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ECM profile on the S25 core and its relationships with chemical compositions

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Abstract

The ECM profile on the S25 core, near the coastal region on Mizuho Plateau, East Antarctica, have been compared with chemical compositions variations. The ECM peaks mainly reflected high concentrations of NO_3^- and hardly coincided with $nssSO_4^{2-}$ peaks. It seems to be difficult to detect past volcanic H_2SO_4 deposition by the ECM on an ice core from the Antarctic coastal region, such as S25 core.

1. Introduction

Electrical conductivity measurement (ECM) developed by Hammer (1980), has been applied by many researchers to investigate the profiles of acidity in an ice core continuously. The ECM peaks have a good relationship with high acidity peaks in an ice core and has been frequently discussed as indicators of volcanic H_2SO_4 deposition. However, the chemical composition of acids except H_2SO_4 also contributes to the ECM currents and it has been suggested that HCl and HNO_3 cause higher currents than H_2SO_4 (Legrand *et al.*, 1987). The ECM signal may be dependent on not only acidic impurities concentrations but also existing state of impurities in ice. It would be much different for the ECM intensity whether acidic impurities exist in grain boundaries or crystal lattices of ice.

In this paper, we show the ECM profile at an ice core taken from the coast of Mizuho Plateau, East Antarctica and discuss the relationship between the ECM intensity and the concentrations of chemical compositions.

2. Sample and method

The ice core was taken at site S25, located at the coast of Mizuho Plateau, East Antarctica (69°01'58"S, 40°28'07"E, altitude 868m), to a depth of 100m by the 26th Japanese Antarctic Research Expedition (JARE-26) in 1986. The S25 core has been stored in the low-temperature room (-20°C) of the National Institute of Polar Research (NIPR) and the ECM was made in the low-temperature room in 1991. The ECM level on the surface of aging ice is depressed, however, the aging effect can be prevented by shaving the ice surface (Schwander *et al.*, 1983). We have performed the ECM immediately after shaving about 1cm of the ice core surface. Unfortunately, the ECM could not be made at depths between 43 and 50m because of heavy pollution by an antifreeze solution. Bulk density of the core was also measured before the ECM conduct. Figure 1 shows the density profile of the S25 core. To measure major ions, the S25 core was cut in the low-temperature room, with the sampling interval of about 5 cm. Water samples (after melting the cut ice) were used for measurements by an ion chromatograph (Dionex 2000i), as was mentioned in detail in Fujii *et al.* (1989).

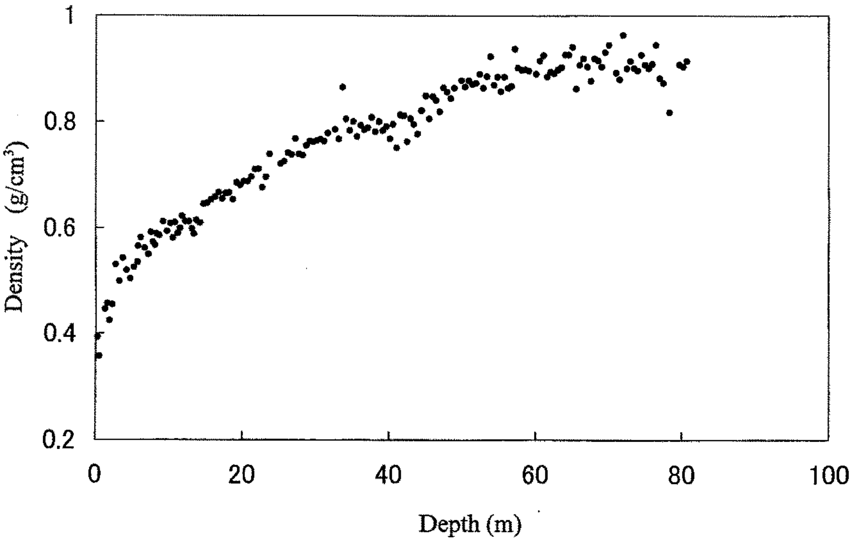

Fig. 1. Density profile of the S25 core.

3. Dating of the S25 core

Site S25 is located in the coastal region, Mizuho Plateau, where a high snow accumulation rate was observed (Watanabe *et al.*, 1988), and strong seasonal variations of hydrogen peroxide (H_2O_2) and non-sea-salt sulfate ($nssSO_4^{2-}$) have been shown in the S25 core (Watanabe *et al.*, 1998; Watanabe *et al.*, 1999). The mean annual net accumulation rate of snow at site S25, based on the counting annual cycles of H_2O_2 and $nssSO_4^{2-}$, was estimated to be about 30 cm a^{-1} water equivalent, showing similarity to the result of stake measurements of snow (Watanabe *et al.*, 1998), and suggests that the whole core represents the records of the last 250 years.

We have also used the firn densification model by Herron and Langway (1980) to estimate the dating of the core. The model shows that plots of $ln(\rho/(\rho_i-\rho))$, where ρ_i is the density of solid ice (0.917 $g \cdot cm^{-3}$) and ρ is the density of the firn, versus depth consist of two linear segments. The first segment is for $\rho<0.05$ $g \cdot cm^{-3}$ and the second is for 0.05 $g \cdot cm^{-3} < \rho < 0.82 \sim 0.84$ $g \cdot cm^{-3}$, corresponding to the first and second stages of densification. Figure 2 shows that the relationship between depth and $ln(\rho/(\rho_i-\rho))$ of the S25 core (the second stage). The $ln(\rho/(\rho_i-\rho))$ is expressed as follows:

$$ln(\rho/(\rho_i-\rho))=0.043D+0.19, \quad (1)$$

where D is the depth of the core. "Pore close off" occurs at $\rho=0.82 \sim 0.84$ $g \cdot cm^{-3}$, below which densification occurs more slowly. Herron and Langway (1980) related the annual accumulation rate A to the slope C of the $ln(\rho/(\rho_i-\rho))$ versus depth relationship as,

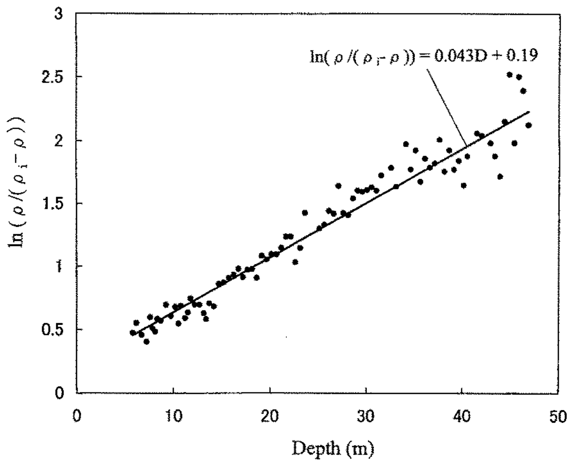

Fig. 2. Relationship between depth and $ln(\rho/(\rho_i-\rho))$ of the S25 core.

$$A=(\rho_i K/C)^2, \quad (2)$$

where K is an empirical constant found from measurements of many cores, Herron and Langway (1980) give as follows:

$$K=575\ exp(-21400/RT), \quad (3)$$

where R is the gas constant and T is the mean annual temperature, which is 257 K at S25. Taking the slop C of regression line of the second stage in Fig. 2 to be 4. 3×10^{-2}, the annual accumulation rate is calculated to be 29 cm a^{-1} water equivalent. The calculated accumulation rate is the similar to the rate value by counting method.

4. ECM profile and chemical compositions

Figure 3 shows the ECM profile along the S25 core, with ages calculated by the firn densification model by Herron and Langway (1980). Because of the increasing density of the firn with depth (Fig. 1), the ECM intensity increases with depth. There are several high ECM peaks, for example, at about 13 m, 34 m, 55 m, 75 m and 95 m depths. High ECM signals have been sometimes treated as signs of large volcanic eruptions, such as Agung 1963, Krakatoa 1883 and Tambora 1815 (Hammer *et al.*, 1980; Langway *et al.*, 1994; Osada, 1996; Kohno *et al.*, 1996). Especially the Tambora 1815 was an explosive eruption and many ice cores from polar regions preserve the signal (Hammer *et al.*, 1980; Legrand *et al.*, 1987; Delmas, 1992; Osada, 1996; Kohno *et al.*, 1996 and 1999). If the ECM peak at about 75 m depth presents a sign of the Tambora 1815 eruption, the mean annual net accumulation rate of snow at site S25 can be estimated to be 31 cm a^{-1} water equivalent. The estimated accumulation rate shows a good correspondence with the result of densification method. Therefore, the signal of the Tambora 1815 may be recorded at 75m depth in the S25 core. The error of the densification method may be about 15 years at 75m depth. However, we need to perform chemical compositions measurements, whether the ECM peak presents the volcanic eruption or not.

Does the ECM signal on the S25 core reflect past volcanic H_2SO_4 deposition? We have compared the ECM profile with the concentrations of chemical compositions in the S25 core. Figures 4 and 5 show comparisons between the vertical ECM profile and $nssSO_4^{2-}$ and NO_3^- concentrations, respectively. Unfortunately, measurements of the chemical compositions were performed only to about 30m in depth. The comparisons present that the large ECM peaks hardly correspond to high $nssSO_4^{2-}$ but have good agreement with high concentrations of NO_3^- (Figs. 4 and 5). Several ECM peaks correspond to relatively high concentrations of $nssSO_4^{2-}$, for example, at 10 m, 19 m, 24 m and 28 m (Fig. 4). However, these peaks also correspond to high NO_3^- (Fig. 5). The result indicates that most of $nssSO_4^-$, which is mainly derived from marine biogenic activity, may not contribute to acidification of snow, while $nssSO_4^{2-}$ concentration is higher than the concentration of NO_3^- (origins and transport processes of NO_3^- in Antarctic snow and ice are not yet well understood (Wolff, 1995)). Figure 6 shows the relationship between Na^+ and Cl^- concentrations in the S25 core. Many samples appear that the $[Cl^-]/[Na^+]$ ratio is lower than that in seawater. Legrand and Delmas (1988) suggested that the deficit of Cl^- relative to Na^+ is mainly due to the presence of Na_2SO_4 as a result of a sea-salt alteration reaction. The $nssSO_4^{2-}$ in the S25 core would exist as mainly Na_2SO_4 which does not contribute to acidification.

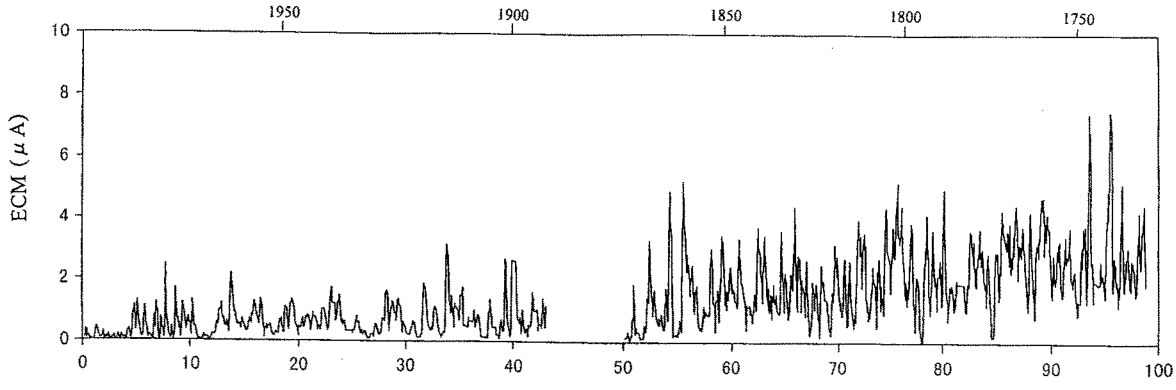

Fig. 3. ECM profile on the S25 core. The profile was obtained by taking a running mean over every 10 cm interval. Ages calculated by the firn densification model by Herron and Langway (1980), are given in numbers.

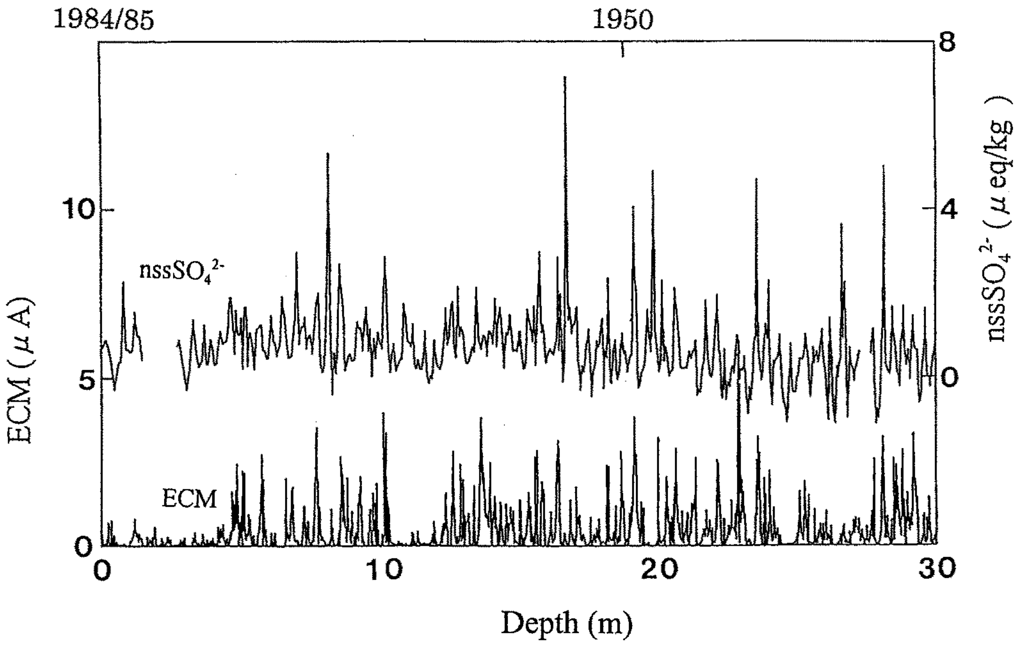

Fig. 4. ECM profile and nssSO_4^{2-} in the S25 core. Ages calculated by the firn densification model by Herron and Langway (1980), are given in numbers.

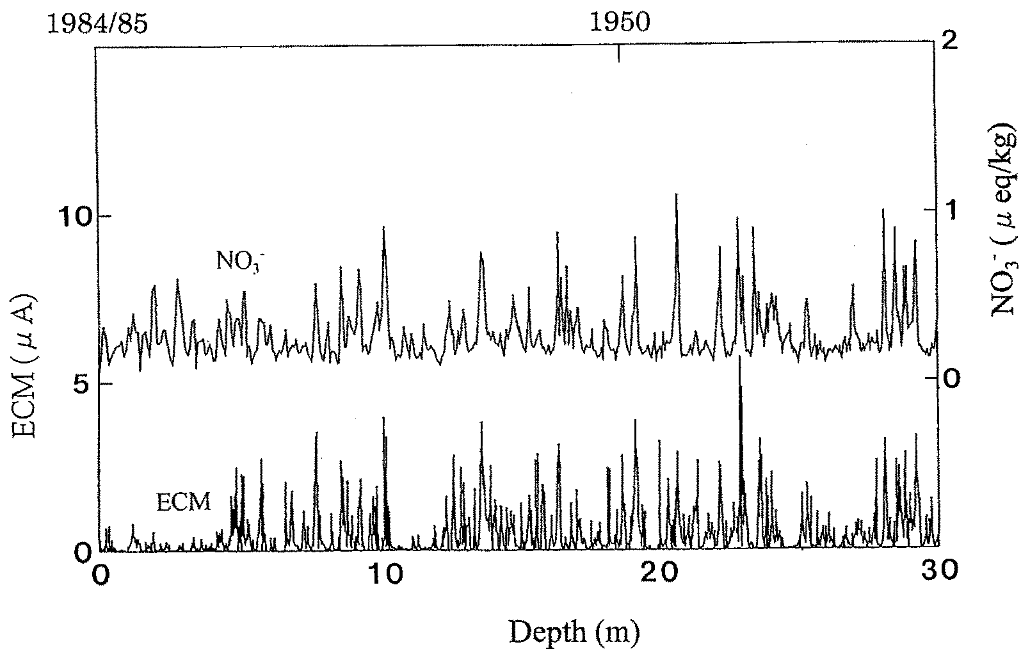

Fig. 5. ECM profile and NO_3^- in the S25 core. Ages calculated by the firn densification model by Herron and Langway (1980), are given in numbers.

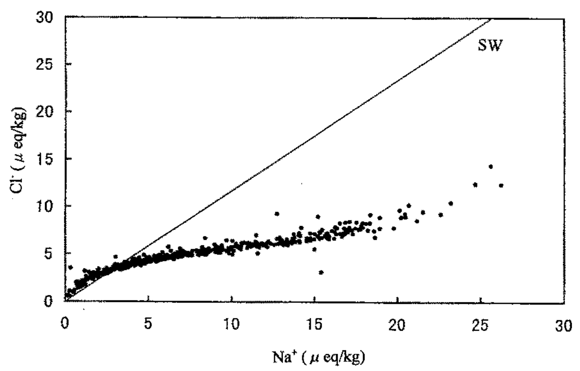

Fig. 6. Relationship between Na^+ concentration and Cl^- concentration in the S25 core. SW shows the ratio in seawater.

Volcanic signals were not detected in an ice core from the Weddell Sea sector in the Antarctica because of high marine-biologically derived SO_4^{2-} deposition in the coastal region (Peel and Mulvaney, 1992). The $nssSO_4^{2-}$ in the S25 core does not seem to show the major volcanic eruptions in this century such as the Agung 1963 (Watanabe *et al.*, 1999). The sign of the Agung 1963 which is one of the most detectable signals (in the 20th century) in inland ice cores (Legrand and Delmas, 1987; Legrand and Feniet-Saigne, 1991; Osada, 1996), is not also seen in the ice core drilled at site H15, about 15 km inland from site S25 (Kohno *et al.*, 1999). Perhaps, it may be difficult to detect volcanic signals in ice cores from coastal regions where marine biogenic sulfur is actively transported.

As mentioned above, the ECM peaks coincide with high NO_3^- concentrations in the S25 core, therefore, the NO_3^- probably exists as HNO_3. Legrand *et al.* (1987) also described that HNO_3 seems to be more effective than H_2SO_4 on the conductivity. Perhaps, the large ECM signals at 55 m, 75 m and 95 m depths may reflect high NO_3^- concentrations.

5. Summary

We performed the ECM on the S25 ice core to 100 m depth. According to the estimated accumulation rate at site S25, the ECM peak at 75m depth may present the signal of the Tambora 1815 eruption, while there are no chemical data at the depth.

The ECM signal on the S25 core have been compared with the concentrations of chemical compositions in the top 30 m. The high ECM peaks had good agreement with high concentrations of NO_3^- and hardly corresponded to high $nssSO_4^{2-}$. The results show that it may be difficult to detect signs of past volcanic eruptions by the ECM intensity on the S25 core.

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