# Effect of accumulation rate on water stable isotopes of near-surface snow in inland Antarctica

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[1] Postdepositional changes in water stable isotopes in polar firm were investigated at three sites characterized by different accumulation rates along the East Antarctic ice divide near Dome Fuji. Water stable isotopes, major ion concentrations, and tritium contents of three 2-4 m deep pits were measured at high resolution (2 cm). Temporally, the snow pits cover the past 50 years with snow accumulation rates in the range of 29–41 kg m<sup>-2</sup> a<sup>-1</sup> around Dome Fuji. Oxygen isotopic profiles in the three pits do not show annual fluctuations, but instead exhibit multivear cycles. These multivear cycles are lower in frequency at Dome Fuji as compared with the other two sites. Peaks of water stable isotopes in the multivear cycles correspond to some ion concentration minima in the pits, although such relationships are not observed in coastal regions. We propose that the extremely low accumulation environment keeps the snow layer at the near surface, which result in postdepositional modifications of isotopic signals by processes such as ventilation and vapor condensation-sublimation. We estimate that oxygen isotopic ratios could be modified by >10% and that the original seasonal cycle could be completely overprinted under the accumulation conditions at Dome Fuji. Moreover, stake measurements at Dome Fuji suggest that the large variability in snow accumulation rate is the cause of the multiyear cycles.

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### 1. Introduction

[2] Water stable isotopes ( $\delta^{18}$ O and  $\delta$ D; WSIs) in polar ice cores are used to derive paleo-temperatures [e.g., *EPICA Community Members*, 2004; *Johnsen et al.*, 2001; *Kawamura et al.*, 2007; *Petit et al.*, 1999; *Uemura et al.*, 2012], because WSIs in polar snow are largely controlled by the difference between the sea surface and condensation temperatures [*Dansgaard*, 1964]. However, it is also known that high temporal resolution data, such as at the seasonal scale, within WSI profiles of firm and ice cores are obscured by modification due to isotopic diffusion [*Langway*, 1967]. Isotopic diffusion between air-filled pores of the firm layer acts

to smooth WSI profiles with depth/time [Johnsen, 1977; Johnsen et al., 2000; Whillans and Grootes, 1985]. Previous studies have assumed that isotopic modifications in firn occurs at isotopic equilibrium between pore space vapor and surrounding snow grains, and used back-diffusion by numerical simulation to reconstruct the original WSI profiles [Johnsen, 1977; Johnsen et al., 2000; Whillans and Grootes, 1985]. Recent studies have investigated vapor-driven diffusion by comparing calculated diffusion rates with those measured in firn by laboratory experiments [Pohjola et al., 2007; van der Wel et al., 2011]. Effects of firn ventilation driven by wind and water vapor advection [Colbeck, 1989; Waddington et al., 2002] have been numerically simulated [Neumann and Waddington, 2004; Town et al., 2008]. These studies demonstrated that changes in isotopic profiles of firn were caused by isotopic equilibrium between the pore space vapor and surrounding ice matrix. Hachikubo et al. [2000] experimentally showed that changes in WSIs are related to the depth hoar formation. Their experiments were conducted using large snow-temperature gradients in a closed and insulated box filled with snow in which changes in WSIs could be measured and revealed that changes of WSIs primarily depended on snow density. Sokratov and Golubev [2009] studied changes in WSIs by sublimation in snow and ice samples under nearly isothermal conditions and showed that large increases of WSIs occurred in the upper several centimeters of surface snow.

[3] An understanding of environments in inland Antarctica with extremely low rates of snow accumulation is important

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**Figure 1.** Locations of the three snow pits (DF, DK, and MP) along the JASE traverse [after *Fujita et al.*, 2011].

for interpreting ice core records. Low accumulation rates result in significant postdepositional modification due to near-surface snow exposure to snow drift and ventilation [Neumann and Waddington, 2004; Town et al., 2008]. Ekaykin et al. [2002] reported that hydrogen isotopic variations of Vostok snow pits corresponded to the accumulation time series obtained from stakes. Neumann et al. [2005] also showed that a WSI record in an ice core at Taylor Mouth did not correspond to temperature variations and concluded that the record was probably affected by multiple sources of snow accumulation (wind-blown snow and storms), which caused postdepositional WSI changes due to vapor motion during prolonged near-surface exposure.

[4] However, few studies have examined the relationship between accumulation environment and WSIs after deposition using field samples taken at ice core drilling sites. Therefore, validation between numerical simulations and field sampling data is currently not sufficient to fully understand the complexities associated with postdepositional WSI changes. Moreover, postdepositional modification of WSIs in firn and its relationship to snow accumulation rate in inland Antarctica are important for interpreting WSI records of deep ice cores.

[5] Here we focus on postdepositional modification of WSI signals using three snow pits acquired at different accumulation environments on the Japanese Swedish Antarctic Expedition (JASE traverse) in the 2007/2008 austral summer. We analyzed

the chemical compositions of the snow pits and compared WSI profiles and major ion concentrations of the pits. Using these data, we will discuss the relationship between snow accumulation rate and postdepositional modification of WSIs in a low-snow-accumulation environment.

### 2. Locations and Methods

#### 2.1. Snow Pits and Analyses

[6] To understand the spatial-temporal variability of the glaciological environment in Dronning Maud Land (DML), a 2800 km route was examined by the JASE traverse across DML in the 2007/2008 austral summer [Holmlund and Fujita, 2009]. The JASE traverse connected several Antarctic stations, namely Syowa-Dome Fuji (DF)-EPICA DML (Kohnen)-Wasa (Figure 1). The Japanese team started from the Syowa station, whereas the Swedish team started from the Wasa station, and the two teams met at the Meeting Point (MP) in December 2007. During this expedition, two 4 m deep snow pits and one 2 m deep snow pit were dug at the DF, DK190 (DK), and MP sites for WSI and chemical analysis [Fujita et al., 2011; Iizuka et al., 2012] (Table 1). The MP site is located 380 km west of the DF station. The DK site is located between these two sites on the traverse route (Figure 1), where a 2 m deep snow pit was dug. The snow samples were kept in a frozen state during transport. WSI ratios ( $\delta D$  and  $\delta^{18}O$ ), major soluble ions, and tritium contents were analyzed at 0.02 m depth intervals at the National Institute of Polar Research in Japan. The WSIs were analyzed by the equilibrium method with a Delta Plus mass spectrometer [Uemura et al., 2007]. The average precisions of WSI determinations were  $\pm 0.5\%$  for  $\delta D$  and  $\pm 0.05\%$  for  $\delta^{18}O$ . The major soluble ions (F<sup>-</sup>, MSA, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) were analyzed by an ion chromatograph (Dionex DX500) in a class 10000 clean room. The precision of these analyses is  $<\pm 2\%$  at the 1 ppb level for all ions. The tritium contents were determined using the liquid scintillation method [Kamiyama et al., 1989, 1997]. Snow densities and stratigraphies including crust layers were also measured along the pit walls with depth resolutions of 0.03 and 0.01 m, respectively.

### 2.2. Dating of Snow Pits

[7] Nonsea salt sulfate (nssSO<sub>4</sub><sup>2-</sup>), which is a useful time marker for dating ice cores and snow pits because it can correspond to volcanic eruptions, is calculated by subtracting the sea salt contribution from the total sulfate concentration ([nssSO<sub>4</sub><sup>2-</sup>]=[SO<sub>4</sub><sup>2-</sup>] - 0.252[Na<sup>+</sup>]) [*Göktas et al.*, 2002].

Table 1. Locations, Accumulation Rates, and Snow Densities of Snow Pits Along the JASE Traverse<sup>a</sup>

Site	Longitude	Latitude	Elevation (ma.s.l.)	Pit Depth (m a.s.l.)	Sampling Date (YYYY.MM.DD)	Snow Density (kg m <sup>-3</sup> )	Accumulation Rate $(\text{kg m}^{-2} \text{ a}^{-1})$	Accumulation Rate (1992–2007) (kg m <sup>-2</sup> a <sup>-1</sup> )
DF	39°47′E	77°18′S	3785	4	2007.12.10-12	$365\pm37$	$29.3 \pm 17.4$	25.6
DK	31°45′E	76°48′S	3733	2	2007.12.20	$368 \pm 43$	$35.5 \pm 13.3$	34.3
MP	43°00′E	74°00′S	3656	4	2007.12.25-26	$372 \pm 29$	$40.9 \pm 13.1$	41.8
DF <sup>b</sup> DF <sup>c</sup>				3.4	1999.1.24	318	$\begin{array}{c} 29.0\\ 27.3\pm19.9\end{array}$	

<sup>a</sup>JASE snow densities were averaged from surface to 2 or 4 m depth by measuring 3 cm depth intervals.

<sup>b</sup>Snow pit the period 1962–1999 by *Iizuka et al.* [2004].

<sup>c</sup>Stake measurements during 1995-2006 by Kameda et al. [2008].



**Figure 2.** Profiles of  $nssSO_4^{2-}$  (black line in left panels) and Na<sup>+</sup> (black line in right panels), Cl<sup>-</sup>/Na<sup>+</sup> (gray line in right panels), and crust layers (thin vertical lines in right panels) of the (a, b) DF, (c, d) DK, and (e, f) MP sites. Vertical lines in the left panels denote the Pinatubo (1992/1993 summer; 1991 eruption) and Agung (1963/1964 summer; 1963 eruption) signals. Gray line in Figure 2a denotes tritium contents and 1964 horizon in the DF pit.

Peaks of  $nssSO_4^{2-}$  produced by volcanic eruptions have a time lag of ca. 1 to 2 year because of transportation from low- or midlatitudes to Antarctica [*Cole-Dai and Mosley-Thompson*, 1997; *Legrand and Delmas*, 1987; *Traufetter et al.*, 2004]. In coastal high-accumulation environments, WSI profiles are also useful for dating snow pits and shallow ice cores, because seasonal cycles of WSI ratios are clearly preserved in firn [*McMorrow et al.*, 2002; *Naik et al.*, 2010]. However, in inland Antarctica, it is difficult to count seasonal signals of WSIs in snow, and as such crust layers, tritium contents, and Na<sup>+</sup> and Cl<sup>-</sup> are commonly used for dating [e.g., *Ekaykin et al.*, 2002; *Iizuka et al.*, 2004].

#### 3. Results

#### 3.1. Accumulation Rates

[8] We detected two eruption signals in the DF pit: 1992/ 1993 Pinatubo (1991 eruption) and 1963/1964 Agung (1963 eruption) at 1.15 and 3.49 m depths, respectively. However, in the other snow pits, we only identified one  $nssSO_4^{2-}$  peak, which corresponded to the Pinatubo eruption at 1.39 m (DK) and 1.75 m (MP) depths (Figures 2a, 2c, and 2e). We also measured a tritium peak at 3.16 m depth in the DF pit, which corresponds to the 1966 fallout from hydrogen bomb tests in 1963 [*Kamiyama et al.*, 1989]. *Iizuka et al.* [2004] collected a snowdrift at the DF station, which had lower Na<sup>+</sup> and higher Cl<sup>-</sup>/Na<sup>+</sup> in summer than in other seasons. However, the seasonal signal of ion concentrations is often obscured by postdepositional modification and erosion of the surface snow. Therefore, we determined summer layers at which the crust layer was found, together with either minima of Na<sup>+</sup> or spikes of Cl<sup>-</sup>/Na<sup>+</sup> at the same depth (Figures 2b, 2d, and 2f).

[9] We detected 49 annual layers in the DF pit and 36 annual layers in the MP pit, resulting in calculated snow



**Figure 3.** Occurrence frequency distributions (bars) and normal distributions (lines) of the annual accumulation rate at the DF site. The blue color denotes the pit accumulation rates, and the white bar and black line denote the accumulation rate determined by stake measurements [*Kameda et al.*, 2008].

 Table 2. Water Stable Isotope Ratios and D-Excesses in the

 Measured Snow Pits

		Average	SD	Maximum	Minimum
DF	δD (‰)	-433.3	22.3	-378.5	-484.1
	$\delta^{18}O(\%)$	-56.3	3.0	-49.0	-63.1
	d-excess (‰)	16.7	2.2	22.6	10.1
DF	$\delta D$ (‰)	-447.2			
(precipitation <sup>a</sup> )	$\delta^{18}$ O (‰)	-57.7			
	d-excess (‰)	14.3			
DK	$\delta D$ (‰)	-423.0	20.3	-362.9	-462.9
	$\delta^{18}$ O (‰)	-54.8	2.7	-46.8	-60.1
	d-excess (‰)	15.2	2.3	21.1	9.6
MP	$\delta D$ (‰)	-408.7	20.5	-339.6	-472.3
	$\delta^{18}$ O (‰)	-52.7	2.6	-44.5	-61.0
	d-excess (%)	13.0	2.1	20.3	8.5

<sup>a</sup>Fujita and Abe [2006].

accumulation rates of  $29.3\pm17.4\,kg\,m^{-2}~a^{-1}$  (DF) and  $40.7 \pm 13.3 \text{ kg m}^{-2} \text{ a}^{-1}$  (MP), based on snow densities observed in the same snow wall of each snow pit (Table 1). The quoted errors are one standard deviation of the mean annual accumulation. Figure 3 shows the frequency distribution of the annual accumulation rates of the DF snow pit and stake measurements during 1997-2008 [Kameda et al., 2008]. Agreement between the two independent measurements suggests that the dating of the JASE snow pits is robust. The accumulation rate at the DK site is estimated to be  $35.5 \pm 13.1 \text{ kg m}^{-2} \text{ a}^{-1}$ , which is an average from 21 annual layers in the 2 m deep snow pit (Table 1). The snow accumulation rate of the DF pit is 0.72 times that of the MP pit, and the annual variability of accumulation at the DF site is larger than that at the MP pit. Snow accumulation rate of DF from 1992 (Pinatubo peak) to 2007 (surface) is slightly lower than that for the whole period (1958–2007) of the snow pit. The accumulation rate in the second half of the 20th century at the eastern part of DML was on average ~15% higher over longer periods of 722 a or 7.9 ka [Fujita et al., 2011]. A wetting tendency was also reported for recent periods from 1999–2005 to 2005–2008 at Dome A [Ding et al., 2011]. This suggests that snow accumulation rates over DML have increased over the long term, but may have been variable in the past few decades.

#### 3.2. Water Stable Isotopes and Ion Concentrations

[10] Averaged  $\delta D$  and  $\delta^{18}O$  values are lower in inland Antarctica than coastal areas, but the deuterium excess (d-excess;  $d = \delta D - 8 \times \delta^{18}O$ ) of the snow pits increases inland (Table 2). The relationship between  $\delta D$  and  $\delta^{18}O$  is given by  $\delta D = 7.46\delta^{18}O - 13.45$  (DF),  $\delta D = 7.88^{18}O + 6.89$ (DK), and  $\delta D = 7.60\delta^{18}O - 6.51$  (MP). Hereafter, we only discuss  $\delta^{18}O$  data and not  $\delta D$  data for the pits, due to the significant correlation between  $\delta^{18}O$  and  $\delta D$  (r=1.00 for DF and r=0.99 for DK and MP; all p < 0.001).

[11] Figure 4 shows  $\delta^{18}$ O profiles versus water equivalent depth, which was obtained by multiplying snow depth by snow density, along with identified summer layers in the pits. It is clear that no seasonal cycle is present, even though a seasonal cycle should be detectable with a 0.02 m sampling interval [Kameda et al., 2008]. As such, it appears that fluctuations of the  $\delta^{18}$ O profiles have multiyear cycles. In particular, the DF pit shows lower-frequency cycles than the other pits.

[12] Table 3 lists correlation coefficients between  $\delta^{18}$ O and ion concentrations in the snow pits. Ions that originate from sea salt (Cl<sup>-</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>), K<sup>+</sup>, and Ca<sup>2+</sup> show significant positive correlations with each other. There are significant negative correlations between  $\delta^{18}$ O and ion concentrations (apart from F<sup>-</sup> and NO<sub>3</sub><sup>-</sup>). Figure 5 shows profiles of MSA, nssSO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and  $\delta^{18}$ O in the pits. It is clear that the  $\delta^{18}$ O peaks coincide with minima in ion concentrations. The relationships between  $\delta^{18}$ O and ion concentrations are more clearly evident in the DF pit than in the other pits (Table 3).

## 4. Discussion

# 4.1. Relationship Between Accumulation and Water Stable Isotopes

[13] Masson-Delmotte et al. [2008] reported the spatial distribution of WSIs in ice/firn cores, noting that  $\delta D$  and  $\delta^{18}O$  have lower values in inland Antarctica than in coastal areas. The same distribution is also evident in the JASE snow pits (Table 2). In an inland region (DF), *Fujita and Abe* [2006] showed that annual averages of WSIs in 2003 weighted by the amount of daily precipitation were -447.2% ( $\delta D$ ) and -57.7% ( $\delta^{18}O$ ), which are similar to those of the DF pit,



**Figure 4.**  $\delta^{18}$ O profiles along water equivalent depth in the (a) DF, (b) DK, and (c) MP pits. Thin vertical lines denote summer layers identified in this study.

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		$\delta^{18}$ O	$F^{-}$	MSA	Cl <sup>-</sup>	$\mathrm{SO_4}^{2-}$	NO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	$K^+$	Mg <sup>2+</sup>
DF	$F^{-}$	-0.02								
(n = 200)	MSA	-0.41	0.18							
. ,	$Cl^{-}$	-0.47	0.51	0.49						
	$SO_4^{2-}$	-0.14	-0.23	0.28	0.04					
	$NO_3^-$	0.06	0.13	0.06	0.00	-0.05				
	Na <sup>+</sup>	-0.58	0.29	0.41	0.84	0.13	0.00			
	$K^+$	-0.46	0.15	0.28	0.67	0.10	0.09	0.78		
	$Mg^{2+}$	-0.58	0.35	0.38	0.82	0.15	0.03	0.98	0.76	
	$Ca^{2+}$	-0.49	0.12	0.26	0.65	0.18	0.15	0.83	0.70	0.83
DK	$F^{-}$	-0.08								
(n = 100)	MSA	-0.40	0.16							
. ,	Cl <sup>-</sup>	-0.43	0.31	0.19						
	$SO_4^{2-}$	-0.30	-0.34	0.19	0.03					
	$NO_3^-$	0.07	0.52	0.23	0.31	-0.17				
	Na <sup>+</sup>	-0.52	0.23	0.16	0.88	0.10	0.18			
	K <sup>+</sup>	-0.50	0.23	0.12	0.84	0.17	0.22	0.96		
	$Mg^{2+}$	-0.51	0.31	0.19	0.91	0.10	0.29	0.99	0.95	
	Ca <sup>2+</sup>	-0.46	0.22	0.06	0.76	0.21	0.27	0.89	0.94	0.89
MP	$F^{-}$	-0.15								
(n = 200)	MSA	-0.32	0.14							
	Cl_	-0.46	0.42	0.14						
	$SO_4^{2-}$	-0.34	0.24	0.42	0.19					
	$NO_3^-$	0.04	0.19	0.24	-0.10	-0.16				
	Na <sup>+</sup>	-0.49	-0.05	0.19	0.91	0.28	-0.09			
	K	-0.50	0.15	0.15	0.91	0.34	-0.10	0.95		
	$Mg^{2+}$	-0.52	0.19	0.19	0.92	0.31	-0.07	0.97	0.96	
	$\tilde{Ca^{2+}}$	-0.41	0.12	0.12	0.68	0.38	-0.08	0.74	0.81	0.76

**Table 3.** Correlation Coefficients Between  $\delta^{18}$ O and Ion Concentrations<sup>a</sup>

<sup>a</sup>Coefficients highlighted in bold indicate significant correlations (p < 0.001).



**Figure 5.** Profiles of MSA,  $nssSO_4^{2-}$ ,  $Na^+$ , and  $\delta^{18}O$  in the DF, DK, and MP pits. Gray shadings denote the depth of  $\delta^{18}O$  peaks.



**Figure 6.** (a)  $\delta^{18}$ O profiles, which spline approximation with 0.25 year intervals, of the DF pit sampled by the JASE traverse (black line; this study) and by *lizuka et al.* [2004] (gray line). (b) Stacked  $\delta^{18}$ O (black line), stacked air temperature by reanalysis data (light blue line), and air temperature by AWS (green line).

although the seasonal amplitude changes were significantly larger than the variability in the pit (Table 2).

[14] We first compared the variations of annual mean  $\delta^{18}$ O in the DF pit with annual air temperatures observed by an automatic weather station at the DF station from 1993 to 2001 [Takahashi et al., 2004], coupled with a reanalysis of annual temperatures from ERA40 [Uppala et al., 2005] and NCEP/NCAR [Kistler et al., 2001]. We used 600 hPa pressure level temperatures for the period 1963-2001, because the annual average air pressure is 605 hPa at the DF site [Saito et al., 2007]. However, we were unable to identify any correlation between  $\delta^{18}$ O and air temperatures at the DF, DK, and MP pit sites. In contrast, the temporal  $\delta^{18}$ O profiles of the 1999 DF pit [Iizuka et al., 2004] and the present study show a significant correlation (r=0.39; p<0.01) (Figure 6a). The sampling site of the DF snow pit dug in 1999 is only a few kilometers from the JASE sampling site, meaning that the atmospheric environment is likely to be similar at the two sites. In order to reduce "stratigraphic noise" found in the low accumulation sites [e.g., Ekaykin et al., 2002], we constructed a stacked isotope profile from the two pits. However, this stacked profile also did not show any correlation with air temperatures (Figure 6b). This suggests other factors playing a role in the formation of the  $\delta^{18}$ O fluctuations, apart from the air temperature fluctuations when the snow was forming. Ekaykin et al. [2004] showed a positive correlation between  $\delta D$  snow pit values and accumulation rate by stake measurements at Vostok when data were smoothed over a 7 year period. They concluded that the  $\delta D$ variability was caused by increased cyclonic activity. We found no correlation between annually averaged  $\delta^{18}$ O and

accumulation rate of JASE snow pits (r=0.01 for DF, r=-0.21 for DK and r=-0.13 for MP). We suppose that influence by postdepositional alteration penetrated deeper than annual layers and thus the relation among  $\delta^{18}$ O and accumulation rates could have disappeared. Moreover, 7 year smoothed  $\delta^{18}$ O profiles and snow accumulation rates at the DF, DK, and MP sites in this study also did not exhibit any correlations (r=-0.06 for DF, r=-0.04 for DK, and r=-0.00 for MP).

[15] Snow accumulation rates at these sites are estimated to be  $15-30 \text{ kg m}^{-2} \text{ a}^{-1}$  at Vostok [*Ekaykin et al.*, 2002],  $18-23 \text{ kg m}^{-2} \text{ a}^{-1}$  at Dome A [*Ding et al.*, 2011; *Jiang et al.*, 2012], and 25 kg m<sup>-2</sup> a<sup>-1</sup> at DF [*Iizuka et al.*, 2004]. However, WSI profiles of fim/ice cores show significant correlations with air temperature at coastal DML regions [*Fernandoy et al.*, 2010; *Naik et al.*, 2010]. This study and the aforementioned studies indicate that deposited snow preserves seasonal cycles of WSIs in high-accumulation regions (> 100 kg m<sup>-2</sup> a<sup>-1</sup>), but not in low-accumulation regions (< 60 kg m<sup>-2</sup> a<sup>-1</sup>).

# **4.2.** Frequency of Water Stable Isotope and Ion Concentration Cycles

[16] Analysis of the three pits shows multiyear cycles in the  $\delta^{18}$ O data (Figure 4). We examined the periodicity of the  $\delta^{18}$ O profiles in these pits by Fast Fourier Transformation (FFT) analysis along water equivalent depth, which was converted from depth with density profile. Frequencies by FFT were converted into years by annual accumulation rates. Figure 7 shows the power intensity and predominant periodicity for  $\delta^{18}$ O, which are found at 2.9, 3.8, 6.1, and 9.9 years at the DF site, 2.1 and 2.9 years at the DK site, and 1.8, 2.3, 4.0, and 6.0 years at the MP site. The higher accumulation areas have a higher frequency of  $\delta^{18}$ O cycles. In this context, we suggest that a decadal cycle is obvious in the DF pit, whereas cycles of a few years are dominant in the other pits.

[17] In another low accumulation region (Vostok station), *Ekaykin et al.* [2002] identified significant oscillations of  $\delta D$  with cycles of 2.5, 5, and 20 years from eight snow pits. The cycles at the Vostok station were consistent with the periods estimated by means of spectral analysis of the



**Figure 7.** Power spectrum density of  $\delta^{18}$ O values in the DF (light blue line), DK (green line), and MP (red line) pits. Gray line denotes a significance level of p < 0.05.

Site	Location	Elevation (m a.s.l.)	$\begin{array}{c} Accumulation \\ (kg  m^{-2}  a^{-1}) \end{array}$	Signs of Correlations Between $\delta^{18}$ O and Ions	Source
Dome Fuji	77°S, 40°E	3810	25	Negative ( $Cl^-$ , $SO_4^{2-}$ , $Na^+$ , $Mg^{2+}$ )	<i>Iizuka et al.</i> [2004]
South Pole	_	2835	71.2	Negative $(Cl^-, Na^+)$	Whitlow et al. [1992]
Amundsenisen (Dronning Maud Land)	75°S, 2°E	2900	77 <sup>a</sup>	Negative (MSA, $Cl^{-}$ , $SO_4^{2-}$ , $Na^+$ , $Mg^{2+}$ , $Ca^{2+}$ )	Isaksson et al. [2001]
Styx Glacier	163°E, 73°S	1800	203	Positive (MSA)	Stenni et al. [2000]
McCarthy Ridge	163°E, 74°S	650	260	No correlation	Stenni et al. [2000]
H72	69°S, 41°E	1241	307	Positive (MSA)	Suzuki et al. [2005]

**Table 4.** Locations and Correlations of  $\delta^{18}$ O in Firn Cores Obtained in Previous Studies

<sup>a</sup>Isakkson et al. [1996].

accumulation time series obtained from stakes and pits. They suggested that atmospheric circulation affected snow accumulation and thus biased WSIs at Vostok. We have found similar multiyear cycles in WSI profiles of snow pits studied at Dome A [*Ren et al.*, 2004] and DF [*Iizuka et al.*, 2004], although previous studies have not described these.

[18] The relationships between  $\delta^{18}$ O and ion concentrations, including MSA and  $SO_4^{2-}$ , show negative correlations even though MSA and  $SO_4^{2-}$  are mainly delivered during the summer season by marine biogenic activity [Legrand et al., 1991]. Table 4 summarizes the relationships between  $\delta^{18}$ O and ion concentrations of selected firn cores and snow pits from previous studies.  $\delta^{18}$ O values for the 1999 DF pit show negative correlations with Cl<sup>-</sup>,  $SO_4^{2-}$ , Na<sup>+</sup>, and Mg<sup>2+</sup>, whereas no significant correlation was found with MSA,  $NO_3^-$ , and  $Ca^{2+}$  [*lizuka et al.*, 2004]. A 6 m deep snow pit dug in 1989, near the South Pole station, had peaks of  $\delta^{18}$ O that often correspond to minima of Cl<sup>-</sup> and Na<sup>+</sup> [Whitlow et al., 1992], although it was not possible to calculate their significance levels. A firn core drilled in the summer of 1991/1992 at Amundsenisen, DML, showed that  $\delta^{18}$ O peaks correlate with minima of major ion concentrations [Isaksson et al., 2001]. Conversely, shallow cores drilled in coastal and high accumulation regions show a positive correlation between  $\delta^{18}$ O and MSA at site H72 [*Suzuki et al.*, 2005] and Styx Glacier [Stenni et al., 2000], and no correlation at McCarthy Ridge [Stenni et al., 2000], where high  $\delta^{18}$ O and MSA values were attributed to a summer signal.

[19] *Iizuka et al.* [2004] suggested that minima of  $nssSO_4^{2-}$ in the 1999 DF pit were formed in summer by sublimationcondensation of water vapor between near-surface snow and the atmosphere. Moreover, some studies have suggested that MSA maxima could move from summer to winter at high latitudes as a result of postdepositional modification [Curran et al., 2002; Delmas et al., 2003]. This process involves removal of gaseous MSA from the snow layers and its return to the free atmosphere, where it may be partly redeposited in the snow layers or remains in the interstitial air [Delmas et al., 2003]. In our study,  $SO_4^{2-}$  concentrations of the DF pit exhibit no correlation with WSIs (Table 3). However,  $\delta^{18}$ O peaks correspond to  $SO_4^{2-}$  minima in the DF pit (Figure 5), possibly because there are two volcanic peaks present in the DF pit record (Figure 2a), which decreases the correlation coefficient between  $\delta^{18}$ O and SO<sub>4</sub><sup>2-</sup>. A significant negative correlation coefficient at DF is found when the volcanic peaks are excluded, whereas those at the other two sites are less significant (Table 5). This suggests that the JASE snow layers may have been modified after deposition, particularly under the low accumulation conditions at Dome Fuji.

# **4.3.** Postdepositional Modification of Water Stable Isotopes and Variability of Accumulation Rate

[20] Isotopic diffusion along isotopic concentration gradients in pore space vapor results in elimination of seasonal cycles with a 0.07–0.08 m diffusion length [Johnsen, 1977]. Therefore,  $\delta^{18}$ O signals shorter than 0.2 m might be eliminated during firnification. In general, the attenuation of the isotopic amplitude depends on ratio between the length of isotopic cycle and the diffusion length. Smaller cycles would disappear in years to decades while the attenuation of longer cycles would be much slower. Johnsen [1977] demonstrated that it takes more than ten thousand years for the isotopic amplitude to be reduced to one tenth of its initial one. In addition, extremely low temperatures should reduce the effects of isotopic diffusion because the diffusion length strongly depends on temperature and porosity of snow and other factors.

[21] Condensation of vapor is expected to be high in nearsurface snow under large temperature gradients [*Neumann* and Waddington, 2004]. Zhou et al. [2002] calculated that water vapor transportation was most active just beneath the surface, where the snow temperature gradient and variation were greatest [*Takahashi et al.*, 2004]. However, low temperatures reaching to  $-80^{\circ}$ C must result in low water vapor pressure and thus lower postdepositional modification. In contrast, during summer, snow surface temperatures reach  $-30^{\circ}$ C and thus water vapor pressures are higher than in winter, and this may cause isotopic modification.

[22] Town et al. [2008] calculated isotopic change associated with wind ventilation. This study showed that a maximum isotopic change of about 10% is possible in winter layers under wind speed conditions of 5 m s<sup>-1</sup> and an annual snow thickness of 0.08 m a<sup>-1</sup>. We estimated the potential modification of  $\delta^{18}$ O at the DF site based on the simulation by *Town et al.* [2008], combined with the daily precipitation data of *Fujita and Abe* [2006]. We first constructed a  $\delta^{18}$ O profile by assuming that daily precipitation formed a snow layer 0.08 m thick, and then examined the profile as if it was sampled at 0.01 m intervals. The amplitude of the  $\delta^{18}$ O profile of precipitation ranged from -65% to -47% (18‰)

**Table 5.** Correlation Coefficients Between  $\delta^{18}$ O and SO<sub>4</sub><sup>2-</sup>, When Volcanic Peaks Are Excluded

Site	Sample Number	Correlation Coefficient $-0.35 \ (p < 0.01)$		
DF	168			
DK	83	-0.25(p < 0.05)		
MP	183	-0.27(p < 0.02)		



**Figure 8.** Annual snow accumulation rates of the (a) DF (light blue line), DK (green line), and MP (red line) snow pits, and (b) determined at the DF site by stake measurements (blue dots). The accumulation rate determined by the stake measurements is the average of 36 stakes, and the standard deviation is also shown [*Kameda et al.*, 2008].

with an average of -57.7%. Site conditions at DF were a wind speed of  $5.9 \text{ m s}^{-1}$  [*Kameda et al.*, 2007] and an annual snow thickness  $0.08 \text{ m s}^{-1}$  [*Fujita and Abe*, 2006]. If the same alteration noted by *Town et al.* [2008] has occurred in the DF snow pit,  $\delta^{18}$ O values in the winter layer would increase from -65% to -55%, and thus the amplitude would be reduced to 8‰ with an average of 53‰. The  $\delta^{18}$ O profile of the DF snow pit (this study) has amplitude of 10%-15% with peaks of -50%, which are similar to summer precipitation values. *Town et al.* [2008] also demonstrated that isotopic peaks corresponding to summer were not changed significantly. Our estimations suggest that postdepositional modification of isotopic compositions associated with wind ventilation [*Town et al.*, 2008] may have altered the initial WSI profile of accumulated snow.

[23] However, if the accumulation rate is constant, isotopic fluctuations are simply modified by a reduction their seasonal amplitudes caused by any of the aforementioned alteration processes. *Kameda et al.* [2008] reported the snow accumulation rate at the DF site as being  $27.3 \pm 19.9$  kg m<sup>-2</sup> a<sup>-1</sup>, based on stake measurements for the period 1995–2006, which is consistent with our DF snow pit data (Table 1). They noted that the 36 stakes occasionally showed negative or zero snow accumulation (8% of the measurements; Figure 3), and also that snow had possibly been exposed at surface for two years. If the snow layer stayed at the surface for such a long period, then the seasonal cycle should be completely eliminated.

[24] Figure 8 shows variations in the accumulation rates of the DF, DK, and MP pits, as well as stake measurements at the DF site [*Kameda et al.*, 2008]. The correlation coefficients of snow accumulation between DF and the other sites are 0.16 (DK; p < 0.05) and 0.39 (MP; p < 0.05). However, snow accumulation measurements at the DF site, based on

snow pit and stake measurements, show no correlation. Some peaks of snow accumulation are consistent amongst the three snow pits, suggesting that these peaks are not affected by local snow drift, but by high precipitation events (i.e., >50% of the total annual accumulation) caused by synoptic weather patterns [*Schlosser et al.*, 2010; *Boening et al.*, 2012]. We suggest that large accumulation rate among the three pits (1991, 2000, and 2004; Figure 8) reflect the influence of high precipitation events.

[25] Furthermore, 36 stake measurements at the DF site showed oscillations of 3-5 years in snow accumulation [Kameda et al., 2008]. Variable accumulation rates change the period of time over which the snow is part of the "surface snow layer." Therefore, any temporal and spatial variations in snow accumulation rate will affect the extent of changes in  $\delta^{18}$ O and ion concentrations at the snow surface by ventilation, vapor condensation-sublimation, and so on. Considering the snow accumulation rates of the three pits, it is evident that the average annual rate is lower at the DF site, whereas the accumulation rate variability is larger at DF (Table 1). Hence, we conclude that low and variable accumulation rates are responsible for the multivear cycles of  $\delta^{18}$ O in the snow pits, and that this occurs through isotopic fractionation caused by postdepositional modification in the "surface snow layer."

#### 5. Conclusions

[26] Stable isotopic and chemical analyses of three snow pits from the JASE traverse show multiyear cycles in the WSI records, which do not correspond to air temperature fluctuations. Fluctuations of WSIs in the DF pit are lower in frequency than the other two pits, and the snow accumulation rate has the lowest but most variable annual average at this site. This large variability in snow accumulation was also observed by stake measurements at the DF site, with oscillations on a timescale of 3-5 years, with some years of negative or zero accumulation [Kameda et al., 2008]. This cyclicity in accumulation is comparable to the  $\delta^{18}$ O fluctuations in the DF snow pit. Moreover, negative correlations were observed between  $\delta^{18}$ O and major ion concentrations. Previous studies have suggested that the  $\delta^{18}$ O of snow or firn shows negative correlations with major ion concentrations in low-accumulation areas, whereas  $\delta^{18}$ O has positive or no correlations with MSA and  $nssSO_4^{2-}$  in high-accumulation coastal regions. We estimated that  $\delta^{18}$ O values in the winter snow layer could increase by >10% after deposition thorough ventilation effects [Town et al., 2008]. Moreover, if the snow layer remained at the surface for two years, then the seasonal  $\delta^{18}$ O cycle could be completely overprinted. Kameda et al. [2008] observed that snow layers had possibly been exposed at the surface for two years. However, large amount of accumulation (twice the average) intermittently characterized the Dome Fuji site. This large accumulation rate variability at Dome Fuji should affect the degree of modification of  $\delta^{18}$ O values, because the snow layer stayed for variable times at the near surface. We conclude that variable accumulation rates in low accumulation snow pit environments result in the formation of multivear cycles in  $\delta^{18}$ O values. This finding has important implications for reconstructing paleoenvironmental information from ancient ice core records.

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