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Citation	GEOPHYSICAL RESEARCH LETTERS, 33(8), Art. No. L08501-Art. No. L08501 https://doi.org/10.1029/2006GL025774
Issue Date	2006-04-25
Doc URL	http://hdl.handle.net/2115/14419
Type	article (author version)
File Information	ohno_2006GL025774.pdf



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Characteristics of salt inclusions in polar ice from Dome Fuji, East Antarctica

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[1] We studied the depth profile of the chemical properties, number concentration and average diameter of micro-inclusions in Antarctic ice from Dome Fuji. Analysis of the data indicated that the distribution of inclusions was not significantly modified during ice sheet flow, although a main constituent $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ changed into another solid phase in the deep ice. In the chemical form, sodium sulfate and magnesium sulfate were dominant in the interglacial and early-glacial ice, but were not detected in the glacial-maximum ice. Instead, the sulfate in the glacial-maximum ice was mainly in the form of calcium sulfate. This is strong support for the hypothesis that the neutralization regime of acid aerosols in the atmosphere and snowpack dramatically changed from chemical reaction with sea salt to that with dust during glacial maxima.

1. Introduction

[2] Knowledge of the location and chemical form of water-soluble impurities in polar ice is essential for understanding various physical aspects of polar ice, including the electrical conductivity [Wolff *et al.*, 1997] and ice grain growth [Alley and Woods, 1996]. More importantly, knowing the micro-structural distribution of impurities is relevant for the reconstruction of past climate from ice cores. The micro-structural distribution determines the mobility of climate proxies, such as water isotopes and soluble impurities, in the ice matrix, and thus affects the post-depositional modifications to the climate signals [Johnsen *et al.*, 2000; Rempel *et al.*, 2001]. Moreover, knowledge of the chemical form of impurities provides clues to the properties of the atmosphere before the air and ice became trapped in the ice sheet. However, study of this topic has been hampered due to difficulty in the *in situ* analysis of the trace constituents in polycrystalline ice.

[3] Recent developments in experimental techniques are overcoming this difficulty and the resulting findings have challenged traditional views. For example, the traditional view has been that impurities segregate in ice grain boundaries [Glen *et al.*, 1977] and a liquid-vein network along triple junctions [Nye and Frank, 1973], the latter of which has been believed to be a critical pathway for diffusion of the climate proxies [Johnsen *et al.*, 2000; Rempel *et al.*, 2001]. However, SEM/EDS observations, mainly on the Dome C ice core [Barnes and

Wolff, 2004], revealed a heterogeneous distribution of trace constituents in grain boundaries, implying an absence of the connected impurity-filled pathway. Moreover, Baker and Cullen [2003], after examining the Byrd and GISP2 ice cores with a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS), found impurity spots on etched ice surfaces well away from grain-boundary grooves, suggesting that some impurities are within ice grains. Later, Ohno *et al.* [2005] used micro-Raman spectroscopy to examine micro-inclusions within ice grains in polar ice from Dome Fuji, and found that the inclusions were mainly sulfate salts with small amount of other soluble salts and insoluble dust. Also, they showed that the inclusions contained a large fraction of the soluble ions. This is consistent with recent high-depth-resolution soluble-ion analyses of Holocene ice from Dome Fuji [Iizuka *et al.*, 2005], which indicated that almost all SO_4^{2-} , Na^+ , and Mg^{2+} existed as sulfate salts in the ice.

[4] However, no study has comprehensively investigated the micro-structural distribution of soluble impurities over a range of depths at one site. As the ice is pressed deeper, various changes can occur, such as relocation, phase changes, and chemical reactions between different components. Also, no study has systematically examined the potential use of the micro-structural distribution as a climate proxy. Here we describe our study of the chemical

properties, number concentration and average diameter of micro-inclusions in deep ice from Dome Fuji and discuss the above points, also using previous results obtained from shallow ice [Ohno *et al.*, 2005].

2. Method and Results

[5] The ice core used in this study was from Dome Fuji station, which is located at the summit of East Dronning Maud Land Plateau (3810 m asl), East Antarctica. This ice core was 2500-m long, covering the past 340 kyr [Hondoh *et al.*, 2002]. At this site, the present-day temperature averages $-58\text{ }^{\circ}\text{C}$ and the accumulation rate averages 32-mm of water equivalent per year. *Dome-F Deep Coring Group* [1998] has more detailed information on the geophysical setting of the station.

[6] We used a microscope to examine micro-inclusions in four $80\times 40\times 5\text{-mm}^3$ ice sections from depths of 1746, 1919, 2280, and 2413 m. The average number concentration and size of the micro-inclusions over a section were measured. Thirty micro-inclusions per section were analyzed using micro-Raman spectroscopy. We used the same experimental procedure as that applied to the shallow ice specimens in Ohno *et al.* [2005] and compare to these previous

measurements.

[7] We found that the inclusions were typically a few micrometers in diameter, with most of them being within ice grains (Figure 1). The measurements also show that the number concentration of micro-inclusions N highly depended on the samples (Table 1). On the other hand, the mean size of the micro-inclusions D was about the same, independent of the samples.

[8] According to the micro-Raman spectroscopy, inclusions in ice from the depths of 1746, 2280, and 2413 m contained the sulfates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hereafter simple salts, and also a sulfate with a split main peak (Figure 2j in *Ohno et al.* [2005]). The results for all depths are in Figure 2. In addition, many samples had the spectrum shown in Figure 3, which clearly has a feature of sulfates [*Socrates*, 2001]. In contrast, the only sulfate detected at 1919 m was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Several inclusions from 1919 m had a weak peak at 1048 cm^{-1} , which may be from a nitrate. In addition, all depths had samples showing the spectrum from SiO_2 and spectra that could not be identified (particularly in the 1919-m ice). The latter are categorized as “others” in Figure 2. No signal was detected from 9 inclusions at 1746 m, 14 inclusions at 1919 m, 2 inclusions at 2280 m, and 1 inclusion at 2413 m, due either to undetectable signals or inherent Raman inactivity.

3. Discussion

3.1. Number concentration and average diameter

[9] There was no noticeable difference in the spatial distribution of micro-inclusions between the deep ice analyzed here (1746-2413 m) and the shallow ice analyzed previously (185-1351 m). Micro-inclusions were often distributed in groups that were mostly within the ice grains. Being within the grains, considerable relocation of the inclusions during ice sheet flow is unlikely. Moreover, we detected no systematic changes in the number and size of micro-inclusions with increasing depth, indicating that there was neither growth nor active formation of the inclusions within the sample depths. This is shown by the numbers N and sizes D in Table 1. On average, the deep ice specimens had N values comparable to those in shallow ice, although the individual N values varied significantly. Below we will argue that this variability can be largely explained by climate changes that affect the total amount of impurity. In addition, we found that the D values were independent of depth. From these findings, we argue that the distribution of each micro-inclusion, even in the deep ice, is nearly

the same as that of the same inclusion when it was first trapped in the ice.

3.2. Volume fraction

[10] In the interglacial ice, the ratio of micro-inclusion volume to total ice volume, hereafter V values, in deep ice (1746 and 2280 m) were a fraction of those from shallow ice (185 and 362 m), although SO_4^{2-} concentrations were almost at the same level in all the specimens measured (Table 1). A possible cause of the low V values is the dissociation of micro-inclusions. However, this possibility is unlikely because sulfates are considered to be stable in the deep ice, judging from the relatively low ice temperatures (Table 1) as compared to the sulfate eutectic temperatures (e.g., $-1.1\text{ }^\circ\text{C}$ for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $-3.9\text{ }^\circ\text{C}$ for $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ [Hall and Sherrill, 1928]). Another possible cause is lack of counter cations. The shallow-ice samples contained enough Na^+ , Mg^{2+} and Ca^{2+} to react with SO_4^{2-} , whereas the 2280-m sample had a significant excess of sulfuric acid and thus about 30% of the sulfate cannot have been present as salts due to the measured lack of the counter cations (Table 1). However, the V value at 2280 m was less than half of those at 185 and 362 m, and this argument does not apply to the case of the 1746-m sample because this ice had no excess

sulfuric acid. These findings imply that in addition to the excess SO_4^{2-} , a substantial amount of sulfate was present as sulfuric acid in the deep ice, despite the existence of the neutralizers. Thus we consider that fewer micro-inclusions were trapped when the deep ice first formed due to differences in the salt-formation conditions and then the additional salts did not form.

[11] The samples from 2413 m had about the same ion-concentration levels as those from 1351 m; these two early-glacial specimens also had almost the same V values, as was expected (Table 1). The 1919-m sample had nearly the same bulk ion concentrations as that of the 576-m LGM specimen, but the V value of the 1919-m ice was about three times larger than that of the shallower ice (Table 1). The most likely reason for this difference is that the deep ice exceptionally contained a large amount of unknown inclusions. The Raman spectra analysis indicated that undetectable species substantially contributed to the V value of the deep ice. About half of the micro-inclusions gave no signal at 1919 m whereas most of samples were Raman-active at 576 m. Judging from the bulk concentrations of impurities and Raman activities, chlorides are candidates for the undetected constituents. However, SEM studies [*Baker and Cullen, 2003; Barnes and Wolff, 2004*] reported that Chlorides were usually found in ice grain boundaries. Thus, if chlorides were the cause, the reason why they preferentially confined as inclusions within ice grains only at 1919 m remains unclear.

3.3. Chemical form

[12] Except for the samples from 1919 m, the composition of micro-inclusions in the deep ice was characterized by the existence of an unidentified sulfate giving the spectrum shown in Figure 3, which was not detected in inclusions from the shallow ice (Figure 2). An unidentified sulfate was frequently found in the deep ice (Figure 2), implying that this sulfate was composed of major ions. In addition, the Raman spectra analysis showed a sudden decrease in the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ content in the deep ice. The composition ratios of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ were calculated by analyzing overlapping peaks from these salts (Figure 4). Although, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was the dominant component of micro-inclusions in all shallow ice samples except for the LGM sample [Ohno *et al.*, 2005], this species was hardly detected in the deep ice. The composition ratios of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ calculated from the sum total of all spectra at a given depth were 85:15 at 185 m, 88:12 at 362 m, 85:15 at 1351 m, 0:100 at 1746 m, 7:93 at 2280 m, and 31:69 at 2413 m. As discussed above, the possibility of dissociation of sodium sulfate in the deep ice is unlikely. The appearance of an unidentified sulfate and sudden decrease of the

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ content occurred simultaneously. From these, we suppose that the unidentified sulfate was sodium sulfate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ that had been present in shallow regions and changed into another phase in deep regions, probably due to the high pressures of the ice load.

[13] Other features are as follows. The double salt containing both SO_4^{2-} and NO_3^- , a characteristic component in the LGM ice, was not found in the 1919-m glacial-maximum ice (Figure 2). The 1746-m ice had relatively large amount of the sulfate with a split main peak (Figure 2). Methane-sulfonate salt was not observed in this experiment, although it existed in the glacial samples of the shallow ice (Figure 2). We offer here no substantial explanations for these findings because a full determination of the salts and more information, such as their eutectic temperatures, would be necessary for the discussion.

3.4. Amount of constituent ions

[14] We estimated the total amount of ions in the simple salts by using the V values and the Raman results. The Raman spectra were used to determine the salt composition. Further details of the estimation method are in *Ohno et al.* [2005]. In this estimate, we assumed that

the unidentified sulfate had the same chemical form and density as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The results suggest that most of the sulfate was confined as salt inclusions in the glacial ice, whereas substantial portions of SO_4^{2-} were not from the simple salts in the interglacial ice (Table 1). The reason for the relatively high values at 1919 m may be an overestimate of the volume fraction of the simple salts in inclusions due to mixing of salts with undetected constituents.

3.5. Implications for climate change

[15] The number of inclusions was found to depend on whether the ice was formed in a cold or warm period (Table 1). The N values in the glacial samples were significantly larger than those in the interglacial samples. The variation of the N values is consistent with previous findings that show that the colder it grows on the earth, the greater the amount of atmospheric aerosols that are carried to the ice sheet [e.g., *Watanabe et al.*, 2003]. These aerosols contain the soluble species that produce micro-inclusions.

[16] The most interesting finding here is that the chemical forms of micro-inclusions in the glacial-maximum ice (576 and 1919 m) were quite different from those in the interglacial

and early-glacial ice (Figure 2). This finding can be explained by the following hypothesis from *Röthlisberger et al.* [2003]. During the Holocene and the last early-glacial period, substantial portions of acid-gas particles (H_2SO_4 and HNO_3) reacted with sea-salt aerosols both during their transport through the atmosphere and while they were in the snowpack. In contrast, during the last glacial maximum, the acids were preferentially neutralized by terrestrial dust [*Röthlisberger et al.*, 2000], which boomed during glacial maxima [e.g., *Fujii et al.*, 2003], instead of reacting with sea salt. In this hypothesis, micro-inclusions are assumed to form mainly through the neutralization of the acid aerosols. The glacial-maximum ice had the high concentrations of Ca^{2+} , which originates mainly from dust, suggesting these samples were dust rich. Consistent with this hypothesis, our analyses of the interglacial and early-glacial ice indicated that most of the SO_4^{2-} combined with Na^+ and Mg^{2+} (sea-salt components), whereas the analyses of the glacial-maximum ice indicated that there was no detectable Na_2SO_4 and MgSO_4 and the sulfate existed mainly as CaSO_4 . Further work along this line of inquiry may provide useful information about past atmospheric chemistry.

[17] **Acknowledgements.** We thank S. Horikawa and Y. Iizuka for valuable discussions, and all of the participants for fieldwork, ice sampling, and logistic support. The present research was supported by a

Grant-in-Aid for Creative Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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Figure captions

Figure 1. Micrograph of micro-inclusions in Dome F ice from 2413 m.

Figure 2. Observed frequency of various salt species in 30 micro-inclusions based on micro-Raman analyses. The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ species were not distinguished because their main peaks were too close to resolve using the spectrometer. The total frequencies at a given depth were not thirty because some inclusions contained more than one salt, or gave no signal. The data from the four shallowest depths are from *Ohno et al.* [2005].

Figure 3. Raman spectra of a micro-inclusion and the surrounding ice at 2413 m in the Dome Fuji ice core. The Raman-frequency range in thick lines on the abscissa axis represents regions of Raman bands from sulfates [*Socrates*, 2001].

Figure 4. Peak fittings for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ in the sum total of all spectra at two ice depths.

Depth (m)	Age (kyr BP)	Temp. (°C)	N (g^{-1})	D (μm)	V	Cl^- ($\mu M/l$)	MSA^- ($\mu M/l$)	NO_3^- ($\mu M/l$)	SO_4^{2-} ($\mu M/l$)	Na^+ ($\mu M/l$)	Mg^{2+} ($\mu M/l$)	Ca^{2+} ($\mu M/l$)
185	5.6 (Holocene)	-54.8	$3.5 \pm 0.4 \times 10^4$	1.7-2.5	$0.8-3.0 \times 10^{-7}$	2.10*	0.08*	0.46*	0.99* (0.40-1.55)	1.84* (0.67-2.54)	0.17* (0.06-0.22)	0.16* (0.01-0.05)
362	12.0 (Holocene)	-52.7	$4.0 \pm 0.5 \times 10^4$	1.8-2.7	$1.0-4.2 \times 10^{-7}$	2.48	0.15	0.20	0.96 (0.50-2.14)	2.15 (0.87-3.72)	0.20 (0.06-0.25)	0.26 (0.01-0.04)
576	24.7 (LGM)	-50.1	$4.3 \pm 0.4 \times 10^5$	1.4-2.3	$0.6-2.6 \times 10^{-6}$	5.36	0.19	1.62	2.48 (1.15-5.29)	5.29	0.89	1.55 (1.15-5.29)
1351	87.8 (early glacial)	-38.6	$1.2 \pm 0.2 \times 10^5$	1.5-2.3	$1.6-7.7 \times 10^{-7}$	1.08*	0.12*	0.28*	1.73* (0.78-3.88)	2.45* (1.06-5.24)	0.35* (0.09-0.47)	0.29* (0.16-0.79)
1746	130.1 (interglacial)	-31.3	$0.9 \pm 0.2 \times 10^4$	1.8-2.7	$0.2-1.0 \times 10^{-7}$	1.03*	0.21*	0.25*	0.99* (0.04-0.21)	1.34* (0.04-0.23)	0.29* (0.02-0.08)	0.27* (0.00-0.02)
1919	157.4 (GM)	-27.7	$7.6 \pm 0.9 \times 10^5$	1.8-2.5	$1.9-6.3 \times 10^{-6}$	5.25	0.28	1.89	2.32 (4.53-15.4)	4.67	1.01	1.82 (4.53-15.4)
2280	244.1 (interglacial)	-19.3	$1.4 \pm 0.3 \times 10^4$	1.8-2.6	$0.3-1.5 \times 10^{-7}$	0.79	0.07	0.20	0.88 (0.12-0.59)	0.45 (0.08-0.36)	0.14 (0.08-0.37)	0.20 (0.01-0.04)
2413	298.8 (early glacial)	-15.9	$1.5 \pm 0.2 \times 10^5$	1.5-2.3	$0.2-1.0 \times 10^{-6}$	3.08*	0.13*	0.45*	1.74* (0.84-3.81)	2.42* (0.95-4.32)	0.48* (0.27-1.23)	0.37* (0.09-0.41)

Table 1. Micro-inclusion survey and soluble ion concentrations in deep ice from Dome Fuji.

N and D are the number concentration and mean diameter of micro-inclusions, and V is the ratio of total inclusion volume to total ice volume. For N , the values represent mean \pm standard error. For D , we estimated the minimum and maximum values. V was estimated from N and D with consideration of their uncertainties. Soluble ion concentrations in melted ice samples were measured using ion chromatography. Measurement errors of ion chromatography are better than $\pm 0.01 \mu mol/l$ [Igarashi *et al.*, 1998]. *From Watanabe *et al.* [2003]. Values in parentheses represent the calculations of the amount of ions trapped in micro-inclusions as the simple salts of $Na_2SO_4 \cdot 10H_2O$, $MgSO_4 \cdot 12H_2O$, and $CaSO_4 \cdot 2H_2O$. The data in the first four rows are from Ohno *et al.* [2005]. Age estimates are from Hondoh *et al.* [2002]. Ice temperatures were estimated from the hole-fluid temperatures.

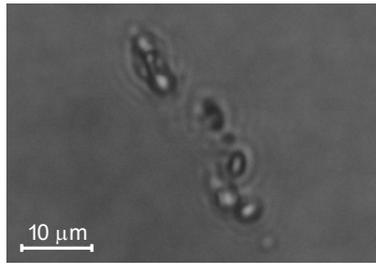


Figure 1. Micrograph of micro-inclusions in Dome F ice from 2413 m.

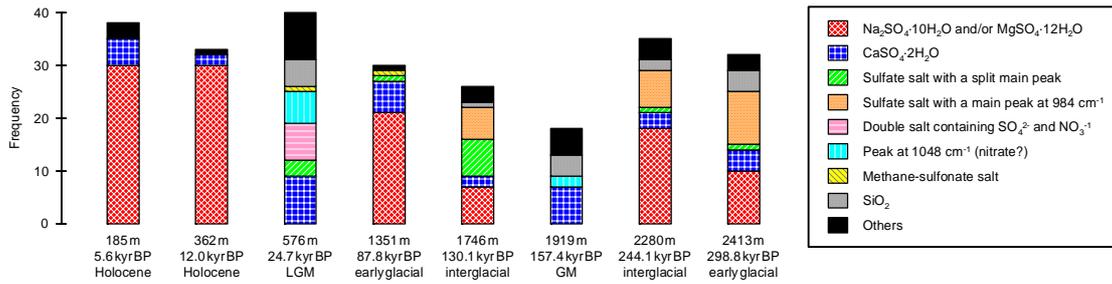


Figure 2. Observed frequency of various salt species in 30 micro-inclusions based on micro-Raman analyses. The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ species were not distinguished because their main peaks were too close to resolve using the spectrometer. The total frequencies at a given depth were not thirty because some inclusions contained more than one salt, or gave no signal. The data from the four shallowest depths are from *Ohno et al.* [2005].

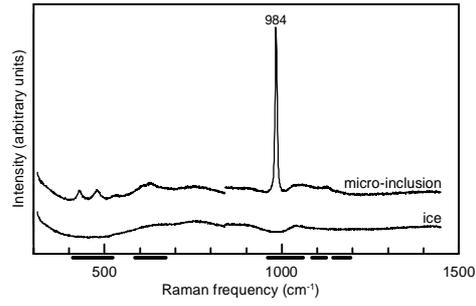


Figure 3. Raman spectra of a micro-inclusion and the surrounding ice at 2413 m in the Dome Fuji ice core. The Raman-frequency range in thick lines on the abscissa axis represents regions of Raman bands from sulfates [*Socrates*, 2001].

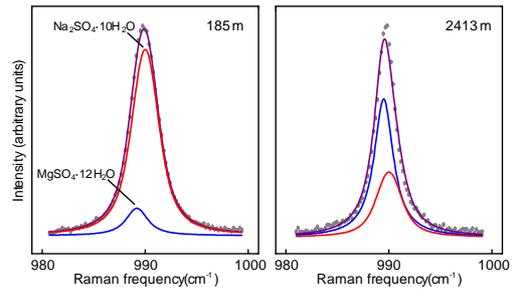


Figure 4. Peak fittings for Na₂SO₄·10H₂O and MgSO₄·12H₂O in the sum total of all spectra at two ice depths.