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Atmospheric Pb variations in Central Asia since 1955 from Muztagata ice core record, eastern Pamirs

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Abstract A Muztagata ice core recovered at 7010 m altitude in East Pamirs provides a Pb concentration record from 1955 to 2000. The result reveals increasing Pb concentrations from 1955 to 1993, with two Pb concentration peaks in 1980 and 1993. After 1993, Pb concentrations in ice core show an obviously declining trend. Analysis shows that the lead in the Muztagata ice core mainly came from anthropogenic emissions from countries in Central Asia, while the local emission had little contribution.

Keywords: Muztagata, ice core, Pb, anthropogenic source.

Measurements of Pb in the well-preserved and dated snow and ice layers in glaciers can be used to reconstruct the past changes of atmospheric lead concentrations and to determine the trends of atmospheric pollution. The lead data obtained from Greenland ice cap revealed severe air pollution in the Northern Hemisphere over the past three millennia. This lead pollution started from as early as Rome times[1], and increased remarkably from the Industrial Revolution to the end of the 1960s, and then decreased during recent decades[2,3]. In Antarctica, increasing Pb concentrations in snow/ice also exists from the early twentieth century to the 1970s, followed by a subsequent decrease[4]. At present, there are few investigations of heavy metals such as Pb in snow and ice in cold alpine glaciers in middle and low latitude areas. The only available lead data are ice cores from Mont Blanc in Europe and Sajama in Southern America, which revealed considerable air pollution on a regional scale since the Industrial Revolution[5,6]. We present here a time series for Pb from 1955 to 2000, which is obtained from an ice core drilled at the Muztagata glacier in the eastern Pamirs.

1 Sampling and analysis

1.1 Ice core drilling and dating

Muztagata glacier (75°06′E, 38°17′N) is located in the eastern Pamirs, near the border of Tajikistan, Kyrgyzstan and Kazakhstan in Central Asia. The summit of Muztagata glacier is 7546 m a.s.l. In the summer of 2003, five ice cores were drilled at 7010 m a.s.l. on the Muztagata glacier. Glaciological parameters for the drill site are as follows: the ice temperature at 10 m depth is –23.09℃ and the temperature near the bedrock is –25.73℃, the mean annual snow accumulation rate is ~ 56 cm (water equivalent) per year, the bedrock depth is 54.8 m and the firn/ice transition is observed at a depth of ~ 33 m.

A 41.6 m ice core (diameter ~ 9.4 cm) was used for analyzing Pb concentrations. This ice core was dated by the clear seasonal variations of ^{18}O, and confirmed by nuclear tests reference layers. The results show that this ice core covered the period of 1955—2003[7].

1.2 Sample preparation

97 one-fourth ice core sections with lengths varying from 12 to 18 cm were taken at various depths of ice core. Because the outer part of the core was probably contaminated during drilling and handing, each section was chiseled into three or four successive veneer layers from the outside to the inside of the section in a class-100 cold room (–15℃). This allowed for obtaining the cylindrical inner part of each core section (diameter 1.5—2 cm). As to the inner cores longer than 13 cm, we cut them into two parts. So a total of 101 discrete samples of 7—13 cm long core section were retrieved from the 97 ice core sections and kept separately in acid-cleaned low-density polyethylene (LADPE) bottles. The same procedure was used to process an artificial ice core of ultrapure water as an analytical blank.

To determine whether the inner part of the core section was free from outside contamination or not, changes in Pb and Al concentrations from the outside to the inside of numbers of ice core sections were analyzed. As an example shown in Fig. 1, such outside-inside concentration profiles of Pb and Al for the

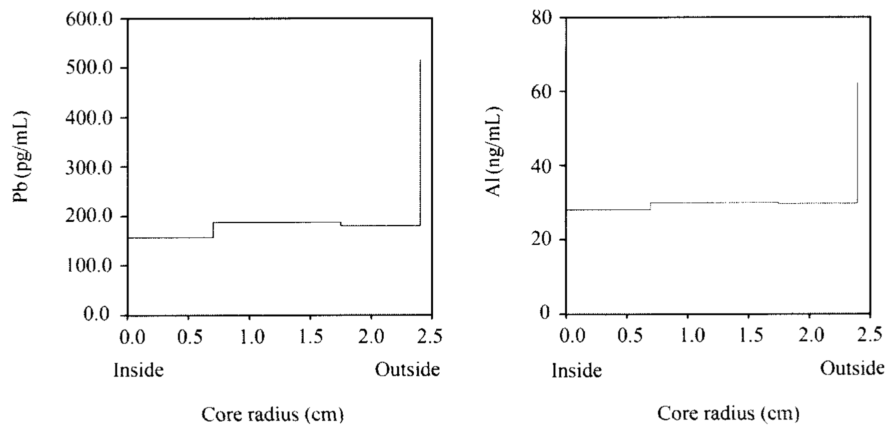

Fig. 1. Pb and Al concentration profiles along a radial transect for ice core M-162 from the Muztagata ice core.

ice core section M-162 show good plateaus in the central part of the section. It indicates that no external contamination had reached the inner core. The procedural blank is 6 pg/g for Pb and 3.7 ng/g for Al (Table 1).

Table 1 Procedural blank of Pb and Al obtained from the analysis of the artificial ice core (pg/g)

	Pb	Al
Reference water used to make artificial ice core	0.94	0.18
The first layer	64	15999
The second layer	15	4240
Inner core	6	3662

1.3 Analysis on Pb and Al by ICP-MS

Before analyzing, the inner core samples were melted at room temperature inside a class-100 bench. Ten milliliter aliquots were poured into acid-cleaned LDPE bottles and acidified with ultrapure nitric acid (Merck “Ultrapur”, 1+200).

The measurements of Pb and Al were performed by a Finnigan MAT ‘element’ ICP-SFMS (Bremen, Germany) in a clean room. The isotope of ^{208}Pb and low resolution (LR, $m/\Delta m$ = 300) were selected for determining Pb concentration, and the ^{27}Al and medium resolution (MR, $m/\Delta m$ = 4000) were selected for Al. Detection limits were calculated to be three times the standard deviations of 1% (*v/v*) HNO_3 solution. The detection limit was 0.43 pg/g for Pb and 472 pg/g for Al. The external calibration curve method was used for the quantification of the analysis. Standard solutions were prepared from a 100 μg/mL single-element stock solution from the National Research Center for Standard Reference Material in China, diluted using Milli-Q Element ultrapure water. The precision of the measurements was obtained from one ice core sample depth from 13.75 to 13.93 m. Precision in terms of relative standard deviations based on five consecutive measurements of the sample is 3.4% and 4% for Pb and Al, respectively.

2 Results and discussion

2.1 Pb concentration in Muztagata ice core

The data of Pb and Al concentrations in 101 samples cover a period of 1955—2000. Fig. 2 displays the variations in the Pb concentrations as a function of the age of ice core. The concentrations show a wider range of values for the samples taken from a one-year ice layer. This is, to some extent, attributed to the influence of artifact sampling, but it mainly reflects the seasonal variations. The large seasonal variations of Pb concentrations were also observed in snow and ice cores from other places such as Antarctica, Greenland and Alps[3,4,8]. The only snow and ice core data of Pb in Northern Hemisphere to which our data can be compared are those obtained from Summit in central Greenland and Mont Blanc in Alps. From the 1950s to 1980s, the mean concentrations of Pb are ~108 pg/g in Greenland[3], ~1332 pg/g[5] in Mont Blanc, and 477 pg/g in Muztagata. The value in Muztagata is 4 fold higher than that in Greenland, but 3 fold lower than that in Mont Blanc. The Mont Blanc is indeed closer to human activity area than Muztagata, while central Greenland is located in the remote Arctic far away from human activity area.

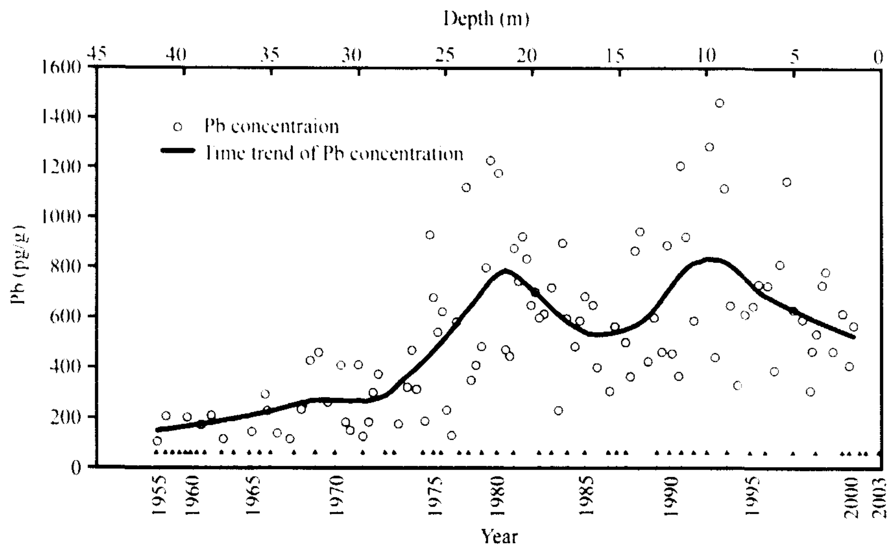

Fig. 2. Temporal variations of Pb concentrations from 1955 to 2000 in Muztagata ice core.

2.2 Temporal trend of Pb from the middle of twentieth century to present

The concentrations of Pb in Muztagata ice core show a clear temporal trend throughout the profile. From 1955 to 1972, the concentrations were ascending slowly, with a mean value of 236 pg/g. An abrupt increase in concentrations is found from1973 to 1980, with a maximum up to 1230 pg/g around 1980. Since then, concentrations decreased abruptly. The Pb concentration is down to 399 pg/g in 1986 but still higher than the average value in the period of 1955—1972. From 1986 to early 1990s, Pb concentrations increased progressively and a high value 1462 pg/g occurred in 1993. Then a decline trend appeared again after 1993 and Pb concentration decreased to 488 pg/g in 2000.

The temporal trend of Pb recorded in Muztagata ice core is distinctively different from that in Summit, central Greenland. From the 1950s to the end of 1960s, Greenland ice core record showed strongly enhanced values in Pb concentration, reaching a maximum around 1969 and then declining[2,3]. Muztagata ice core Pb record displayed a slight increase from 1955 to 1972, abruptly ascended during the periods of 1973—1980 and 1986 to early 1990s, and then decreased since 1993. In fact, the Pb in Greenland and Muztagata ice cores has different source regions. Greenland ice core Pb record mainly reflects emissions from North America and West Europe[3—5], but Muztagata ice core Pb record mainly receives pollutants from Central Asia.

2.3 Contribution from natural sources

Glaciers receive all of their water and other materials from the atmosphere, and Pb in snow and ice also comes from atmospheric lead through dry and wet deposition. Lead emits to atmosphere from both natural and anthropogenic sources. Worldwide natural emissions of Pb to the atmosphere originate mainly from soil and rock particles, sea salt spray, volcanoes, wild forest fires and biogenic sources[9]. Al is a major constituent of the Earth's crust[10] and can be used as an index to calculate Pb contribution from rock and soil dust. Based on the crustal Pb/Al ratio[10] and Al concentrations (8—326 ng/g) in our samples, the rock and soil dust contribution to Muztagata ice core Pb ranges from 1 to 33 pg/g. It accounts for about 0.22 to 5.7% (average: 1.9%) of concentrations measured in the ice core. Contributions from other natural sources cannot be evaluated from our data. On a global scale, the contributions to Pb from other natural sources are very uncertain and lower than those from rock and soil dust[11]. It can be convinced that there is a small contribution to Pb from natural source in Muztagata ice core. The very large excess Pb (~90%) above natural contribution is probably mainly derived from anthropogenic sources, which resulted in the heavy atmospheric lead pollution in Muztagata region.

2.4 Anthropogenic sources

Anthropogenic sources for atmospheric lead include leaded gasoline combustion, coal and oil combustion in electric power stations and heating and industrial plants, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration, and kiln operation in cement plants[11]. The local source emitting lead to atmosphere in Muztagata region is mainly the combustion of alkyl lead additives in transportation. In Muztagata region, the traffic has expanded rapidly since 1990 and the unleaded gasoline was only used after 2000. It means that atmospheric lead emission from local source would also be increasing during the period from 1990 to 2000. This case reverses the changing trend of Pb concentrations in Muztagata ice core since early 1990. Thus we believe that the local lead emission has a small contribution to Pb in Muztagata ice core.

The five countries in central Asia (Tajikistan, Kyrgyzstan, Kazakhstan, Turkmenistan and Uzbekistan), which are now called Central Asia new independent states (NIS) and located in the upwind region of Muztagata, are thought to be the main source regions for Pb observed in Muztagata ice core. A recent report reveals that heavy metals (such as Pb, Cu, Zn) emitting to atmosphere are becoming a major pollution in the Central Asia NIS, especially since the 1950s[12]. These pollutants can be easily transported for a long distance by strong westerlies and deposit on the wind-downward area such as Muztagata. The major source emitting lead to atmosphere in Central Asia NIS is non-ferrous industries producing Pb and Cu. The second is leaded gasoline combustion in transportation[13,14]. For example, the total atmospheric lead emission in 1990 in Central Asia NIS is 6078.5 ton, of which about 60% comes from non-ferrous industries and about 35% comes from traffic[13]. In addition, most of total atmospheric lead released from Kazakhstan[13,14].

Previous studies[2−6] suggested that the temporal trends of Pb concentrations in ice cores are similar to those of annual emission fluxes in corresponding sources. However, because of the long-term isolation of Central Asia NIS from the rest of the world during the former Soviet Union (FSU) period, few data of emission of pollutants were opened to public. The only data published in recent several years (1990—1996)[15] are not allowed to compare with the longer time series of Pb in Muztagata ice core.

To some extent, the increase of pollutant emission flux accompanies the development of economy. Therefore, some reasonable explanations for the temporal trend of Pb in Muztagata ice core can be obtained when considering the specific status of Central Asia NIS. The economy of FSU increased generally from 1955 to 1989[16] and the economy of Central Asia NIS has a similar progress during the same time period. As shown in Fig. 2, the concentrations of Pb in Muztagata ice core generally present an ascending temporal trend from 1955 to 1989. It is in agreement with the general economic status of Central Asia NIS during the same time. After early 1990s, the economy of Central Asia NIS fell into a decline because of the disintegration of FSU, leading to a significant decrease of pollutant emission in this area[13,15]. As shown in Fig. 3, from 1990 to 1996, the annual lead emission in Kazakhstan decreased from 1770 ton to 380 ton, reducing by about 80%. As to Uzbekistan, it decreased from 608 ton to 300 ton, reducing by about 50%. A marked decline trend of Pb in Muztagata ice core after the early 1990s (Fig. 2) is in good agreement with the above changes. The two peaks of Pb in ice core occurring in around 1980 and 1993 can be explained by the two large scale arms races between FSU and USA. Due to large high-grade base metal deposits (Pb, Cu, and Zn), Central Asia NIS have enormous metallurgical and heavy and armament industries and played an important role in arms race during the FSU period. The abrupt increase in Pb concentration in Muztagata ice core since 1973, peaking around 1980, is probably attributed to vast emission of pollutants from the first large scale arm race between FSU and USA, which was aimed at routine armament and missile nuclear weapon and had persisted from 1972 to around 1980. The decline trend

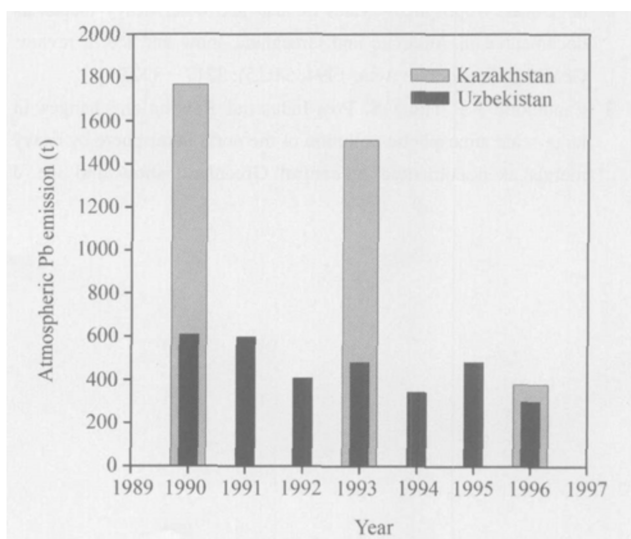

Fig. 3. The emission fluxes of atmospheric Pb from Kazakhstan and Uzbekistan during 1990—1996[15].

of Pb in ice from 1981 to 1985 reflected the moderate state status of arm race in this period. And the subsequent increase of Pb concentrations until 1993 probably results from the second large scale arm race, which was carried out when USA set forth the Star Wars in 1985 and persisted from 1986 to the disintegration of FSU.

3 Conclusions

This study presents preliminary data on changes in Pb deposited on Muztagata glacier in the past decades, and provides an interesting insight into air pollution for Pb in Central Asia. It is surprised to find so high values of Pb in an ice core obtained from high altitude above 7000 m. It is necessary in the future to extract new high altitude ice cores from other locations in Pamirs and other abutting places to confirm this initial result. In addition, more available lead emission data of Central Asia NIS need to obtain for elucidating the detailed characteristics of Pb variations in Muztagata ice core.

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