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An assessment of variations in mercury deposition to Antarctica over the past 34,000 years

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Abstract We performed a comparison analysis of the variations in Mercury (Hg) concentrations and the precipitation proxies (e. g., ^{18}O values and ^{10}Be concentrations) in the Dome C ice core. The results showed that there were significant correlations between Hg and $\delta\,^{18}O$ values, ^{10}Be concentrations, indicating that the accumulation rate in Dome C is one of the key factors controlling the variations of Hg concentrations in the past 34,000 years, and implying that Hg concentrations in ice core can be used as another reliable proxy of precipitation rate in Antarctica. Based upon the high-resolution $\delta\,^{18}O$ values, we estimated the variations in mercury deposition flux to Antarctica over the past 34,000 years. The highest mercury deposition flux is about 3.80 pg cm^{-2} yr^{-1} during the Last Glacial Maxium (LGM) as high as 3.5 times of the mercury deposition flux (about 1.08 pg cm^{-2} yr^{-1}) in Holocene due to the fluctuations in natural mercury emissions such as the oceanic biological emissions.

Key words mercury deposition flux, precipitation rate, LGM, Holocene, Antarctic Dome C ice core.

1 Introduction

Mercury (especially methylmercury) has attracted attentions as a potentially dangerous environmental pollutant because of its toxicity and its ability to bioaccumulate in the food chains (Harada 1995; Bargagli *et al.* 1998; Watras *et al.* 1998; Dietz *et al.* 2000). Free from the local human activities, mercury profiles in remote area provide numerous helpful knowledge to understand the influence of natural factors in the global mercury cycles, e. g., natural mercury emissions, air temperature (Appelquist *et al.* 1978; Nriagu1989; Vandal *et al.* 1993; Fitzgerald *et al.* 1998; Gobeil *et al.* 1999; Martínez-Cortizas *et al.* 1999; Bindler 2003).

Antarctic ice core is a kind of perfect material to evaluate the trace element background values because of its homogenization, accurate dating, and free from local human activities (Fitzgerald *et al.* 1998). Vandal *et al.* (1993) firstly reported mercury concentrations in subsamples from Antarctic Dome C ice core. The results showed that Hg concentrations were 5 -6 times higher in LGM than in Holocene in accordance with 5 -6 times larger of oceanic productivity during LGM in comparison with today (Saigne and Legrand 1987). Hence, Vandal *et al.* (1993) suggested change in pre-anthropogenic Hg concen-

trations should be linked to the variations in the oceanic biological productivity, and preliminary estimated the mercury deposition flux during LGM and Holocene. However, the continuous changes of the mercury deposition flux to Antarctica during the past 34,000 years on the basis of the high-resolution precipitation rate have not yet been reported so far.

The $\delta^{18}O$ values, ^{10}Be concentrations in ice core have been used as reliable proxies of precipitation rate (Raisbeck *et al.* 1981; Jouzel *et al.* 1987; Qin and Ren 2001). Raisbeck *et al.* (1981) reported the concentration profiles of cosmogenic ^{10}Be in deep ice core from Dome C and Vostok, Antarctica. In these cores from both origin they found a concentration of ^{10}Be approximately two times larger in late glacial period than in the Holocene ice due to a lower precipitation rate on the Antarctic plateau during glacial periods, compared to interglacial periods (Raisbeck *et al.* 1987).

In this paper, we compared the Hg concentrations with $\delta^{18}O$ values and ^{10}Be concentrations in deep ice core from Dome C, and calculated the mercury deposition fluxes to Antarctica on the base of the high-resolution $\delta^{18}O$ values of Dome C in the past 34,000 years.

2 Data Collection

Dome C (74°39′S, 124°10′E) is 3,240 m a. s. l (Fig. 1) with −53.5 ℃ mean annual air temperature. The Dome C Antarctic ice core is 906 m in length spanning approximately 40,000 years before the present. It was obtained during the 1977 − 1978 Antarctic field season as part of the International Antarctic Glaciological Project by thermally drilling method. The Dome C data set including $\delta^{18}O$ isotope and age data related to depth were published by Lorius *et al.* (1979), Here, we downloaded these data from the web site http://www.ngdc.noaa.gov . Hg and ^{10}Be concentrations were cited from Vandal *et al.* (1993) and Raisbeck *et al.* (1981), respectively.

3 Discussion

3.1 Comparison between the Hg concentrations and $\delta^{18}O$, ^{10}Be in Dome C ice core

The variations of Hg concentrations and $\delta^{18}O$ values, ^{10}Be concentrations in Dome C ice core over the past 34,000 years were given in Fig. 2. As seen in Fig 2a, Hg concentrations show a significant negative correlation with$\delta^{18}O$ values ($r = -0.910$, $n = 14$). This is attributed to the air temperature and the accumulation rate decrease with $\delta^{18}O$ values decline (Jouzel *et al.* 1987; Qin and Ren 2001). The low accumulation rate could increase the concentrations of all kinds of aerosols, trace element and dust particles, e. g., NO_3^-, light carboxylic-acids, Pb and dust particles in Dome C ice core (Raisbeck *et al.* 1987; Legrand and Deangelis 1999; Rothlisberger *et al.* 2000; Qin and Ren 2001). In Fig. 2b, changes in Hg and ^{10}Be concentrations in Dome C ice core over the past 34,000 years were similar. The higher concentrations occurred in LGM due to arid climate and lower concentrations in Holocene corresponding to humid period (Raisbeck *et al.* 1981). As $\delta^{18}O$ and ^{10}Be concentrations in ice core have been used as proxies of precipitation, we proposed that Hg concentrations in ice core may be a potential proxy of the accumulation rate due to its significant correlation with $\delta^{18}O$ and ^{10}Be.

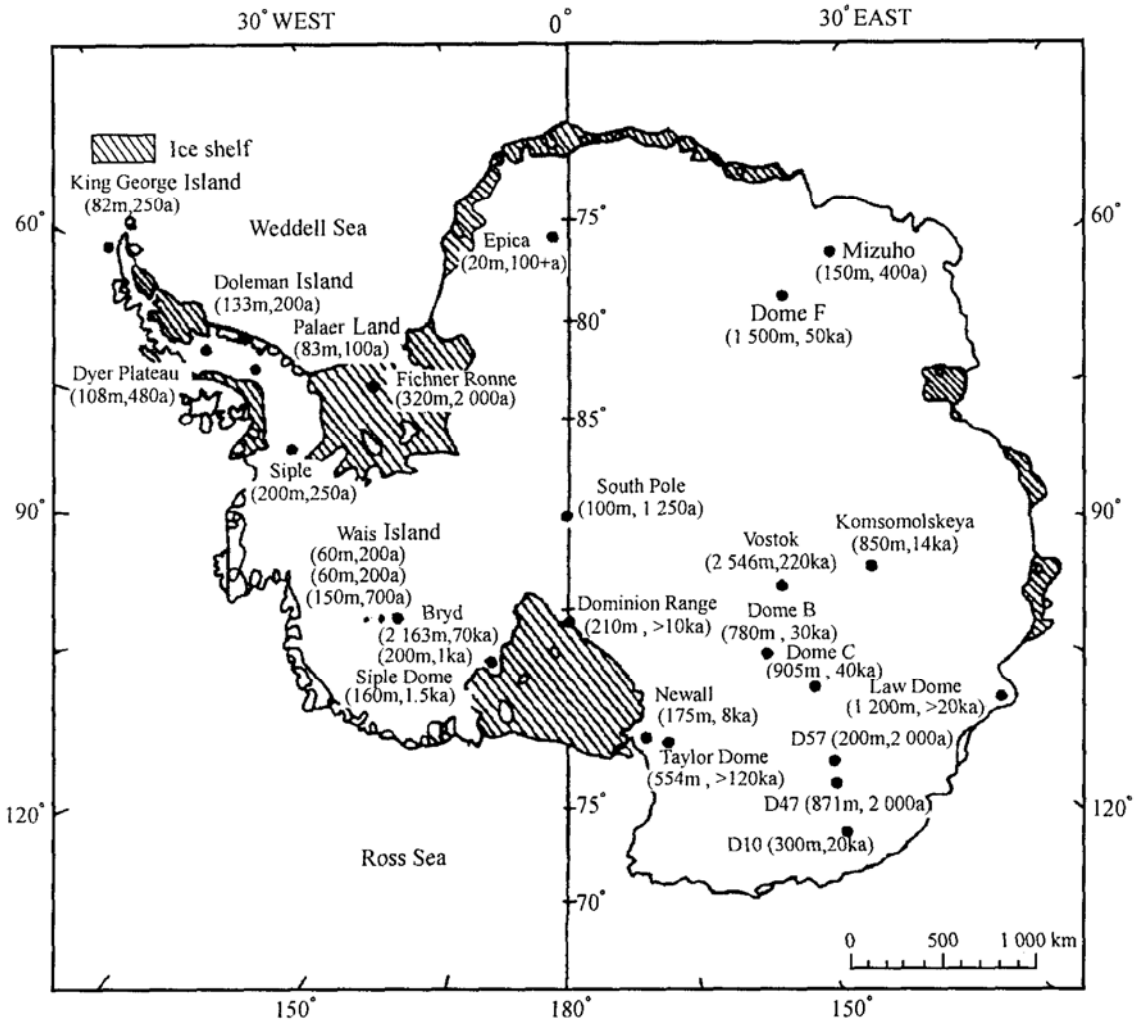

Fig. 1. Location of Dome C ice core.

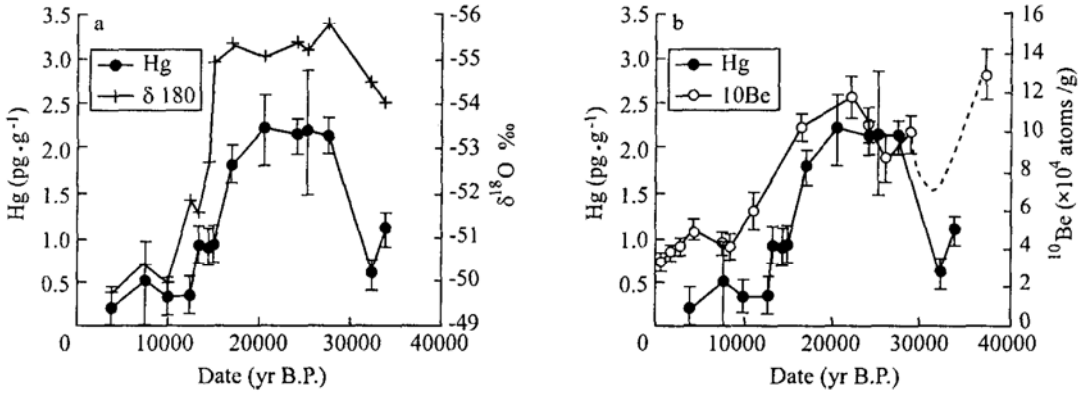

Fig. 2a. Comparison variations between the Hg concentrations and $\delta^{18}O$ values in Dome C ice core over the past 34,000 years ($r = -0.910$, $n = 14$); 2b. Comparison variations between the Hg concentrations and ^{10}Be values in Dome C ice core over the past 34,000 years, the dash line is given as guess because lack of data.

3.2 Calculation of accumulation rate

We defined a modern $\delta^{18}O$ values as 1.0, corresponding to an accumulation rate at 3.7 cm yr^{-1} in Dome C. The other$\delta^{18}O$ values related to Hg concentrations in the ice core were then normalized based upon modern $\delta^{18}O$ values and accumulation rate (seen in Fig. 3).

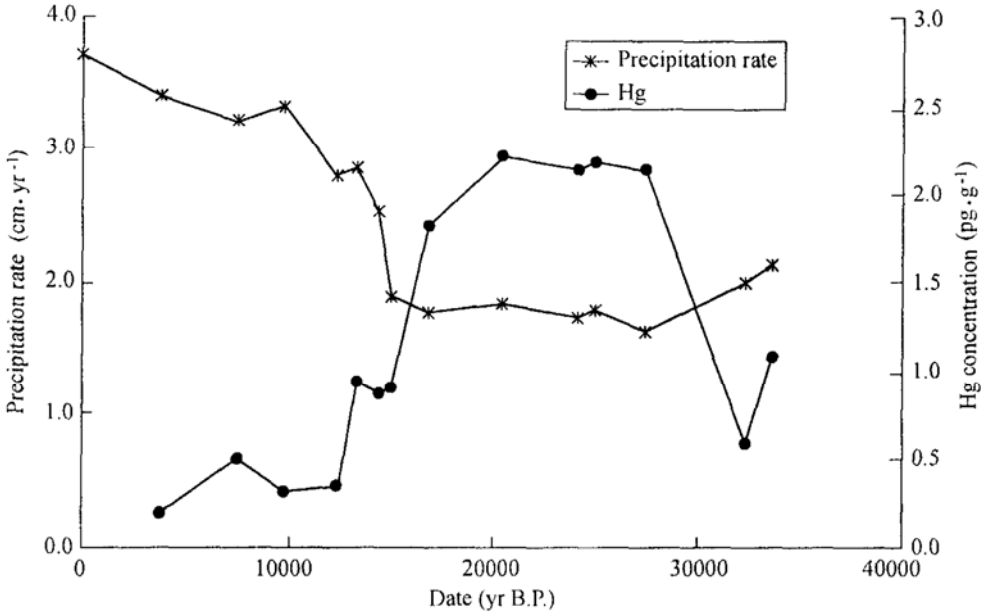

Fig. 3. The change of the precipitation rate in Antarctica recalculated from the $\delta^{18}O$ values in Dome C ice core during the past 34,000 years.

3.3 Assessment of Hg deposition flux

The Hg deposition fluxes were calculated as the following equation:

$F = [Hg] \times \rho \times \nu$

Where,

F: the deposition flux (pg cm^{-2} yr^{-1});

$[Hg]$: the concentration of Hg in ice core subsample (pg g^{-1});

ρ: the density of water(1g cm^{-3});

ν: water accumulation rate (cm yr^{-1}).

As seen in Fig. 4, four different climatic period were defined as: early Last Ice Age (Period Ⅰ, 34,000 – 28,000 yr B. P.), LGM (Period Ⅱ, 28,000 – 18,000 yr B. P.), transition from LGM to Holocene period (Period Ⅲ, 18,000 – 11,400 yr B. P), Holocene (Period Ⅳ, 11,400 – 4,000yr B. P.). During the above four periods, there was a dramatic variations of mercury deposition flux to Antarctica. The highest flux approximately 3.80 pg cm^{-2} yr^{-1} occurred in LGM period, about 3.5 times larger compared with the ones in Holocene. A detailed comparison with Vandal's results was listed in Table 1. The value in

Holocene given here was comparable with the previous result (Vandal et al. 1993), while, the mercury deposition flux to Antarctica during other three periods (Period Ⅰ, Ⅱ, Ⅲ) was slightly larger than the Vandal's values. This should be ascribed to the fact that Vandal et al. (1993) used an overvalued water accumulation rate data in the three periods of Ⅰ, Ⅱ, Ⅲ.

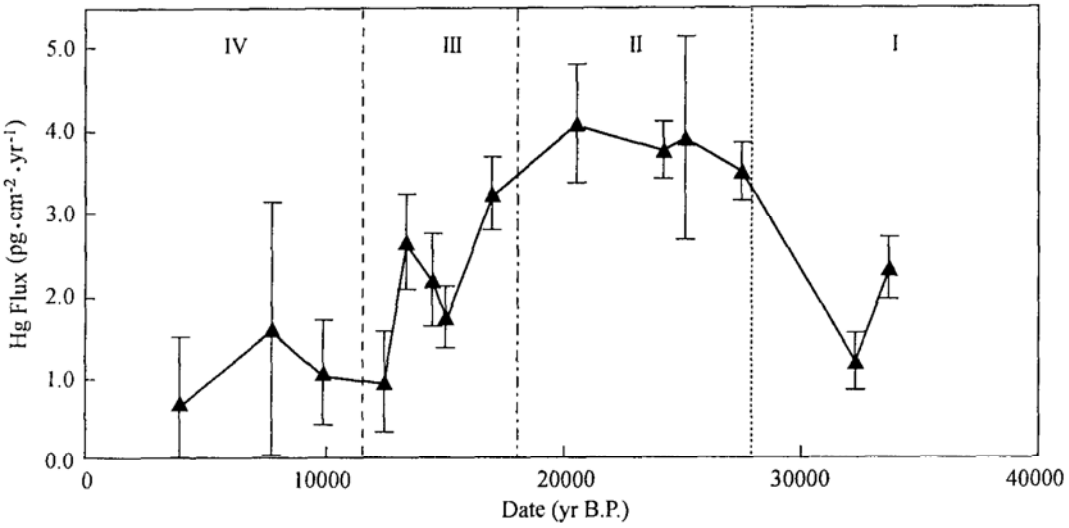

Fig. 4 Change of the mercury deposition flux to Antarctica over the past 34,000 years.

Table 1. The assessment of variations in mercury deposition flux to Antarctica over the past 34,000 years

Period	Hg concentrations ($pg\ g^{-1}$)	Hg deposition flux ($pg\ cm^{-2}\ yr^{-1}$)	Hg deposition flux* ($pg\ cm^{-2}\ yr^{-1}$)
Holocene	0.33	1.08	0.90
Transition from LGM to Holocene	0.96	2.13	/
Last Glacial Maxium (LGM)	2.17	3.80	3.10
early Last Ice Age	0.84	1.75	1.30

* reported by Vandal *et al.* (1993).

3.4 Influencing factors of mercury deposition flux

There are different views on the variations of mercury deposition to Antarctica during the Last Glacial period. Vandal et al. (1993) suggested that the oceanic productivity emission dominate the mercury concentration in the pre-anthropogenic period, while total mercury from volcanic eruptions, dust deposition and sea-salt transition only account of 5%−10% in proportion of mercury deposition to Antarctica. However, Martínez-Cortizas et al. (1999) argued that the higher mercury deposition flux during LGM was due to the cold condensation effect in the period. However, if atmospheric mercury deposition flux increases, while mercury emission into atmosphere is insufficient, atmospheric mercury reserves will decrease. Hence, Vandal et al. (1993) interpretation seems reasonable. In fact, the modern mercury deposition flux sharply reaches about 380 pg cm^{-2} yr^{-1} over the South Ocean due to the booming anthropogenic mercury emission (Mason *et al.* 1994).

Finally, we know that there are two dominant factors, the accumulation rates in ice

core and the mercury deposition fluxes, directly influencing the Hg concentrations in subsamples of ice core.

4 Conclusion

In our results, we observed a dramatic variation of mercury deposition flux to Antarctica during the past 34,000 years from the continue archives of Dome C ice core. The highest mercury deposition flux to Antarctica about 3.80 pg cm^{-2} yr^{-1} occurred in LGM period, about 3.5 times larger than in Holocene period. The natural mercury emissions such as oceanic biological emission are the predominant sources in the pre-anthropogenic mercury pollution. In addition, we suggested that Hg concentrations in ice core be used as another reliable proxy for precipitation rate.

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