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Na_2SO_4 and $MgSO_4$ salts during the Holocene period derived by high-resolution depth analysis of a Dome Fuji ice core

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ABSTRACT. We analyzed the profiles of ionic chemical species in three 500 mm sections of an ice core from Dome Fuji, Antarctica, dated 3.0, 8.9 and 13.3 kyr BP (before present), and compared the profiles to those in the surface snow. The 3.0 and 8.9 kyr sections are from the Holocene and the 13.3 kyr section slightly predates the Holocene. The analyses were done on 2 mm thick slices within each section. At each depth, the primary ionic species were Na^+, H^+, Cl^- and SO_4^{2-}. The SO_4^{2-}, Na^+ and Mg^{2+} levels varied with depth in each section over distances ranging from several millimeters to several centimeters. Also, the correlation coefficients between Na^+ and SO_4^{2-} and between Mg^{2+} and SO_4^{2-} for each depth were 0.90 or greater, in contrast to the value of 0.59 or less in the surface snow (defined here as 0–3.4 m from the surface). These results suggest that almost all Na^+ and Mg^{2+} in the Holocene ice exists as Na_2SO_4 and $MgSO_4$ salts, and the formation of these salts occurs not only in the atmosphere during transport, but also in the firn layer.

1. INTRODUCTION

Ice-core research is widely conducted to reconstruct regional and global paleoclimates. Ice cores drilled from the inland regions of polar ice sheets are particularly important for reconstructing climates for the past several hundred thousand years, a time period that includes several glacial cycles. In the interior of Antarctica, long-term paleoclimate studies have been carried out for ice cores from Byrd (e.g. Johnsen and others, 1972), Vostok (e.g. Legrand and Delmas, 1988; Petit and others, 1999), Dome Fuji (e.g. Watanabe and others, 2003a,b), EPICA DML (e.g. Oerter and others, 2004) and EPICA Dome C (e.g. EPICA community, 2004).

However, analyses of short-term climatic fluctuations in the ice cores from inland Antarctica have not been done. This is mainly because, owing to the low annual snowfall rates, the annual layers are too thin to provide sufficient material for chemical analyses. Reworking by wind mixes the surface snow, and occasionally a region in inland Antarctica has no net accumulation throughout a year. Furthermore, in this region post-depositional processes are expected to have a larger influence on the variations of chemical concentrations and on the oxygen/hydrogen isotope ratio than is observed in other regions of Antarctica. The post-depositional processes include:

1. sublimation, condensation and volatilization in surface snow (Sturm and Benson, 1997; Kreutz and others, 1998) and
2. molecular diffusion in firn or ice (Johnsen and others, 2000; Livingston and George, 2002; Barnes and others, 2003).

The sublimation, condensation and volatilization processes have been studied in ice cores from Greenland and Antarctica (e.g. Dibb and others, 1994; Bergin and others, 1995; Dibb and Jaffrezo, 1997; Röthlisberger and others, 2002; Iizuka and others, 2004). These processes have been studied in detail for volatile species including:

1. NO_3^- (Legrand and Delmas, 1986; Dibb and others, 1998; Honrath and others, 1999; Munger and others, 1999; Wagnon and others, 1999),
2. H_2O_2 (Neftel and others, 1984; Sigg and Neftel, 1991; Hutterli and others, 2001, 2003; Röthlisberger and others, 2003),
3. HCHO (Hutterli and others, 1999, 2002, 2003; Röthlisberger and others, 2003) and
4. Cl^- (Röthlisberger and others, 2003).

In general, these studies found that concentrations of volatile substances in snow layers become lower than those in precipitation owing to their escape from the snow to the atmosphere, particularly in regions with low snow accumulation rates such as inland Antarctica.

The molecular diffusion process of ion species in deep ice has also been studied (e.g. Barnes and others, 2003). Diffusion smooths out the initial variations of chemical concentrations, particularly in regions with low snow accumulation rates such as inland Antarctica. Regarding the molecular diffusion process, Barnes and others (2003) showed that only events of magnitudes that significantly exceed the background fluctuation in the SO_4^{2-} and Cl^- levels are detectable after 11 000 years in the Dome C ice core, and post-depositional movement is negligible for Na^+.

From 1995 to 1996, the Japanese Antarctic Research Expedition (JARE) conducted a deep ice-coring project at Dome Fuji (77°19′ S, 39°40′ E; 3810 m a.s.l.). The project team recovered ice down to 2503 m, which covers the past 340 kyr (Fujii and others, 2002; Watanabe and others, 2003b). The present annual accumulation rate at Dome Fuji is about 30 mm w.e. (Kameda and others, 1997) and the annual layer thickness of the Dome Fuji ice core is estimated to be 25–35 mm for the Holocene period (Watanabe and others, 2003a). In the Dome Fuji region, the snow layers down to 3.4 m depth have summer minima in both the

Table 1. Average concentrations, standard deviations and median absolute deviations of eight ion species (μmol L^{-1}) at depths of 0–3.4 m (surface snow), 119, 298 and 415 m (Holocene ice). The acidity, H^+ in the final column, was estimated using the following equation: $[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] + [CH_3SO_3^-] - ([Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}])$ (μeq L^{-1})

		$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	H^+
Surface snow (0–3.4 m)	Average	0.15	1.78	0.65	1.19	1.13	0.02	0.13	0.13	3.22
	Standard deviation	0.10	0.40	0.94	0.56	0.64	0.02	0.07	0.05	1.22
	Median absolute deviation	0.07	0.31	0.44	0.42	0.48	0.01	0.05	0.04	1.02
119 m ice	Average	0.09	1.90	0.18	0.95	1.68	0.07	0.16	0.20	0.81
	Standard deviation	0.02	0.26	0.04	0.39	0.71	0.09	0.07	0.06	0.38
	Median absolute deviation	0.01	0.16	0.03	0.31	0.56	0.03	0.06	0.04	0.30
298 m ice	Average	0.05	1.30	0.41	1.08	1.07	0.05	0.11	0.13	2.26
	Standard deviation	0.02	0.33	0.05	0.32	0.63	0.06	0.08	0.14	0.35
	Median absolute deviation	0.02	0.21	0.03	0.23	0.40	0.02	0.05	0.06	0.20
415 m ice	Average	0.18	0.92	0.22	1.09	2.08	0.10	0.26	0.22	0.38
	Standard deviation	0.03	0.30	0.05	0.41	0.75	0.02	0.08	0.05	0.37
	Median absolute deviation	0.03	0.21	0.04	0.33	0.58	0.01	0.06	0.03	0.24

non-sea-salt SO_4^{2-} and Na^+ concentrations (Iizuka and others, 2004). If the post-depositional processes have little effect, short-term fluctuations should occur in the Dome Fuji ice core. In this paper, we present high-resolution depth profiles of soluble ions from the Holocene period and discuss chemical reactions that probably occurred during the post-deposition processes.

2. ANALYTICAL PROCEDURE

We selected 500 mm long ice sections at three well-separated depths: 119 m (119.291–119.770 m), 298 m (298.403–298.878 m) and 415 m (415.352–415.818 m). The ages of these ice sections are 3.0, 8.9 and 13.3 kyr, respectively, and their annual accumulation rates are estimated to be 27, 29 and 27 mm of ice, respectively, based on $\delta^{18}O$ values that are considered to show good correlation with annual accumulation rates (Watanabe and others, 2003a). The section from 13.3 kyr BP corresponds to the beginning of the Antarctic Cold Reversal and is thus not strictly from the Holocene. Nevertheless, all sections are more recent than the Last Glacial Maximum and are in or near the Holocene. For convenience, we refer to all three sections as 'Holocene ice' even though the oldest slightly predates the Holocene.

For each ice section, we sliced 3 mm of ice from the outside of the section to decontaminate the surface. This was done on a clean bench in a cold room using a clean ceramic knife. The cleaned ice section was sliced every 2 mm of depth, and each sliced fraction was sealed in a clean polyethylene bag (Whirl Pak®). The estimated thickness error of each sample was <0.5 mm. Thus we obtained 230–240 samples from each 500 mm section.

After melting an ice sample in the pack, it was filtered through a pore size of 0.45 μm. We used an ion chromatograph (Dionex 500) to analyze the liquid for the eight major soluble ions: Cl^-, NO_3^-, SO_4^{2-}, $CH_3SO_3^-$ (MSA), Na^+, K^+, Mg^{2+} and Ca^{2+}. The concentration of soluble ions was measured with an estimated error of <5% (Igarashi and others, 1998). As a reference, we analyzed an ice section frozen from ultra-pure water using the same method, including the same type of bag, and found no peaks on the chromatograph. This result indicated that any contamination from our method would probably not affect our results.

3. RESULTS

The data, listed in Table 1, show that the primary anions are Cl^-, with average concentrations ranging from 0.92 to 1.90 μmol L^{-1}, and SO_4^{2-}, ranging from 0.95 to 1.19 μmol L^{-1}. The primary cation is Na^+ with average concentrations ranging from 1.07 to 2.08 μmol L^{-1}, and the calculated concentrations of H^+ range from 0.38 to 3.22 μmol L^{-1}. The concentrations of $CH_3SO_3^-$, NO_3^-, K^+, Mg^{2+} and Ca^{2+} are significantly lower than those of the primary ions.

The depth profiles of Cl^- are similar in all three Holocene ice sections, as are the profiles for NO_3^- (Fig. 1). Except for a few spikes in the Cl^- profiles, the Cl^- and NO_3^- profiles are relatively uniform and smooth. In contrast, the SO_4^{2-} and Na^+ profiles have fluctuation periods ranging from several millimeters to several centimeters (Fig. 2). Also, the 298 m section has slightly smoother SO_4^{2-} and Na^+ profiles than those of the 119 and 415 m ice sections.

The Cl^- and Na^+ profiles are consistent with the recent study by Barnes and others (2003), who found that events in the Cl^- profile disappear by diffusion but are retained in the Na^+ profile. However, in contrast to the Barnes and others study, our SO_4^{2-} profiles retain millimeter-order fluctuations in deep ice. This contrast is discussed in section 5.

4. SMOOTHING OF Cl^- AND NO_3^- PROFILES BY POST-DEPOSITIONAL PROCESSES

We now compare the high-resolution depth profiles of soluble ions in the Holocene ice with those in the surface snow. The surface snow down to 3.4 m was analyzed at a similar resolution to the Holocene ice (Iizuka and others, 2004). The SO_4^{2-} and Na^+ concentrations of the surface snow have roughly the same average as those of the Holocene ice (Table 1) with similar fluctuation periods (Fig. 2). This suggests very little smoothing of SO_4^{2-} or Na^+ by post-depositional processes.

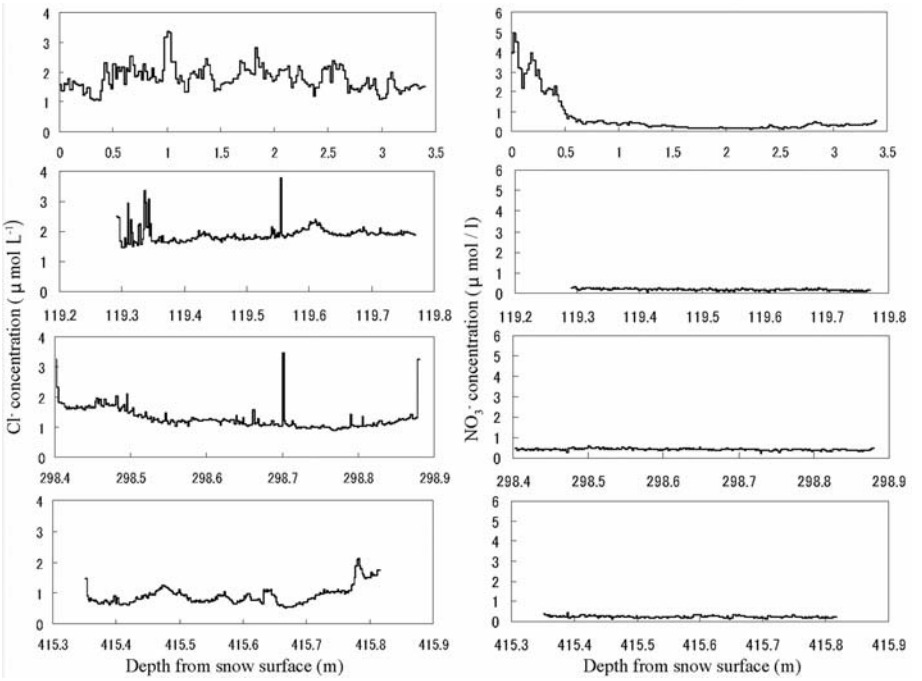

Fig. 1. High-resolution depth profiles of Cl^- and NO_3^- concentrations at depths of 0–3.4 m (surface snow), 119, 298 and 415 m. The 119 and 298 m sections are from the Holocene, the 415 m section slightly predates the Holocene but, for simplicity, all three will be called 'Holocene ice'. Analyses were made every 20 mm of depth for surface snow and every 2 mm of depth for the Holocene ice.

Unlike the SO_4^{2-} and Na^+ trends, the Cl^- and NO_3^- profiles in the Holocene ice are much smoother than those in the surface snow. The average concentrations of NO_3^- in the Holocene ice sections are much lower than those in surface snow. This decrease in concentration indicates that the smoothing below 0.6 m depth is due to volatilization of NO_3^- from the snow to the atmosphere (Legrand and Delmas, 1986; Dibb and others, 1998; Honrath and others, 1999; Munger and others, 1999; Wagnon and others, 1999; Röthlisberger and others, 2002). Also, the snow accumulation rate of the Dome Fuji region is lower than 40 mm w.e. a^{-1}, which means that Cl^- loss by volatilization can occur (Röthlisberger and others, 2003). If we assume that the average Cl^-/Na^+ ratio in the surface snow (1.57 mol L^{-1} (mol L^{-1})$^{-1}$) is the initially deposited ratio at Dome Fuji, and that this is constant throughout the Holocene, then the Cl^- loss in the Holocene ice sections is estimated to be 27.9%, 23.0% and 71.8% of its initial concentration for the 119, 298 and 415 m deep sections, respectively.

The residual Cl^- in the Holocene ice (i.e. 72.1%, 77.0% and 28.2% of the initial Cl^- in the 119, 298 and 415 m ice) shows smoother profiles than those observed in the surface snow (Fig. 1). The median absolute deviations of the Cl^- profiles are 0.16, 0.21 and 0.21 μmol L^{-1} for the 119, 298 and 415 m ice sections, respectively (Table 1), values that are significantly lower than the surface snow value of 0.31 μmol L^{-1}. We argue that this smoothing is a result of significant diffusion of Cl^-. (This is in addition to the post-depositional loss by volatilization.) Moreover, the Cl^- profiles are relatively smooth by the time the ice reaches 119 m depth, and apparently little additional smoothing has occurred below 119 m (Fig. 1). As 119 m is close to where the firn transforms to ice, the smoothing process of Cl^- is probably due to its diffusion in firn.

The Cl^- profiles also contain a few spikes. Most Cl^- spikes occur at the same depth as Na^+ spikes (Fig. 2), which suggests that some of the Na^+ and Cl^- did not diffuse in the Holocene ice but instead formed NaCl salt by anion–cation trapping (Livingston and George, 2002). Alternatively, sea-salt NaCl may not have transformed to HCl and Na_2SO_4. Although these spikes are dramatic changes to the profile, their occurrence is rare. Overall, we think that the binding of Na^+ with Cl^- is insignificant compared to the binding of Na^+ with SO_4^{2-}, as discussed in detail below.

5. POST-DEPOSITIONAL $NA_2SO_4{\cdot}10H_2O$ AND $MGSO_4{\cdot}12H_2O$ SALT FORMATION

In the surface snow the correlation coefficients between anions and cations are low, except for the high value ($r^2 = 0.89$) between Na^+ and Mg^{2+} (Table 2). Moreover, the ratio of Mg^{2+} to Na^+ in the surface snow is equal to that of sea salt, suggesting that most Na^+ and Mg^{2+} comes from sea salt. The Cl^- is also derived from NaCl and $MgCl_2$ in sea salts; however, this is not reflected in the correlations in Table 1. The reason for this lack of correlation is that the depth profiles of Na^+ and Cl^- in the surface snow may be disturbed by various processes including:

1. chemical reactions of NaCl and H_2SO_4 during transport through the atmosphere (Legrand and Delmas, 1988),
2. ion fractionation on the snow surface by sublimation and condensation (Iizuka and others, 2004) and
3. volatilization of HCl from the surface snow (Röthlisberger and others, 2003).

We suggest that the same processes apply to the depth profile of Mg^{2+} (with $MgCl_2$ taking the place of NaCl). Due to these processes, the surface snow probably has various combinations of salts (NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$)

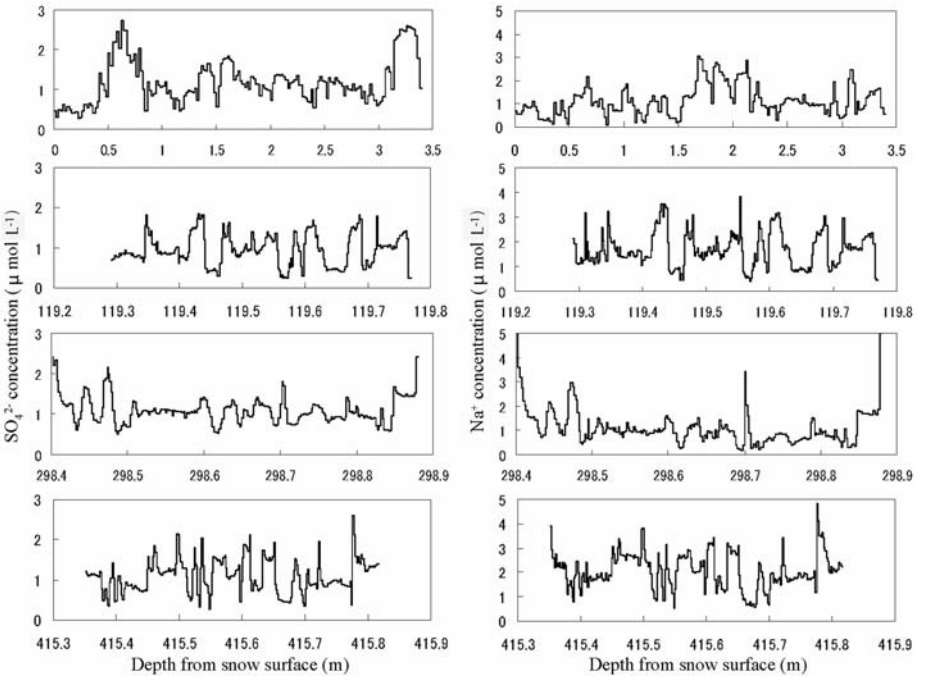

Fig. 2. High-resolution depth profiles of SO_4^{2-} and Na^+ concentrations in the surface snow and Holocene ice. Analyses were made in the same manner as described for Figure 1.

Table 2. Correlation coefficient matrix for the eight measured ion species in the surface snow and in the Holocene ice. Correlation coefficients exceeding 0.9 are in bold

		$CH_3SO_3^-$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Surface snow	$CH_3SO_3^-$	1							
	Cl^-	0.05	1						
	NO_3^-	0.08	–0.27	1					
	SO_4^{2-}	0.30	0.26	–0.42	1				
	Na^+	0.13	0.59	–0.34	0.40	1			
	K^+	0.11	0.38	–0.10	0.39	0.64	1		
	Mg^{2+}	0.17	0.50	–0.30	0.59	0.89	0.67	1	
	Ca^{2+}	0.03	0.25	–0.27	0.25	0.21	0.11	0.25	1
119 m ice	$CH_3SO_3^-$	1							
	Cl^-	0.62	1						
	NO_3^-	–0.02	–0.05	1					
	SO_4^{2-}	–0.18	0.16	–0.15	1				
	Na^+	–0.01	0.43	–0.13	**0.94**	1			
	K^+	0.43	0.75	0.22	0.10	0.35	1		
	Mg^{2+}	–0.12	0.22	–0.23	**0.96**	**0.94**	0.04	1	
	Ca^{2+}	–0.02	0.34	0.41	0.22	0.33	0.45	0.20	1
298 m ice	$CH_3SO_3^-$	1							
	Cl^-	0.49	1						
	NO_3^-	0.42	0.32	1					
	SO_4^{2-}	0.13	0.36	–0.04	1				
	Na^+	0.30	0.71	0.12	**0.90**	1			
	K^+	0.24	0.70	0.23	0.49	0.69	1		
	Mg^{2+}	0.33	0.57	0.11	**0.93**	**0.95**	0.62	1	
	Ca^{2+}	0.28	0.53	0.25	0.36	0.53	0.62	0.48	1
415 m ice	$CH_3SO_3^-$	1							
	Cl^-	0.12	1						
	NO_3^-	0.02	–0.19	1					
	SO_4^{2-}	–0.03	0.45	–0.27	1				
	Na^+	–0.04	0.54	–0.10	**0.92**	1			
	K^+	–0.07	0.27	0.19	0.43	0.55	1		
	Mg^{2+}	–0.08	0.57	–0.20	**0.93**	**0.95**	0.42	1	
	Ca^{2+}	0.14	0.44	0.22	0.34	0.50	0.73	0.42	1

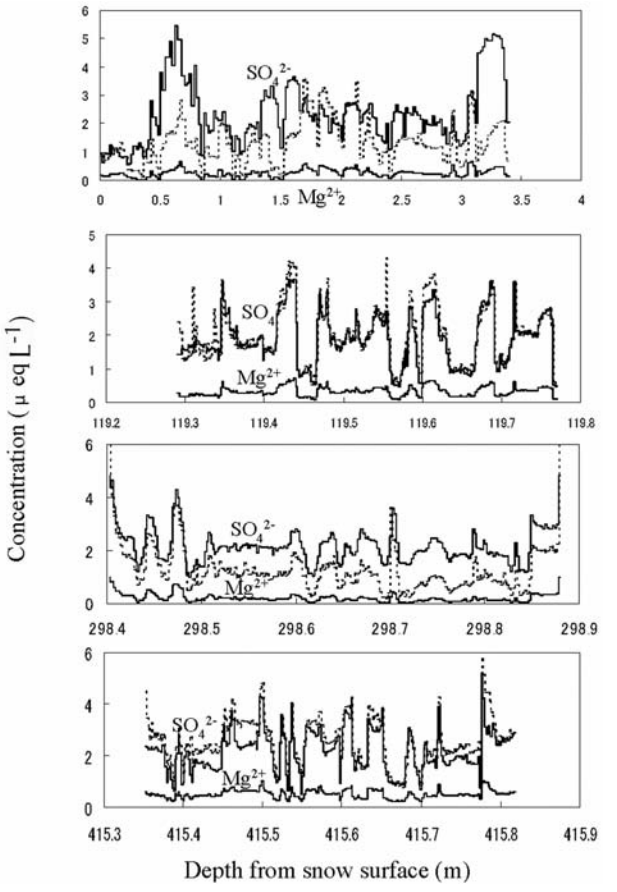

Fig. 3. High-resolution profiles of SO_4^{2-}, Mg^{2+} and the sum of Mg^{2+} and Na^+ in the surface snow and Holocene ice. The SO_4^{2-} and Mg^{2+} profiles are solid black lines and the sum of the Mg^{2+} and Na^+ profiles is a dotted line. These concentrations are in equivalent ($\mu eq\,L^{-1}$).

and acids (HCl and H_2SO_4), with the result that it has low correlation coefficients between cations (Na^+ and Mg^{2+}) and anions (Cl^- and SO_4^{2-}).

However, in the Holocene ice the correlation coefficients between Na^+, Mg^{2+} and SO_4^{2-} are greater than 0.9 (bold entries in Table 2). Hence, some redistribution processes must have caused these ion pairs to become closely correlated in the deep ice. Moreover, the profile for SO_4^{2-} is nearly equal to that for the sum of Na^+ and Mg^{2+} in molar equivalents in the 119 and 415 m ice sections (Fig. 3). In the 298 m section these two profiles have the same peak and trough positions, but the amount of SO_4^{2-} generally exceeds the sum of Na^+ and Mg^{2+}. These results suggest that almost all Na^+ and Mg^{2+} ions in the Holocene ice coexist with SO_4^{2-}. In the 298 m ice, 73.2% of the SO_4^{2-} is estimated to have existed as a compound with Na^+ or Mg^{2+}.

According to the thermodynamic phase diagram for Na_2SO_4 and $MgSO_4$ in Usdowski and Dietzel (1998), the salts $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ should exist at the temperature and average Na^+, Mg^{2+} and SO_4^{2-} concentrations found in the Holocene ice. The existence of these salts in our samples is further supported by the findings of Ohno and others (2005), in which most of the soluble impurities in the Dome Fuji ice core consisted of salt inclusions within ice grains. Moreover, they found that the inclusions were primarily $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ in the Holocene ice. Taken together, these results suggest that almost all the Na^+, Mg^{2+} and SO_4^{2-} existed as salts of $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$. The formation of the post-depositional salts is mostly completed within the firn because the high correlation coefficients between Na^+, Mg^{2+} and SO_4^{2-} occurred in the 119 m ice. These sulfate salts have eutectic points of –1.56 and –3.67°C for $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$, respectively and thus would exist as a solid in firn and ice. This solidity means that Na^+ and Mg^{2+} would have low mobilities in the Holocene ice.

We argue that the excess amount of SO_4^{2-} in the 298 m section is due to the relatively low cation concentrations in that section (Table 1) and this excess SO_4^{2-} exists with H^+ in the form of liquid H_2SO_4. The shape of the SO_4^{2-} profile is nearly the same as that of the sum of the Na^+ and Mg^{2+} profiles. When we subtract the two curves, the excess SO_4^{2-} is found to have a smooth profile, much like that of Cl^-. The smooth profile suggests that the excess SO_4^{2-} was fully diffused, as would occur if this SO_4^{2-} combined with H^+ to form liquid H_2SO_4, which readily diffuses in firn or ice. Following this smoothing process our findings for the SO_4^{2-} agree with those of Barnes and others (2003).

We interpret our findings to mean that the salts of $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ can form within the firn when liquid-phase SO_4^{2-} diffuses to relatively immobile Na^+ and Mg^{2+}, reacts and then becomes relatively immobile. It is also known that these salts form in the atmosphere (Legrand and Delmas, 1988), and thus some salts probably originated in the firn and some in the atmosphere; but whatever the source, the salts should be relatively immobile and have a more rapidly fluctuating profile. The key points here are that the SO_4^{2-} ions that form salts of $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ become essentially immobile, whereas the SO_4^{2-} ions that form an acid remain mobile and thus should have a smooth profile.

To summarize, our findings can be explained by the following processes:

1. liquid-phase SO_4^{2-} diffuses within the firn (Barnes and others, 2003),
2. SO_4^{2-} becomes immobile after reacting with Na^+ or Mg^{2+},
3. Na^+, Mg^{2+} and SO_4^{2-} remain as $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ salts in ice (Ohno and others, 2005) and
4. liquid-phase SO_4^{2-} is present in the ice if the Na^+ or Mg^{2+} concentrations are insufficient to react with all of the SO_4^{2-}.

Our findings also suggest that the low mobility of Na^+ and Mg^{2+} in deep ice should be useful for reconstructing the past Holocene environment with millimeter resolution, which corresponds to several months in the Holocene (Watanabe and others, 2003b). There will be some inherent uncertainties in the procedure; for example, the levels of $Na_2SO_4{\cdot}10H_2O$ in the ice include sources from chemical reactions in the atmosphere and thus do not solely reflect the past climate (Legrand and Delmas, 1988). In addition, some years have no net snow accumulation. Nevertheless, there is a need for additional climate analysis methods for the Holocene, and the levels of Na^+ and Mg^{2+} in deep ice show promise as one such method.

6. CONCLUSIONS

We have analyzed the ion profiles in ice-core sections from 3.0, 8.9 and 13.3 kyr BP, and compared the profiles to the ion profiles in the top 3.4 m of the core. We found that the correlation coefficients among Na^+, Mg^{2+} and SO_4^{2-} in the Holocene ice exceed 0.9 (Table 2), whereas the surface snow has low correlation coefficients between Na^+ and SO_4^{2-} and also between Mg^{2+} and SO_4^{2-}. The analyses indicates the presence of the salts of $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$, and the amount of these salts relative to the other ions suggests some of the salt forms within the firn through a process in which liquid-phase SO_4^{2-} diffuses towards relatively immobile Na^+ and Mg^{2+} and then reacts. Of the total SO_4^{2-} concentration, the component that is probably bound in the salts of $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$ has millimeter-order fluctuations in the depth profiles, whereas the remaining SO_4^{2-}, which we argue was part of the acid of H_2SO_4, has smooth profiles. Na^+ and Mg^{2+} are expected to have a low mobility in the Holocene ice since they form the solid salts $Na_2SO_4{\cdot}10H_2O$ and $MgSO_4{\cdot}12H_2O$. The low mobility of Na^+ and Mg^{2+} should be useful for reconstructing the past Holocene environment with millimeter resolution.

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