Mt. Everest Ice Core Record of Atmospheric Cu, Zn, Cd, Pb, and Pb Isotopes Variations in Central Asia during the Past 800 Years

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Abstract

Recent century scale time records for As, Mo, Sn, Sb, Bi, U, and Cs from Mt. Everest ice cores documented that a significant perturbation in the natural cycles of these elements took place during the second half of the 20th century due to increasing emissions of anthropogenic pollutants largely from fossil fuel combustion and non-ferrous metals production in central Asia. To evaluate to what extent human activities in central Asia have affected the natural atmospheric cycles of other heavy metals over time, Cu, Zn, Cd, and Pb concentrations and Pb isotopes were determined at 143 depth intervals from high-altitude Mt. Everest ice cores, covering an 800-year time period from 1205 to 2002 AD. This is the first reliable long-term time series of changes in the occurrence of Cu, Zn, Cd, and Pb and Pb isotopes in the remote Himalayan atmosphere. Our data show that these metals were primarily of natural origin up until the 1960s and significant increases in concentrations and crustal enrichment factors are observed from the 1970s onward. Such changes are attributed to massive emissions of anthropogenic Cu, Zn, Cd, and Pb from various anthropogenic sources in India. The Pb isotopic compositions provide clear evidence that anthropogenic Pb emitted from the use of leaded gasoline and coal combustion in India has affected the remote Himalayan atmosphere.

Key words: Trace elements, Mt. Everest ice core, anthropogenic perturbation, Pb isotopes

Introduction

The snow and ice offer valuable opportunities to reconstruct a unique record of changes in atmospheric compositions over time. In this context, there have been many efforts to unravel the pollution history by various trace elements from snow and ice cores retrieved from various locations in polar region and middle latitudes in the Northern Hemisphere (e.g., Hong et al., 1994; Krachler et al., 2008; McConnell and Edwards, 2008; Schwikowski et al., 2004). These investigations have provided useful time series that document man-made perturbation to atmospheric trace element cycles over tens of hundreds of time periods.

In contrast, comparatively little is about the evolution of atmospheric trace element cycles in Asia, despite the fact that Asia has become the largest emission source of trace elements into the atmosphere as a result of rapid economic and industrial developments (Pacyna and Pacyna, 2001). Very recently, century scale time records for As, Mo, Sn, Sb, Bi, U, and Cs were obtained from the analysis of Mt. Everest ice cores (Hong et al., 2009; Kaspari et al., 2009). They revealed that significant atmospheric pollution for these elements took place during the second half of the 20th century in response to increasing emissions of anthropogenic pollutants largely from fossil fuel combustion and non-ferrous metals production in central Asia.

We present here the historical record of the changing occurrence of atmospheric Cu,

Zn, Cd, and Pb evidenced from Mt. Everest ice cores covering the last 800 years from 1205 to 2002 AD. To date, this is the first time that these metals have been determined in high-altitude Himalayan snow and ice for century-scale historical records.

Materials and Methods

Two firn/ice cores (108.8 m [ER-a] and 95.8 m [ER-b] in length, respectively) were drilled on the East Rongbuk (ER) glacier on the northern slope of Mt. Everest (28°03'N, 86°96'E; altitude 6518 m; mean snow accumulation rate of 50 cm H_2O yr^{-1}) in 2002 (Hong et al., 2009). Dating of the cores was based on a combination of several methods such as the counting of annual layers of δD and chemistry back to 1534 AD, at a depth of 98 m, identification of major volcanic events, and use of a flow model from a depth of 98 m down to the bottom. The dating error is estimated to be ±0 year at 1963 and ±5 years at 1534 AD and progressively increase with depth from 98 m down to the bottom. Details of the dating are given by Kaspari et al. (2009) and Hong et al. (2009).

A total of 102 core sections covering the period from 1205 to 1966 AD (26.6 to 105.7 m in depth) and 1972 to 2002 AD (1.3 to 26.5 m in depth) were selected from the ER-a and ER-b cores, respectively. Each core section was mechanically decontaminated using ultraclean procedures (Hong et al., 2000). A total of 143 samples were obtained after dividing the inner core with more than 20-cm-long inner core length.

Aluminum, Cu, Zn and Pb concentrations were determined separately using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Sciex, ELAN 6000) and Cd using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) (Element2, Thermo Fisher Scientific, Bremen, Germany) equipped with an Apex high-sensitivity inlet system (Apex IR, Elemental Scientific Incorporated, Omaha, Nebraska, United States) (Hong et al., 2009). Pb isotopic compositions were also analyzed at Curtin University of Technology using an isotope ratio thermal ionization mass spectrometer (Triton, Thermo scientific). In addition, cations (Na^+, NH_4^+) and anion (SO_4^{2-}) were determined using a Dionex 320 ion chromatograph equipped with CS 12/As 11 columns. Finally, Sc was previously measured using ICP-SFMS (Hong et al., 2009).

Results and Discussion

The Cu, Zn, Cd, and Pb concentrations determined in 143 depth intervals are at the pg/g level with mean concentrations of 67 pg/g for Cu, 154 pg/g for Zn, 2 pg/g for Cd, and 34 pg/g for Pb, respectively. From our data, large variations in concentrations for each metal are evidently linked to the short-term (intra-annual and inter-annual variations), which is well characterized by higher concentrations during the non-monsoon season and lower concentrations during the summer monsoon season as documented in high-altitude Himalayan snow and ice (Kaspari et al., 2009). Such variability in concentrations results from the spring input of crustal dust from central Asia during the non-monsoon season and increased regional precipitation during the monsoon season.

Fig. 1a shows the long-term time trends of changes in concentrations of Cu, Zn, Cd, and Pb during the past 800 years. For the pre-1900 period, whilst variability in concentrations is observed for all metals, this variability does not fluctuate beyond two standard deviations. In contrast, during the middle to late 20th century, concentrations increased significantly with the most pronounced increase observed in Cd concentrations.

To evaluate the contribution from rock and soil dust, the crustal enrichment factors (EF) were calculated by using both Al and Sc as a conservative crustal element. We have used elemental composition in Tibetan Plateau soils as a reference crustal composition (Li et al., 2009). Fig 1b shows that EFs are notably constant with time, with only a few values greater than twice the standard deviation for the pre-1900 period. The relatively low mean and standard deviations of EFs of 3.0±0.7 for Cu, 2.2±0.5 for Zn, and 2.7±1.1 for Pb, respectively, indicate that for these metals, the contribution from rock and soil dust is essentially important. Conversely, very high mean EF value for Cd (12) implies that Cd inputs into the remote high-altitude Himalayan atmosphere are dominated by sources other than crustal dust. Other significant natural sources of Cd to the atmosphere are volcanoes and continental and marine biogenic emissions (Nriagu, 1989). Our data however do not allow us to make quantitative estimates of such contributions in our samples. Despite that, a lack of significant changes in EFs for the pre-1900 period suggests that Cu, Zn, Cd, and Pb in our samples are principally natural in origin

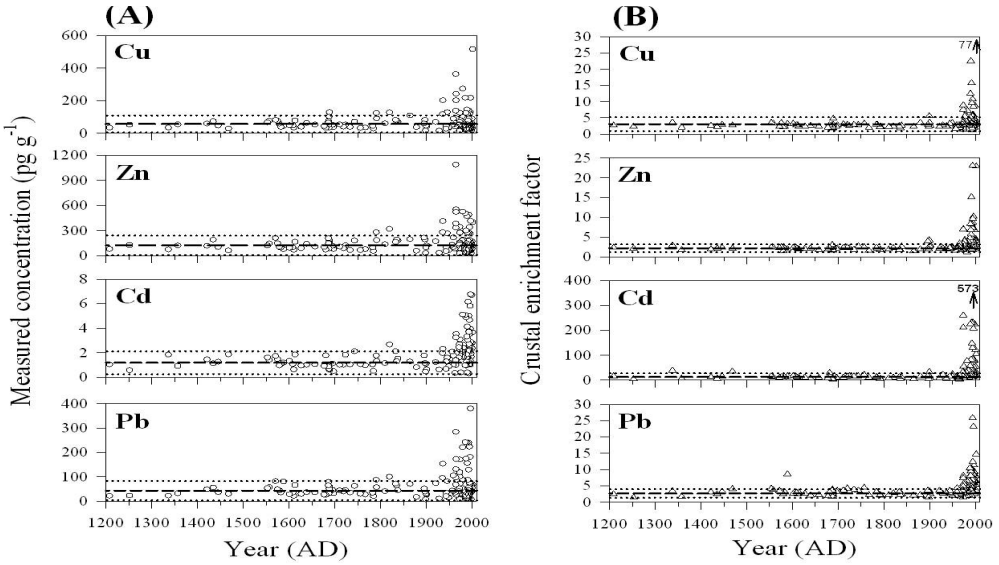

Figure 1. Changes in concentrations (a) and crustal enrichment factors (b) of Cu, Zn, Cd, and Pb from 1205 AD to 2002 AD in ice cores from Mt. Everest. Dashed and dotted lines represent the mean value and twice the standard deviation, respectively, for each metal during the time period prior to 1900 AD.

during this time, with significant contributions from rock and soil dust for Cu, Zn, and Pb and probably from volcanic and biogenic sources for Cd. This situation is different from the distinct pre-1900 pollution history for Cu, Zn, Cd and Pb in various regions of the Northern Hemisphere as well documented in ice cores from Greenland, the Canadian Arctic, and European Alps (e.g., Hong et al., 1994; Krachler et al., 2008; McConnell and Edwards, 2008; Schwikowski et al., 2004).

Fig. 1b shows that significant increases in EFs are observed during the recent decades, with slight different patterns from one metal to another. Compared to the other metals, the increase ratio of the Cd EFs since the 1970 appears the most dramatic, showing the highest mean increase factor of ~6 in the beginning of 1990s. Previous investigations of different trace elements in the same ice core revealed that the EF values have increased significantly for Bi, U, Cs, As, Mo, Sn, and Sb since the middle of the 20th century due to the influx of anthropogenic pollutants of these elements, largely from fossil fuel combustion and non-ferrous metals production (Hong et al., 2009; Kaspari et al., 2009). Therefore similar increases in the Cu, Zn, Cd, and Pb EF values in our data since the 1970s provide further evidence for rising atmospheric pollution for these metals in the remote high-altitude atmosphere in central Asia during the corresponding time period.

The correlations of Cu, Zn and Pb with respect to crustal fraction show very significant correlations (r^2 = 0.89 for Cu, 0.91 for Zn, and 0.78 for Pb, respectively) with respect to crustal fraction, which is likely to reflect similar transport and deposition of their pollutants and crustal dust probably due to the crustal dust scavenging during the transport from their source regions to the high altitude Himalayan atmosphere. By comparison, less significant correlation (r^2 = 0.36) is observed for Cd. Therefore it seems reasonable to assume that the crustal dust scavenging of Cd pollutants is less effective during the transport and a significant part of Cd pollutants is transported independently of mineral dust as well as the other metals.

Changes in $^{206}Pb/^{207}Pb$ ratio from 1900 AD to 2002 AD are shown in Fig. 2. For the pre-1900, $^{206}Pb/^{207}Pb$ ratio ranged from 1.191 to 1.214 with a mean value of 1.201. As seen in Fig. 2, major deviations from background level of the 206Pb/207Pb ratio are observed during the post-1970 period. Significantly lower $^{206}Pb/^{207}Pb$ ratios (~1.16) occur between 1988 and 1994. Based on the profile of major decrease in $^{206}Pb/^{207}Pb$ ratios in response to significant increase in the Pb EFs from the 1970s onwards, we interpret major decrease in $^{206}Pb/^{207}Pb$ ratio to be indicative of an anthropogenic Pb input. The most probable anthropogenic sources for Pb inferred from Pbisotope ratios were leaded gasoline consumption and coal combustion in India.

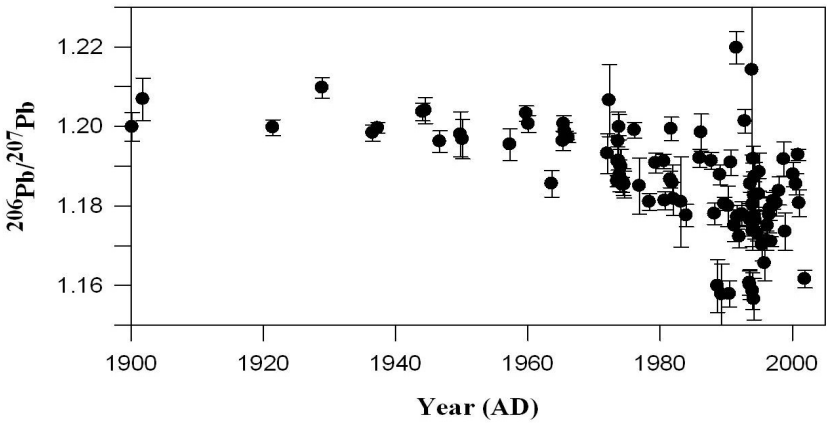

Figure 2. $^{206}Pb/^{207}Pb$ ratios from 1990 AD to 2002 AD in ice cores from Mt. Everest. Uncertainties shown are 95% confidence intervals.

Conclusion

Our data clearly show that significant atmospheric Cu, Zn, Cd, and Pb pollution in the remote high-altitude Himalayan atmosphere has occurred from the 1970s onwards. Such atmospheric pollution is attributed to massive emissions of anthropogenic pollutants of these metals from fossil fuel combustion and non-ferrous metals production in India. The use of leaded gasoline in India was also a large source for the increase in anthropogenic Pb input. Increased Pb concentrations and EFs and lowered $^{206}Pb/^{207}Pb$ ratios during the corresponding time period indicate the influence of less radiogenic anthropogenic Pb.

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