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High-resolution atmospheric cadmium record for AD 1776–2004 in a high-altitude ice core from the eastern Tien Shan, central Asia

Chaomin WANG,[1] Yaping LIU,[2] Wangbin ZHANG,[1] Sungmin HONG,[3] Soon Do HUR,[4] Khanghyun LEE,[5] Hongxi PANG,[1] Shugui HOU[1]

[1]*School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing, China*
[2]*State Key Laboratory of Cryospheric Sciences, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, China*
[3]*Department of Ocean Sciences, Inha University, Incheon, Korea*
[4]*Korea Polar Research Institute, Incheon, Korea*
[5]*Environmental Measurement and Analysis Center, National Institute of Environmental Research, Environmental Research Complex, Incheon, Korea*
Correspondence: Shugui Hou <shugui@nju.edu.cn>

ABSTRACT. Two ice cores drilled to the bottom were recovered from Miaoergou flat-topped glacier (43°03′19″ N, 94°19′21″ E; 4512 m a.s.l.), eastern Tien Shan, central Asia, in 2005. A high-resolution record of cadmium was established by applying inductively coupled plasma mass spectrometry to one of the ice cores (57.6 m), covering a 228 year period from AD 1776 to 2004. The results showed long-term variations of atmospheric transport and deposition of cadmium at high altitudes. Trend analysis based on the sequential Mann–Kendall test and the analysis of crustal enrichment factors of the cadmium shows that natural contribution, mainly from rock and mineral dust, dominated the atmospheric cycles of cadmium during the period AD 1776–1957, which was confirmed by the significant correlation between the winter North Atlantic Oscillation (NAO) index and annual cadmium concentration. The concentration of cadmium increased sharply from AD 1957 to 2004, suggesting increasing influence from human activities, such as metals production. The ice-core record indicated increasing atmospheric cadmium pollution in response to rapid economic growth after AD 1957 in the region.

KEYWORDS: ice chemistry, ice core

INTRODUCTION

With increasing industrialization and economic development, the environmental and health risks associated with heavy metals have attracted attention all over the world (Mu and others, 2012; Riederer and others, 2013; Chen and others, 2014; Erdakos and others, 2014; Eichler and others, 2014; Ha and others, 2014; Lavoie and others, 2014; Majzlan and others, 2014; Zohar and others, 2014). Because of their ability to disperse in the atmosphere over long distances (up to thousands of kilometres) heavy metals have the potential to create environmental and health risks after long-term exposures (Pacyna and Pacyna, 2001; Szymańska-Juchniewicz and others, 2009). Source identification and quantification of heavy metals is one of the key steps for controlling their emission and effectively reducing their environmental impacts. As a result of rapid industrial and economic development, Asia has become the most significant source of anthropogenic heavy metals emitted into the atmosphere (Pacyna and Pacyna, 2001). Snow and ice cores from the Himalaya (Hong and others, 2009; Kaspari and others, 2009), Pamir (Li and others, 2006, 2008) and the Tien Shan (Li and others, 2007a; Liu and others, 2011; Shi and others, 2011) have been used in previous studies to evaluate the historical impact of industrialization on the atmospheric loading of heavy metals in the region. However, existing studies have rarely determined the concentration of heavy metals for a relatively long period of time with high temporal resolution.

In this study, we present the first high-resolution time series for cadmium (Cd) obtained from the analysis of an ice core from the eastern Tien Shan, central Asia. It covers a 228 year period from AD 1776 to 2004. Cadmium was chosen because it is a ubiquitous heavy metal with no known nutritive function, but can affect human health even with low-level exposure. Chronic, low-level exposure to cadmium is linked to cardiovascular and kidney diseases, decreased bone density (increased fractures) and cancer (lung, pancreatic, breast, bladder). It may also cause increased environmental risks (Gallagher and others, 2010; Engström and others, 2011; Sorooshian and others, 2012; Riederer and others, 2013). The glaciers in the study region are close to the Gobi Desert and serve as the major water supply for the extremely arid Hami area (Fig. 1). Therefore, people living in this area could be exposed to higher risks of adverse health effects, such as cancers and other chronic diseases, from cadmium pollution.

MATERIAL AND METHOD

Study area and ice-core sampling

The Tien Shan are located in a remote area of central Asia, surrounded by vast dust source areas, such as the Taklimakan Desert, the Mongolian Gobi Plateau and the Gurbantunggut Desert (Fig. 1). Moisture is primarily delivered from the west and the north (Wake and others, 1990). It is suggested that 87% of snow accumulation forms

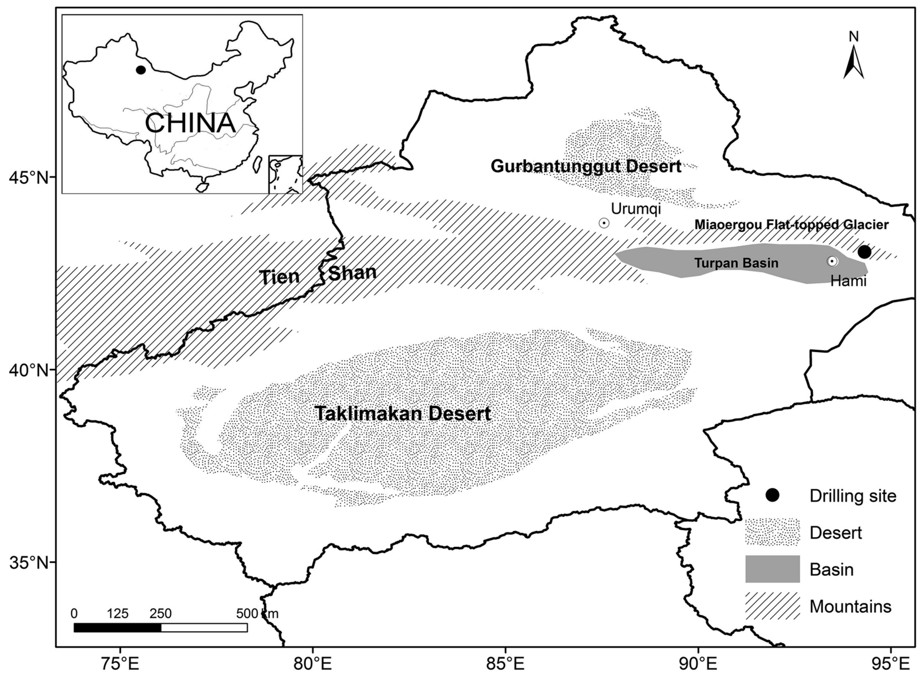

Fig. 1. Location of the Miaoergou flat-topped glacier in the eastern Tien Shan, China. The black dot shows the position of the drilling site (43°03′19″ N, 94°19′21″ E; 4512 m a.s.l.).

from precipitation originating from the Aral–Caspian closed basin, the eastern Mediterranean Sea and the Black Sea, with the remaining 13% from the North Atlantic (Aizen and others, 2006). Therefore the Tien Shan are an ideal site for studying the long-range transport of atmospheric heavy metals.

In AD 2005, two ice cores to bedrock (58.7 m for core 1 and 57.6 m for core 2) were recovered from a dome on Miaoergou glacier (43°03′19″ N, 94°19′21″ E; 4512 m a.s.l.) (Liu and others, 2011) (Fig. 1). The low borehole temperatures at the drilling site (–7.2°C at 10 m depth and –8.2°C at the bottom) allowed good preservation of ice-core records (Liu and others, 2009). The ice cores were transported frozen to the State Key Laboratory of Cryospheric Sciences (SKLCS), Lanzhou, China for processing. This study is based upon the records obtained from core 2. The partitioning depth of the firn and the ice part of core 2 was 17.49 m, dated at AD 1950 according to annual-layer counting. Core 2 (~9.4 cm in diameter) was split axially into two halves. One half was used to obtain the ^{210}Pb dating samples (~300 g each sample). A total of 20 samples were obtained for the measurement of ^{210}Pb activity. The other half was sampled continuously at intervals of ~4–5 cm on the ultra-clean bench in a cold room (–20°C). A total of 1205 samples were obtained for the analysis of trace elements, stable oxygen isotopes and major ions. After initial decontamination, the ice-core samples for trace element analysis were put in clean low-density polyethylene (LDPE) bags for further decontamination. All samples were obtained with a non-polluting cutting process in the cold room.

Chemical analysis

The decontamination of the ice-core samples, the acidification of samples acidified to 1% HNO_3 for 7 days and the measurements of major ions, stable oxygen isotopes and β activity were performed in the SKLCS, following the procedures in Liu and others (2011). Decontamination was conducted in a class 100 laminar-flow clean bench, located inside a –12°C cold room. First, ~5 mm of ice was shaved off both ends of each ice section, using a clean stainless scalpel. The core section was then placed in the lathe and the first ~5 mm thick veneer layer was shaved off. This procedure was repeated twice more. The remaining core section was then held with homemade tongs and another ~5 mm of ice was shaved off from both ends. Finally, the remaining inner core section was placed into a clean LDPE bag. The ice chips shaved off during decontamination were collected for measurements of β activity using a MINI20 low-background α/β counting system (CANBERRA EURISYS) at SKLCS.

The decontaminated inner core sections were melted at room temperature (~20°C) inside a class 100 clean bench in a class 10 000 clean room at SKLCS. Two aliquots (15–20 mL) were taken for each of the measurements of major ions, microparticles and trace elements. Compared with the much higher concentrations of trace elements in the Miaoergou samples, the effects from absorption of the container were insignificant. The samples for trace element measurements were acidified to 1% with Fisher 'Optima' grade ultrapure HNO_3, and allowed to react with the acid for 7 days. They were then frozen until measurements were taken. According to Koffman and others (2014) and Osterberg and others (2006), at least 70% cadmium concentration can be reached with acidification at 1% for 7 days.

Measurements of major ions and δ^{18}O were performed at SKLCS. Major cations and anions were analyzed using a Dionex 600 and ICS-2500 ion chromatograph (with a detection limit of 1 ng g^{-1}) respectively. Stable-oxygen isotopic ratios were measured using a Finnigan MAT-252 mass spectrometer (accuracy 0.05‰). Measurement of ^{210}Pb activity was performed at the University of Bern using an α-energy spectrometer (ORTEC, ruggedized, 300 and 450 mm^2) with 45% typical counting yields (Wang and others, 2014). Measurements of trace elements were

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performed at the Korea Polar Research Institute (KOPRI) using an inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer Sciex, ELAN 6100). Prior to measurements, the samples were melted at room temperature, inside a class 10 clean bench located in a class 1000 clean room. External calibration curves were used for quantification. The ICP-MS data were blank-corrected, by subtracting the procedure blank values (Liu and others, 2011). The detection limit (DL) and procedure blank value of cadmium in this study are 0.7 pg g^{-1} and <DL respectively (Liu and others, 2011). The accuracy of the method was verified by analyzing a riverine water reference (SLRS-4, River Water Reference Material for Trace Metals, National Research Council of Canada, Ottawa). The measured and certified values for cadmium concentration with the mass number 114 are 14 $\pm$ 1 pg g^{-1} and 12 $\pm$ 2 pg g^{-1} respectively. The measured and certified values for crustal element Ba concentration with the mass number 138 are 12.3 $\pm$ 0.1 ng g^{-1} and 12.2 $\pm$ 0.6 ng g^{-1} respectively. A good agreement between the measured and the certified values was observed for cadmium and barium.

Dating of the ice core

The ice core was dated by a combination of different methods. First, the δ^{18}O values and concentrations of crustal species (Ca, Ba) in the ice core showed clear annual cycles. Lower δ^{18}O values in the records are usually associated with winter precipitation, and higher δ^{18}O values with summer precipitation (Hou and others, 1999). The crustal species in the eastern Tien Shan snow and ice show clear seasonal variability, with higher concentrations in winter and spring due to strong dust input, and lower concentrations in summer due to heavy precipitation (Li and others, 2007a). The Miaoergou ice core was dated by counting the annual layers of these elements in the continuous records back to AD 1776 at a depth of 49.9 m. The estimated dating uncertainty was $\pm$1 year for this period. In addition, the measurement of ^{210}Pb activity indicated an age of AD 1851 $\pm$ 6 at a depth of 41.5 m (Wang and others, 2014). Moreover, the ice core was dated with essentially zero uncertainty at AD 1963 based on the β-activity horizons produced by global atmospheric thermonuclear tests in the Northern Hemisphere. The results of these three dating methods were highly consistent in this study.

The surface ice-core section was dated at AD 2004 according to extensive field investigations and mass-balance measurements from Li and others in AD 2004 and 2005. They concluded that the surface ice layer was well preserved despite the weak ablation process in Miaoergou glacier (Li and others, 2007b). Miaoergou glacier has a snowline elevation of ~4100 m a.s.l., an average annual temperature of –7°C and mean annual net accumulation of ~200 mm a^{-1} (Li and others, 2007b). The elevation of the ice core in this study is 4512 m a.s.l., well above the snowline. The high elevation and the low temperature make it possible that the surface ice layer was well preserved in AD 2005.

RESULTS AND DISCUSSION

Character of the data

Cadmium concentrations in the ice-core records are presented in Figure 2. There was great variability, with concentrations ranging from 1 to 235 pg g^{-1}. The mean cadmium values for the pre-1957 and post-1957 periods were ~10–29 pg g^{-1} respectively. The variability in cadmium concentration was linked to short-term (interannual and intra-annual) changes in the sources and transport of dust. The concentration peaks were associated with dust storm activities and strong winds during winter and spring. The low concentrations were probably caused by decreased dust flux, as well as heavy precipitation during summer, which would have washed out aerosol on the trajectory towards Miaoergou, thus diluting the cadmium.

Variations in concentrations and crustal enrichment factors

The sequential Mann–Kendall (MK) test was used to investigate the temporal trend of cadmium concentrations in the Miaoergou ice core from AD 1776 to 2004. Results are presented in Figure 3. The MK test is a rank-based non-parametric method that has been widely applied for trend detection due to its robustness against the influence of outliers and its reliability for biased variables (Chen and others, 2007; Hamed, 2008; Zhan and Lu, 2009; Ye and others, 2013). The sequential MK test was often used to determine the approximate time when abrupt changes occur. The MK statistic was calculated at each year for both forward and backward time series (UF_k and UB_k respectively). The intersection of UF_k and UB_k located within the confidence interval indicates the beginning of a step change (Moraes and others, 1998; Zhang and others, 2011). Figure 3 shows the MK test results for cadmium concentrations in the Miaoergou ice-core records. The UF_k curve suggests no significant trends in the cadmium concentration before AD 1957. However, cadmium concentrations started to increase significantly after AD 1957, the year when UF_k and UB_k curves intersect (within the 95% confidence interval), suggesting the beginning of an abrupt change in concentration trends.

The crustal enrichment factor (EF) of cadmium was calculated to evaluate the relative contribution of natural sources (e.g. rock and soil dust) and other sources (Fig. 2). The EF is defined as the concentration ratio of a given element to that of a conservative crustal element, normalized to the same concentration ratio characteristics of the upper continental crust (Wedepohl, 1995). Using barium (Ba) as a crustal reference element, for example, the calculation of EF for cadmium (Cd) is

$$\mathrm{EF(Cd)} = \frac{(\mathrm{Cd/Ba})_{\mathrm{ice}}}{(\mathrm{Cd/Ba})_{\mathrm{crust}}}$$

EF values between ~0.1 and 10 usually indicate dominant input from natural rock and soil dust. EF values significantly larger than ~10 often suggest significant contribution from other sources. Results show that the post-1957 EF values were >10, indicating that sources other than rock and soil dust became prominent for cadmium concentrations in the atmosphere. Occasional deviation of EF values before 1957 can be attributed to changes in the dust composition associated with other possible natural causes such as sea-salt spray, wild forest fires and continental and marine biogenic processes (Nriagu, 1989). The significant increase of cadmium concentration after AD 1957 is most likely attributable to anthropogenic input, as previous investigation of different heavy metals in the same ice core found similar increases of EF values as a result of anthropogenic emissions (Liu and others, 2011).

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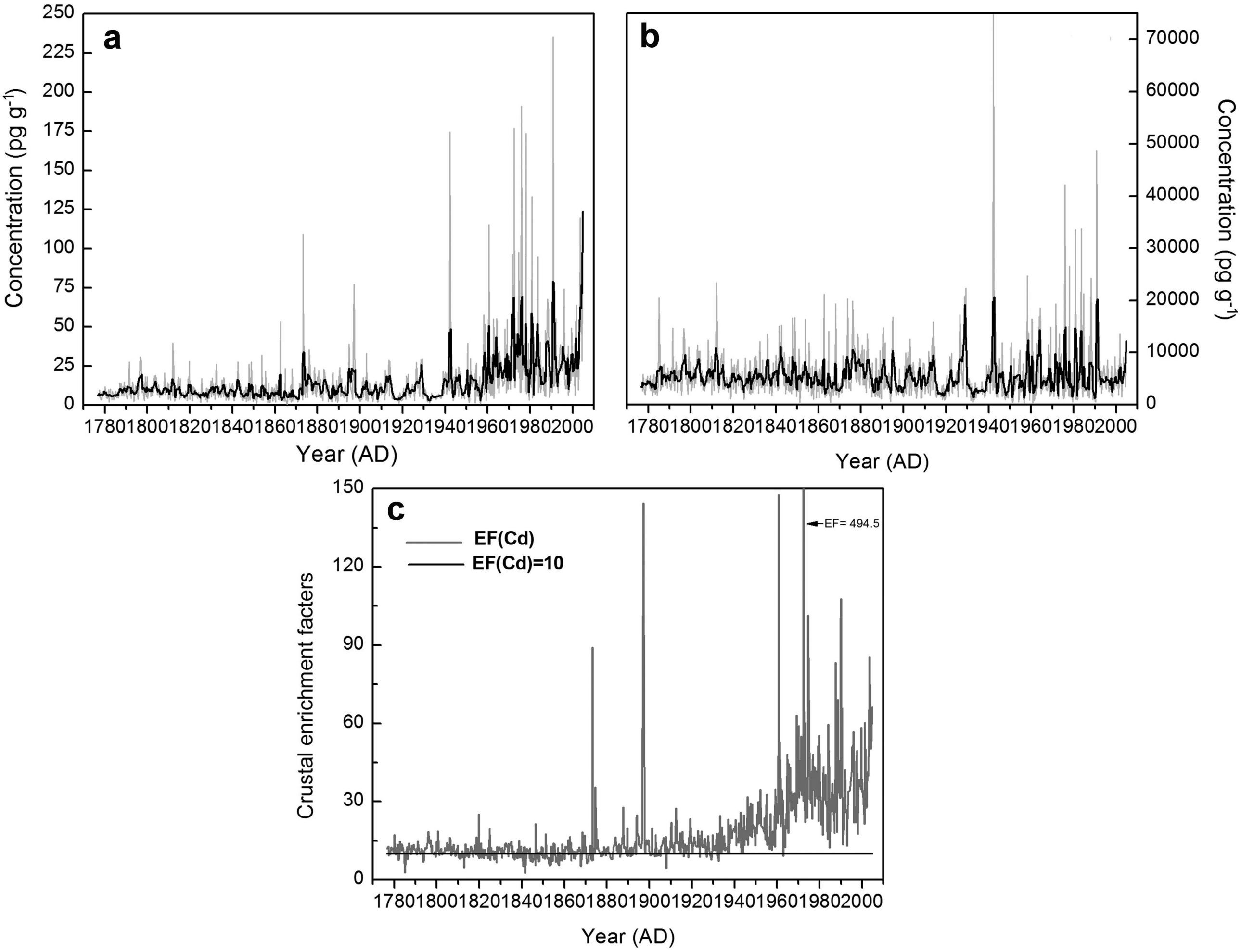

Fig. 2. Cadmium concentration (a), barium concentration (b) and the crustal enrichment factors (EF) of cadmium (c) in the Miaoergou ice core during AD 1776–2004. Solid lines show the five-point running average trends. The horizontal solid line in (c) shows the EF value of 10.

Correlation between North Atlantic Oscillation (NAO) index and cadmium concentration in the Miaoergou ice core

The North Atlantic Oscillation (NAO) is one of the most prominent and recurrent patterns of atmospheric circulation over the middle and high latitudes of the Northern Hemisphere during the cold season (November–April). The NAO is linked to climate variability from the eastern seaboard of the USA to Siberia and from the Arctic to the subtropical Atlantic (Hurrell and others, 2003). The NAO is also linked to the Asian climate (e.g. precipitation, temperature) on seasonal to decadal timescales (Wang and others, 2013; Gong and others, 2014; Lauterbach and others, 2014; Yim and others, 2014). Reanalysis data for the NAO index (AD 1701–1957) (Cook and others, 1998) were obtained from the US National Climatic Data Center (NCDC)/US National Oceanic and Atmospheric Administration (NOAA), and analyzed to examine the impact of the winter NAO on cadmium concentration in the Miaoergou ice core.

The smoothed annual winter NAO index showed a significant negative correlation with the smoothed annual cadmium concentration ($r = -0.48$, $p = 0.05$) as well as with the smoothed annual barium concentration ($r = -0.455$, $p = 0.1$) for the period AD 1776–1957 (Fig. 4), implying a possible connection between the winter NAO and the heavy-metals loading process in central Asia. It is possible that the winter NAO set up the dynamical conditions for dust storm occurrences in the western region of central Asia, the major source of cadmium concentration. Previous studies also show that the winter NAO index is inversely correlated with the dust flux over the Tibetan Plateau and

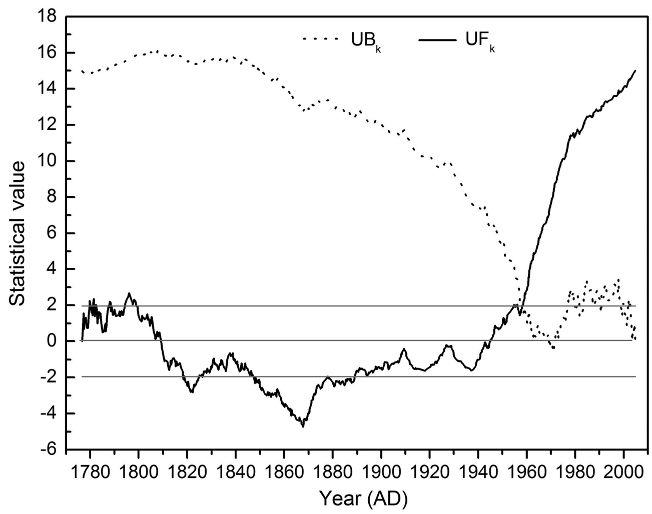

Fig. 3. The sequential Mann–Kendall test statistics for forward (UF_k) and backward (UB_k) sequences of cadmium concentrations in the Miaoergou ice core during AD 1776–2004. The horizontal gray lines represent the 95% confidence level.

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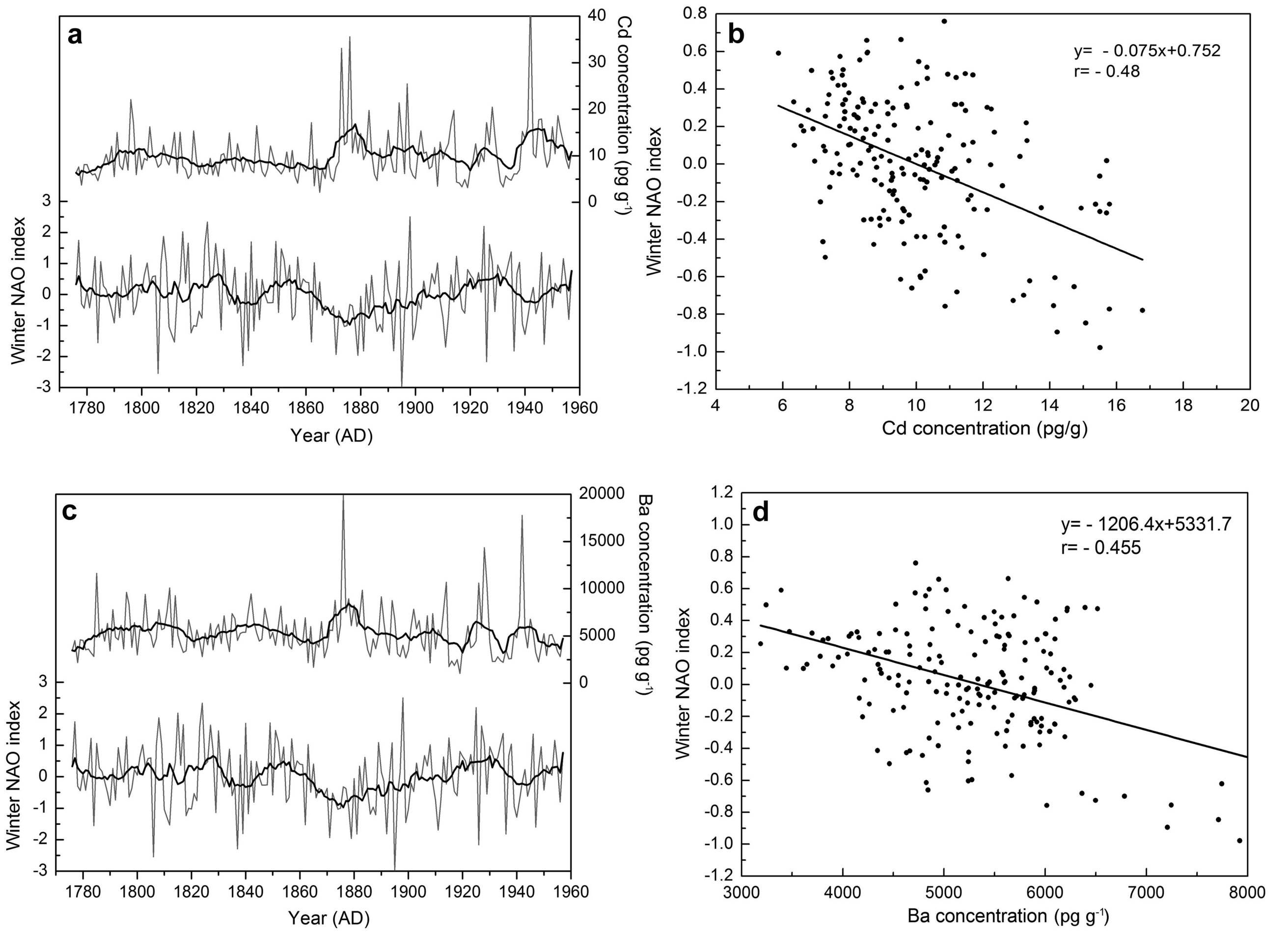

Fig. 4. (a, c) Comparison between the normalized time series of the winter NAO index and annual cadmium (a) and annual barium concentration (c) in the Miaoergou ice core during AD 1776–1957. The gray lines represent the original annual data, and the thicker black lines the 11 year running average. (b, d) Correlation between the smoothed winter NAO index and the smoothed annual cadmium (b) and barium (d) concentrations.

northwest China (Xu and others, 2007; Dong and others, 2013; Zhao and others, 2013). Therefore, the significant negative correlation between cadmium concentration and the winter NAO index during AD 1776–1957 further confirmed that natural sources (e.g. rock and soil dust) were the major contributors of cadmium to the Miaoergou ice core.

Anthropogenic sources of cadmium in the Miaoergou ice core from AD 1957 to 2004

Major anthropogenic sources of cadmium in recent decades include conventional thermal power plants, fossil fuel combustion, non-ferrous metal production, and iron and steel ferroalloys manufacturing (Pacyna and Pacyna, 2001; Hong and others, 2009; Kaspari and others, 2009; Eichler and others, 2014). Atmospheric trace element levels in the Miaoergou area are closely related to the variability in air mass trajectories under the influence of the westerlies (Liu and others, 2011). As a result, upwind countries like Russia, Kazakhstan and Uzbekistan could be important sources, given their large cadmium emissions into the atmosphere (Kakareka and others, 2004). However, despite the observed weakening of the westerlies and decrease in the associated spring dust storms in northwest China in the past half-century (Zhao and others, 2013), cadmium concentrations in the Miaoergou ice core increased during AD 1957–2004. This suggests stronger impacts of anthropogenic emission on Miaoergou glacier in the past half-century.

The significant increase of cadmium in the Miaoergou ice core reflects increasing pollution from heavy-metal emissions in central Asia during recent decades. As shown in Figure 5, metals production in the Soviet Union, Russia and China has greatly increased since the 1950s, suggesting that increasing human activities since the 1950s could have caused the large increase of cadmium in the Miaoergou ice core during AD 1957–2004. Miaoergou cadmium concentrations peaked during the 1970s, declined slightly in the 1980s and increased again during the period AD 1990–2004. Increased cadmium concentrations during the second half of the 20th century were also observed in snow and ice from the Siberian Altai (Eichler and others, 2014), the European Alps (Barbante and others, 2004) and central Greenland (Candelone and others, 1995) (Fig. 6). The cadmium peak in the 1970s could be a result of significant industrial production of iron and steel, lead/zinc and other metals in the former Soviet Union during the 1970s (CIA, 1981; Peck and others, 2004). The collapse of the Soviet economy at the end of the 1980s caused a dramatic decrease in metal production (Kang, 2013; Fig. 5), leading to a decline in cadmium concentrations. The recent increase in cadmium from the Miaoergou ice core contrasts with the decrease of cadmium recorded in other Northern Hemisphere ice cores during recent decades (Fig. 6) due to controls on emissions in industrial regions such as Europe and North America (Barbante and others, 2004; McConnell and Edwards,

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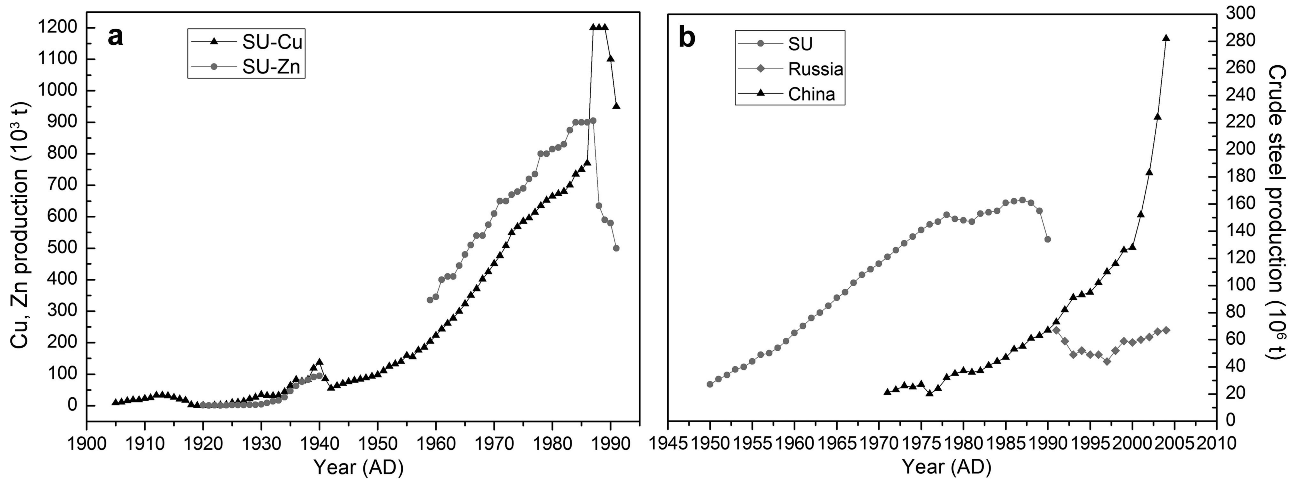

Fig. 5. (a) Russian/Soviet production of primary blister copper (Cu) and primary smelter zinc (Zn) during 1905–91 (Nutter, 1962; Bureau of Mines, 1932–93). (b) Crude steel production of the Soviet Union, Russia and China during 1950–2004 (http://www2.ttcn.ne.jp/honkawa/5500.html).

2008). This increasing trend of cadmium in central Asia, however, could be caused by the growing energy demand and increasing industrial production, as well as less strict emission controls in the region (Pacyna and Pacyna, 2001).

Local industrialization in Xinjiang Province also followed a similar timeline. Before AD 1949, local industrial production mainly consisted of traditional handicrafts, with a very low level of industrial production. From the 1950s to 1970s,

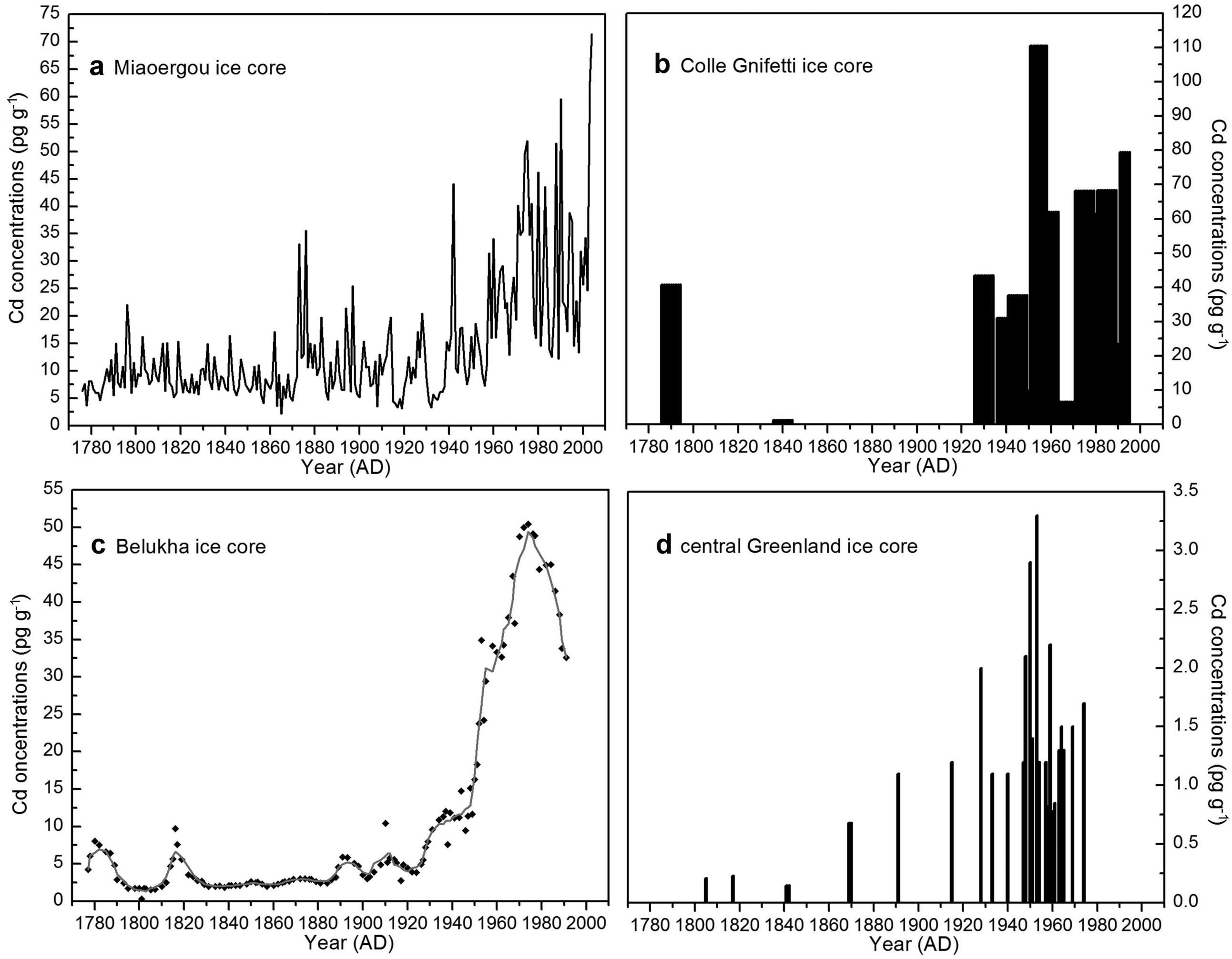

Fig. 6. Cadmium concentrations in (a) the Miaoergou ice core from eastern Tien Shan for the period AD 1776–2004, (b) the Colle Gnifetti ice core from the European Alps for the period AD 1787–1995 (Barbante and others, 2004), (c) the Belukha ice core from the Siberian Altai for the period AD 1776–1991 (Eichler and others, 2014) and (d) the central Greenland ice core for the period AD 1805–1974 (Candelone and others, 1995).The gray line in (c) represents the five-point smoothing result.

many modern industrial and mining enterprises were created, forming a modern network of industries in Xinjiang. Since AD 1978, the reform of state-owned industry has generated new momentum for industrial development (Wang, 2010). The fast and comprehensive industrialization at the beginning of the 21st century in Xinjiang and neighboring regions may have caused the large increase of cadmium in the Miaoergou ice core during AD 2000–04.

CONCLUSIONS

A high-resolution atmospheric cadmium record was established for the period AD 1776–2004 from a 57.6 m ice core recovered from the eastern Tien Shan. Trend analysis based on the sequential MK test and the analysis of crustal enrichment factors of the cadmium show that natural contributions, mainly from rock and mineral dust, dominated the atmospheric cycles of cadmium for most of the record until AD 1957. This was confirmed by the significant correlation between the winter NAO index and annual cadmium concentration. Cadmium concentration increased dramatically from AD 1957 to 2004, suggesting increasing cadmium contributions from human activities (e.g. metals production). Therefore the Miaoergou ice core clearly records the increasing atmospheric cadmium pollution resulting from rapid economic growth since 1957.

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