# IRON FLUX OVER THE SUBARCTIC PACIFIC ESTIMATED BY AN ICE-CORE RECORD FROM MT. WRANGELL, ALASKA

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## INTRODUCTION

Iron is an essential nutrient for phytoplankton and plays an important role in the control of phytoplankton growth (Martin et al., 1989). Iron enrichment experiments carried out in the western and the eastern subarctic Pacific reveal that the iron limits phytoplankton growth in these areas (e.g. Tsuda et al., 2003). Possible sources of iron dissolved in surface seawater in the Sea of Okhotsk or Oyashio regions in the western subarctic Pacific are thought to be the iron-rich intermediate waters transported to surface by upwelling (e.g. Nishioka et al, 2007) and atmospheric dust (e.g. Duce and Tindale, 1991), that are lifted by dust storms generated over the Asian continent.

In order to estimate the contribution of atmospheric dust to phytoplankton groth, it is neccesary to quantitate the flux of air borne iron over the ocean. Several studies succeed at simulation of the transport process of chemical species in the atmosphere (e.g. Uno et al, 2001; Takemura et al., 2002), and at estimation of the deposition flux of chemical substances from the atmosphere (Uematsu et al., 2003) at the eastern Asia region. However, Uno et al.2003 show the case that simulate value of dust concentration differ by more than one order from the observation value of that in at the remote islands in Japan, and states the difficulty of quantitative prediction of dust because of complexities in accurately calculation dust emissions. It is need to validate the output of model studies with observation data of aerosol concentrations and/or deposition fluxes. However, sufficient data on aerosol concentration and deposition have not been collected especially on the North Pacific.

Ice-core is one of suitable archives to extract deposition of chemical substances from atmosphere. Glaciers developing in the high mountains of Kamchatka and Alaska record continuous time-series of dry and wet deposition of aerosol over a few hundreds years (Shiraiwa and Yamaguchi, 2002; Shiraiwa et al., 2003). Those glacier are cold enough to prevent vertical migration of the deposited substances by melt water. Moreover, annual accumulation rate in high mountain is significantly higher than that in polar region. Therefore, the high resolution records of iron deposition can be reconstracted from these ice-cores with year to year resolution.

In this study, we reconstruct the flux of air borne iron by means of analyses of an icecore obtained from Mount Wrangell in Alaska (Shiraiwa et al., 2004). Continuous iron profiles of ice-cores have hardly been reported apart from an ice-core from Law Dome in Antarctica by Edwads et al., 2006 because of difficulties of measurement owing to low content of iron in ice-cores and high risk of contamination. This study reports the first iron profile in an ice-core obtained from the northern North Pacific region.

#### SITE AND SAMPLE

Mount Wrangell ( $62^{\circ}$ N, 144W, 4317m a.s.l.) is located in the lee area along pathway of atmospheric dust from Asian continent to the North America (Figure 1), and is a glacier-mantled shield volcano (Benson and Motyka, 1978). The summit caldera is crowned by a 4 x 6 km oblong, 1 km deep glacier. A 50.29-m long ice-core was drilled by an electric mechanical drill on the summit of Mount Wrangell in 2003 (Shiraiwa at al., 2004). The ice-cores had been transported to the Institute of Low Temperature



Science, Hokkaido University by a freezer cargo and have been analyzed on stable isotope of water molecule, tritium content, insoluble particle (Yasunari et al, 2007), visible stratigraphy, detailed density (Kanamori, 2007), and dissolved ion species. Water equivalent depth (m w.eq.) of ice core was determined by the detailed density profiles (Kanamori, 2007). Age of ice-cores was estimated by the seasonal variation of hydrogen isotope ratio of water molecule and tritium content, and visible volcanic ash layer emitted from Mount Spurr eruption in 1992 observed in 26.82m w.eq. (Yasunari et al., 2007). The bottom of the ice-core at 50.29-m deep corresponds to 29.0m w.eq. and 1991 A.D. Since the average of annual accumulation was 2.4-2.6m w.eq., behavior of iron flux can be extracted with high time resolution.

## EXPERIMENTAL

We used upper 30m of ice-core for analysis of iron concentration, which covers from 2003 to 1997. The ice-cores have been cut and divided into several parts along vertical axis with a band saw for each analyses described as above. For iron determination, a quarter part of ice-cores were used. The ice-cores were cut horizontally into approximately 0.25-m long sections. The outer of ice-cores are awfully contaminated with iron by drilling instrument made of metal during ice-core drilling and by blade of band saws during processing described as above. Therefore, we carried out decontamination procedure with extreme caution. After 20-mm thickness of surface of ice sample was shaved with a ceramic knife in a clean bench settled in a cold clean room (class 10,000, -20°C), the ice samples were melted in 500-mL Teflon containers in ambient temperature. Melted samples were decant to 15-mL polypropylene bottles and were acidified with nitric acid of ultra pure glade (Kanto Kagaku) to 1% immediately after melting to prevent hardly soluble elements from being deposited and adsorbing on the wall of bottles. The samples were stored for several weeks before analysis because hardly soluble elements including iron are dissolved gradually into nitric acid

solution. It takes a few weeks until concentrations of these elements become stable. All materials used for sample preparation process and sample storage were cleaned in a 4M nitric acid bath for 24 hours.

Concentration of iron in the sample was determined by a graphite furnace polarized Zeeman type Atomic Absorption spectrophotometer (Hitachi model Z-2700) with pyro-coated cuvett and standard analysis condition.

#### **RESULT AND DISCUSSION**

A concentration profile of iron in the ice-core is shown in Figure 2 with that of  $\delta D$ profile. The iron concentrations showed relative high value in the layers above winter layers identified by minimum of  $\delta D$  in each year. The profile of  $\delta D$  shows seasonal variation with minimum in winter and maximum in summer. Therefore, the iron concentrations in the ice-core increase in ice/snow layers corresponding to spring in each year when the frequency of Kosa (Yellow dust) phenomena observed in Japan increases. Three peaks of iron concentration over 500nM, appeared in 2002 and 2001, when significant Kosa phenomena were observed in Japan (Nishikawa et al., 2003). Therefore, the profile of iron concentration in



Figure 2. Profiles of iron concentration and  $\delta D$  of ice-core obtained from Mount Wrangell. Dashed lines indicate minimum of  $\delta D$  corresponding to the winter layer.

the ice-core seems to reflect the variations of activity of dust storm in Asian continent.

Deposition flux of iron over snow surface at the summit of Mount Wrangell is given by multiplying the concentration of iron by relevant water equivalent depth. The profile of annual and springtime fluxes of iron are shown in Figure 3a and b. Annual flux of iron ranged from 3.0 to 29 mg/m<sup>2</sup>·yr. The values of iron flux are comparable to that estimated by Duce and Tindale, 1991. The iron fluxes in springtime ranged from 2.5 to 21 mg/m<sup>2</sup>·yr, and made up 55-95% of annual fluxes. Annual variation of number of Kosa days and total number of Kosa days reported by Japan Meteorological Agency (Nishikawa and Mori, 2003) are similar to the variations of iron fluxes except for the datum in 2000. Consequently, it is reasonable to suppose that the iron flux on the snow surface at the summit of Mount Wrangell reflects the dust emission in Asian continent.

The iron fluxes at three peaks observed in 2002 and 2001 layers marked by "I", "II", and "III" in Figure 2 were 9.53, 6.43, and 15.0 mg/m<sup>2</sup>, respectively. Each value is thought to be the iron flux supplied by one dust event. Generally, 2-10% of air borne iron can be dissolved in seawater (e.g. Fung et al, 2000). When 2% of the average flux of three events of  $10 \text{mg/m}^2$  is dissolved in the 30-m deep mixing layer in seawater, the concentration of

dissolved air borne iron in seawater becomes 0.12nM. This increase of dissolved iron supplied by one dust event can impact on the concentration of dissolved iron in surface seawater in the Sea of Okhotsk of sub nM order (Nishioka et al., 2007).

Iron fluxes estimated by icecore records do not correlate directly with deposition fluxes over subarctic North Pacific as well as dust emission fluxes in Asian continent. The chemical signals in ice-cores are formed via several processes such as emission, transportation, scavenging, and deposition. However, there are still large uncertainties in estimates



Figure 3. Annual variation of flux of iron (a), springtime flux of iron (b), the number of Kosa phenomena days (c), the total number of Kosa phenomena days in all meteorological station

of these processes. It is also need to evaluate the representativeness of ice-core records. A icecore reserve record of depositional substances at only a certain point. Additionally, drilling site of ice-cores in mid latitude as Alaska or Kamchatka is high mountain area far from sea surface. In order to precisely estimate the flux of chemical substances over subarctic Pacific with ice-core records, spatial distribution and vertical structure of Asian dust should be taken into consideration. Namely, ice core studies should be combined with simulative studies of chemical transport models in the new phase.

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