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 \textasciitilde 1980 A.D.
- South Pole Ba is 23 times above background as a result of local human activities.

**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 \textasciitilde 23) since 1980 A.D. The Ba crustal enrichment factor (EFc) values rise from \textasciitilde 3 before 1980 A.D. to \textasciitilde 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 sulfuric 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 (Mazzer 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
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 been 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.

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 MΩ) 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...
identify any known historical eruptions in the deeper part of the record.

3. Results

3.1. Variations in elemental concentrations for the period 1541–1999 A.D.

Fig. 3 shows variations in Ba concentration from the US ITASE-02-6 ice core for the period from 1541 to 1999 A.D. Concentrations vary from 0.01 to ~3000 ng/L, with a mean concentration during the entire period of ~28.3 ng/L. Low background concentrations of Ba (average of ~12.9 ng/L) are observed between 1541 and 1980 A.D. (Fig. 3, Table 1). During this period maximum Ba concentration is 252.8 ng/L. Since 1980 A.D. Ba concentrations increase significantly by a factor of ~23, reaching a mean value of ~296 ng/L, varying from a minimum values of 5.2 ng/L up to a maximum values of 3118 ng/L. No other measured elements have such a significant increase since 1980 A.D.

3.2. Concentration versus flux

To investigate if observed changes in chemistry are related to changes in accumulation rate, we calculate Ba annual deposition flux. Ba flux is calculated by multiplying Ba concentrations in the ice by the annual water-equivalent accumulation rate (weq = density × annual layer thickness). Fig. 3 shows Ba concentration and flux for the period 1541–1999 A.D. Both concentration and flux show similar variability and increase in late 20th century. This indicates that the US ITASE-02-6 Ba concentrations are independent of accumulation rate and that the variability exhibited in the record is likely not a function of changes in snow accumulation.

3.3. Crustal enrichment factor

Atmospheric dust is one of the major sources for trace elements in ice cores. Ba has been used as a proxy for crustal dust input to Antarctica in several studies (Vallelonga et al., 2002; Van de Velde et al., 2005; Hong et al., 2012). To investigate the importance of crustal dust attribution for Ba in the US ITASE-02-6 ice core, we calculate a mean crustal Enrichment Factor (EFc) for Ba using the following equation:

\[
EFc = \frac{\left[\frac{[\text{Ba}]_{\text{sample}}}{[\text{La}]_{\text{UCC}}} + \frac{[\text{Ba}]_{\text{Ce}}}{[\text{Ce}]_{\text{UCC}}} + \frac{[\text{Ba}]_{\text{Pr}}}{[\text{Pr}]_{\text{UCC}}} + \frac{[\text{Ba}]_{\text{Ti}}}{[\text{Ti}]_{\text{UCC}}} \right]}{4}
\]

Upper continental crust (UCC) values of La, Ce, Pr, and Ti are from Wedepohl (1995) (Fig. S1). We calculate a mean EFc using four reference elements to reduce the potential bias from any one crustal reference element. The four crustal reference elements (La, Ce, Pr, and Ti) were chosen because their EFc ratios to one another in the US ITASE-02-6 ice core are close to ~1. Therefore, they are a good proxy for crustal dust for this study.

Fig. 3 shows Ba EFc values for the study period. Usually, elements with EFc lower than 10 are considered non-enriched and as such are considered delivered almost entirely from crustal dust (Duce et al., 1975). Variations of EFc in elements between 0 and 10 are attributed to the differences in the composition of crustal dust reaching the study site (Tuncel et al., 1989; Suggaard-Andersen et al., 2007). Our calculations show that for the period from 1541 to ~1980 A.D., Ba EFc values are very low (mean of 2.8) (Table 1).

This indicates that the major source for the Ba during this time is crustal dust. Since 1980 A.D. Ba EFc values increase significantly to a median value of 32.1 indicating that other sources besides crustal dust were introduced during recent decades. Therefore the recent increase in Ba concentration is not related to an increase of crustal dust input to Antarctica.

3.4. Oceanic enrichment factor

To evaluate possible contributions to Ba concentrations from marine aerosols we calculated a Ba oceanic enrichment factor (Efo). Efo values for Ba were calculated according to the following equation:
Ocean elemental abundances are from Lide (2005). Fig. 3 shows that Ba is highly enriched relative to ocean water over the entire record, indicating that the marine contribution for Ba at US ITASE-02-6 is negligible and is not the cause of the Ba rise since 1980 A.D.

Both Efc and Efo calculations suggest that during the period from 1541 to ~1980 A.D. most of the Ba originated from rock and soil dust, however since 1980 A.D. another source, most likely anthropogenic emissions, became more significant.

4. Discussion and conclusion

In order to determine whether the post 1980 A.D. Ba increase is local, or if it represents a higher Ba loading (e.g., increased atmospheric transport) to the entire Antarctic continent, we compared Ba concentrations in the US ITASE-02-6 ice core with other available Antarctic glaciochemical Ba records (Figs. 1 and 4, Table 1). Table 1 shows that all of the sites have mean Ba concentration values similar in magnitude to pre-1980 A.D. US ITASE-02-6 values both before and after 1980 A.D. Law Dome has the lowest Ba concentration, what could be explained by higher snow accumulation at this site.
The US ITASE-02-6 average concentration for the whole analyzed period is 28.3 ng/L and is relatively stable during the entire record except for recent decades. Since ~1980 A.D. Ba concentrations in the US ITASE-02-6 ice core increase dramatically, reaching a mean values of 296 ng/L. Other glaciological records that cover recent decades, such as US ITASE-00-2, US ITASE-01-4, US ITASE-02-1, Dome Fuji (Hong et al., 2012), Coats Land (Planchon et al., 2002) and Law Dome (Vallelonga et al., 2002), do not demonstrate a notable rise since 1980 A.D. (Fig. 4). Therefore it is most likely that the increase in Ba concentrations at US ITASE-02-6 since 1980 A.D. can be attributed to a local source.

We also calculate Ba EFC values for the other sites. Ba EFC values for other US ITASE ice core records were calculated using the same method as described in section 3.3. We were not able to do the same EFC calculations for the Dome Fuji, Law Dome and Coats Land records, since they did not have companion measurements for La, Ce, Pr and Ti (crustal reference elements used in this study). For Coats Land we used previously published Ba EFC values based on calculation using Al as a reference element (Planchon et al., 2002). Calculated Ba EFC values are shown in Table 1 and Fig. 5. Other US ITASE (US ITASE-01-4, 02-1, and 03-1) and Coats Land records have mean Ba EFC values below 10 both before and after 1980 A.D., indicating that crustal dust is the primary source for Ba in Antarctic ice. None of the other Antarctic records show increases in Ba EFC values since 1980 A.D., as is evident in US ITASE-02-6 record (Fig. 5). This further suggests that an increase in Ba concentrations during recent decades at South Pole is most likely caused by local source pollution.

Anthropogenic release of Ba is primarily associated with industrial processes involved in the mining, refining, and production of Ba and barium-based chemicals, and fossil fuel combustion (Miner, 1969). Since other Antarctic records do not demonstrate a rise in Ba concentrations we exclude any global or hemispheric-scale sources of Ba pollution, such as mining and production of Ba and barium-based chemicals. Barium in the form of organometallic compounds is also used as an additive to diesel fuels to reduce smoke emissions from diesel engines (Miner, 1969; Schroeder, 1970; Ng and Patterson, 1982). The US ITASE-02-6 ice core was collected 5 km from the Amundsen–Scott South Pole Station. This is an active station that requires a large amount of industrial processes involved in the mining, re-anything needed here. Is it 2014 or 2013?}

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.03.009.

References


