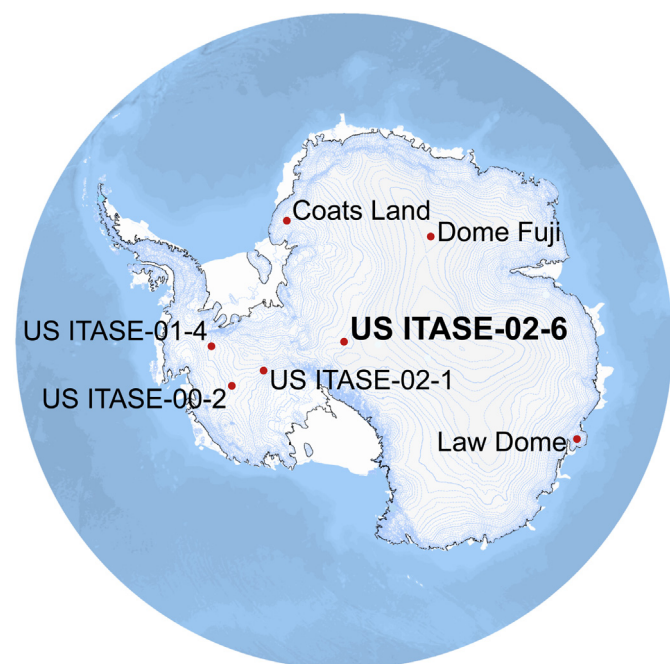


Fig. 1. Location of US ITASE-02-6, 02-1, 00-2 and 01-4 ice core drilling sites in Antarctica. Also shown are locations of the Dome Fuji (Hong et al., 2012), Coats Land (Planchon et al., 2002), and Law Dome (Vallelonga et al., 2002) snow pit sampling and firm/ice core drilling sites.

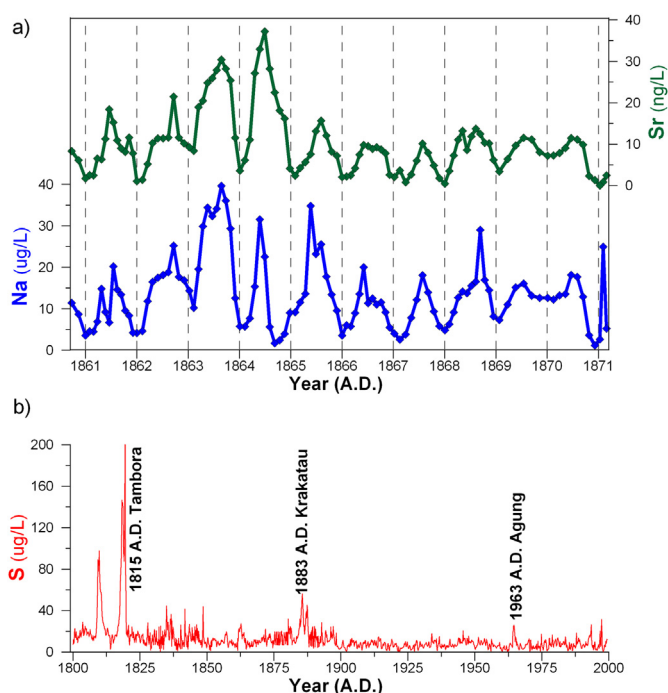


Fig. 2. US ITASE 02-6 ice core timescale development: a) example of annual variations in Na (ug/L) and Sr (ng/L) concentrations; b) S record (ug/L) showing peaks attributed to major tropical volcanic eruptions.

The interferences were minimized by using a ESI Apex desolvating sample introduction system. This study is focused on changes in Ba concentration in the US ITASE-02-6 ice core chemistry record. Detection limit for Ba (defined as three times the standard deviation of MilliQ (>18.2 M Ω) deionized water blanks passed through the entire melter system) is 0.31 ng/L, equivalent to ~1.1% of the Ba mean concentration over the analyzed period (Table S1).

2.2. Dating of the ice core

The US ITASE-02-6 ice core record was annually dated, using a CCI software package (Kurbatov et al., 2005), by matching seasonal peaks from Na and Sr (Fig. 2a) and identification of major historical volcanic eruptions (Fig. 2b). Most of the Na in Antarctic ice is delivered from open ocean sources. Peaks in Na concentrations in Antarctic ice cores are observed to occur primarily in winter/spring due to more intense atmospheric circulation and transport at this time (Legrand and Mayewski, 1997). We found that Sr in the South Pole record also exhibits a well-defined seasonal signal, peaking in winter/spring similar to Na (Fig. 2a), so it can also be used for annual layer counting. Major historical volcanic events, such as the 1963 A.D. Agung, 1883 A.D. Krakatoa and 1815 A.D. Tambora eruptions, identified by large peaks in S concentration, were used as absolute time horizons during timescale development (Fig. 2b). On the basis of our dating, US ITASE-02-6 covers the period from the 1541 to 1999 A.D. We developed the timescale for the top part of the record by counting annual layers from the well-known and easily-identified 1963 A.D. Agung eruption to the top of the core. We estimate a maximum dating error of ± 3 years between the 1963 A.D. Agung and 1883 A.D. Krakatoa eruptions, and ± 2 years between the 1883 A.D. Krakatoa and 1815 A.D. Tambora eruptions. We did not estimate dating error for the section below the 1815 A.D. Tambora eruption, because we were not able to unambiguously

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