### Calcium speciation of particles trapped in Greenlandic ice core associated with neutralization reaction of calcite in the atmosphere

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Aerosol has various influences on the surface environment of the earth, and one of the influences is its global cooling effect including direct and indirect effects. The indirect cooling effect is caused by hygroscopic aerosols which act as cloud condensation nuclei (CCN) and form clouds that can reflect sunlight. However, hygroscopicity of aerosol differs depending on the chemical species that constitute the particles. Therefore, it is important to clarify the chemical species in aerosols to estimate the degree of the indirect cooling effect. Sulfate, one of the major species of aerosols, has high CCN activity, because it is considered that most of sulfate is present as ammonium sulfate ( $(NH_4)_2SO_4$ ) with high hygroscopicity (Pilinis et al, 1989). On the other hand, it is reported that calcite ( $CaCO_3$ ) in mineral particles reacts with sulfuric acid ( $H_2SO_4$ ) during atmospheric transportation and forms gypsum ( $CaSO_4 \cdot 2H_2O$ ) (e.g. Jones and Prospero 1996; Takahashi et al., 2009). In our previous study, sulfate species of aerosol collected in Higashi-Hiroshima, Japan were determined, which suggests that atmospheric neutralization reaction of  $CaCO_3$  in mineral dust with  $H_2SO_4$  causes suppression of forming  $(NH_4)_2SO_4$  decreases hygroscopicity of sulfate aerosols.

Greenlandic ice sheet preserved natural and anthropogenic trace gases and particles transported from continents in the Northern hemisphere (Delmas 1992), which is one of the important samples to reconstruct various factors on climate change of the past, and to contribute to the more accurate prediction of the climate in future. Therefore, determination of amount of CaSO<sub>4</sub>·2H<sub>2</sub>O in mineral dust, or identification of the neutralization process of CaCO<sub>3</sub>, in ice sheet has a potential to reconstruct the variation of sulfate species in aerosols that have information of atmospheric chemical reactions in the past, which will help us to know the CCN activity of sulfate aerosols in the Northern hemisphere. However, there is no study on quantitative determination of CaSO<sub>4</sub>·2H<sub>2</sub>O in mineral dust in ice sheet. In this study, calcium speciation experiments of particles trapped in Greenlandic ice sheet were conducted. Ice core were drilled at southeast Greenland, SE Dome (67.2°N, 36.4°W) in 2015. The parts of the ice dated as 1971, 1978, 1987, 1995, and 2004 were sublimated in low-temperature room (−20°C) to obtain trapped particles using the method in lizuka et al. (2009, 2012). Calcium-bearing particles in the trapped particles were identified by micro X-ray Fluorescence ( $\mu$ -XRF) mapping. Subsequently, calcium species of the particles were determined by micro X-ray absorption fine structure ( $\mu$ -XAFS) spectroscopy. As a result of the calcium speciation, CaSO<sub>4</sub>·2H<sub>2</sub>O fraction to total calcium in 1971, 1978, and 1987 were lower than CaCO<sub>3</sub> fraction. In contrast, CaSO<sub>4</sub>·2H<sub>2</sub>O fraction in 1995 and 2004 were higher than CaCO<sub>3</sub> fraction. It is considered that chemical reaction of CaCO<sub>3</sub> in mineral dust with H<sub>2</sub>SO<sub>4</sub> was more active in recent 20 years. On the other hand, sulfate ion (SO<sub>4</sub><sup>2</sup>-) concentration in ice core decreased from late 1970s. The trend of  $SO_4^{2-}$  was consistent with emission record of  $SO_2$  in industrial countries at the time, however, emission amount of SO<sub>2</sub> increased in East Asia in recent 20 years, especially in China (Crippa et al., 2016), which is also an important source of mineral dust in Greenlandic ice sheet. Therefore, it was considered that calcium species in the mineral particles trapped in the ice sheet reflected chemical reactions of calcium with H<sub>2</sub>SO<sub>4</sub> in China. These results suggested that suppression of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> formation in the Northern hemisphere was associated with the neutralization reactions of CaCO<sub>3</sub> with H<sub>2</sub> SO<sub>4</sub> in East Asia.

Keywords: aerosol, ice core, cloud condensation nuclei, neutralization reaction, calcium speciation, X-ray absorption fine structure (XAFS)

### Greenland ice core records of biomass burning aerosol and BVOCs over the past 60 years

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It is vital to fully understand climate feedback mechanism within climate system in order to improve prediction of future climate by simulation model. However, biogeochemical feedback is not fully understood. Both the biomass burning aerosol and Biogenic volatile organic compounds (BVOCs) are thought to have a potential as chemistry feedback in response to climate change. Biomass burning aerosol is emitted from burning of forests and savanna for colonization and agriculture, burning of agricultural waste, and substances burned for fuel. BVOCs such as isoprene and monoterpenes are important precursors of secondary organic aerosol (SOA) come from terrestrial vegetation and marine plankton. However, substantial role of those aerosols in climate system is still uncertain. In order to better understand roles of biomass burning aerosol and BVOC in climate system, it is needed to explore link between climate and those emissions on various time scale. In this study, we reconstruct variability of biomass burning activity and emission of BVOC over the past 60 years based on novel approach, organic molecule tracers analyses in Southeastern Greenland-Dome (SE-Dome) ice core, which provides high-time resolution reconstruction of past environment. Organic molecular tracers such as biomass burning and biogenic SOA tracers are detected in SE-Dome ice core. Levoglucosan, which is produced by pyrolysis of cellulose and hemicellulose and thus is a tracer of biomass burning, showed sporadic peaks in the years of 1961, 1964, 1994, 1998 with the largest peak in 1964. In contrast, dehydroabietic acid, a specific tracer of the pyrolysis of conifer resin showed high peak at 1959, 2003 and showed a gradual increasing trend from 2009. The concentrations of isoprene SOA tracers (2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol) are also dominant in SE-Dome ice core samples. Erythritol, is an analog of 2-methyl erythritol, a tracer species for isoprene SOA showed positive correlation with sugar compounds (arabitol, fructose, glucose) and with Dehydroabietic acid from the ice core with 95% confidence level. These results suggest that erythritol comes from continental sources. Monoterpene SOA traces are not found in SE-Dome ice core. Air mass backward trajectory showed that North America is the main source region of aerosols, indicating aerosols in SE-Dome region are transported mainly from North America. This study showed that general biomass burning tracers such as levoglucosan have been sporadically transported over the southeast Greenland and levoglucosan data matches with eastern USA fire history. In contrast, the ice core record of dehydroabietic acid indicated that fires of boreal conifer forest have occurred in North America during the last decades and transported to southeastern part of Greenland. The causes of historical variability of SOA tracers are complex and depend on atmospheric circulation, changes in vegetation cover and other factors such as temperature, tropospheric oxidative capacity.

Keywords: Isoprene SOA tracer, Biomass burning, levoglucosan, BVOC

### A 60-year record of isotopic compositions of nitrate preserved in the high-accumulation dome ice core, South East Greenland

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Nitrate ( $NO_3$ ) is one of the major anions found in snow.  $NO_3$  deposition results from reactions between nitrogen oxides ( $NOx = NO + NO_2$ ) and atmospheric oxidants. Global main sources of NOx are fossil fuel and biomass burning, biogenic soil emissions, and lightning, and a recent increase in  $NO_3$  in ice cores has been associated with increasing anthropogenic emissions of NOx. Based on the changes in  $NO_3$  concentration, however, it is difficult to identify specific sources of NOx which takes into account for the changes in  $NO_3$  concentrations, hindering the development of mitigation policy of anthropogenic pollution and its effect on the environment.

Isotopic compositions of  $NO_3^-$  reveal changes in the nitrogen source and its formation pathways, but ice core records for  $NO_3^-$  concentrations and its isotopic compositions are problematic because of post depositional loss of  $NO_3^-$  via photolysis. In this study, we analyzed isotopic compositions of  $NO_3^-$  preserved in the high-accumulation dome ice core, South East Greenland. South East Greenland has a dome whose elevation is higher than 3000 m a.s.l. with high accumulation rate (about 1 m yr<sup>-1</sup>) in water equivalent. High elevation and accumulation rate gives high-time resolution reconstruction of past environment, and provides negligible effect of the post depositional loss of nitrate ( $NO_3^-$ ). In fact, the nitrogen isotopic compositions for  $NO_3^-$  are generally lower than those reported in Summit, Greenland, suggesting negligible effect of post depositional loss of  $NO_3^-$  in this site. In the presentation, we present changes in  $NO_3^-$  concentration and its isotopic composition through recent 60 years, and discuss the changes in the source and formation pathways of nitrate.

Keywords: stable isotope, nitrate

Isotopic constrains on post-depositional processing of snow nitrate in eastern Dronning Maud Land, East Antarctica.

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Stable isotopic ratio of nitrate in deep ice core would be valuable information for paleo-atmospheric analysis. However, post-depositional change should have an effect on the information. In previous study, this process is pointed out as physical release or photochemical reaction of nitrate on snowpack surface. Furthermore, the reactions are rare source of nitrogen oxides(NOx) for clean atmosphere in Antarctica. To determine the mechanism of the process, isotopic composition of N(d15N) is used as an indicator for nitrate photolysis. Nitrate photolysis as post-depositional change enriches d15N for remaining nitrate on snowpack. Thus, the isotope composition(d15N) enable us to estimate how post-depositional process work in the Antarctic Plateau. In order to test spatial variation of isotopic compositions, between coastal site and inland site, here we present latitudinal variation of d15N value of NO<sub>3</sub> in surface snow in eastern Dronning Maud Land, East Antarctica. Snow samples were collected from the surface to depths of 80 cm and 30 cm at low- and high-elevation sites during the 54th Japanese Antarctic Research(JARE), and the surface to depth 50 cm at coastal sites during 57th Japanese Antarctic Research, respectively. The d 15N of nitrate in snow were considerably increased from coastal to inland based on sample collected in 54th JARE. For the snow pit analysis in 57th JARE from surface to 180 cm, d15N ranged from -8.5 permil to +30.5 permil, and there no appreciably change. In contrast, spatial variability was observed in coastal sites samples within 100 km in JARE57. It suggests that the nitrate source would be different in the small area. The NO<sub>3</sub> mass fraction f of pit samples on each depths were evaluated using measured d15N values, assuming initial d15N value(-10 permil), NO<sub>3</sub> concentrations, and atmosphere-snow fractionation constant  $^{15}\,\varepsilon$  (-60 permil) for  $\,\delta$  15N based on a Rayleigh-type process (Frey et al., 2009; Berhanu et al., 2014). From the calculation, f in the pit samples ranged 0.51 to 0.97. This value would be corresponding to nitrogen oxides flux value at the same site in JARE57. In detail, high concentration NO and HONO were emitted from snow surface. NO<sub>2</sub>, however, wasn't detected from snow surface and in the atmosphere.

Keywords: isotope, Nitrate

#### State dependence of climatic instability over the past 720,000 years from Antarctic ice cores and climate modelling

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Climatic variabilities on millennial and longer timescales with a bipolar seesaw pattern have been documented in palaeoclimatic records, but their frequencies, relationships with mean climatic state, and mechanisms remain unclear. Understanding the processes and sensitivities that underlie such changes will underpin better understanding of the climate system and projections of its future change. We investigate the long-term characteristics of climatic variability using a new ice-core record from Dome Fuji, East Antarctica, combined with an existing long record from the Dome C ice core. Antarctic warming events over the past 720,000 years are most frequent when the Antarctic temperature is slightly below average on orbital time scales, equivalent to an intermediate climate during glacial periods, whereas interglacial and fully glaciated climates are unfavourable for a millennial-scale bipolar seesaw. Numerical experiments using a fully coupled atmosphere-ocean general circulation model (AOGCM) with freshwater hosing in the northern North Atlantic showed that climate becomes most unstable in intermediate glacial conditions associated with large changes in sea ice and the Atlantic Meridional Overturning Circulation (AMOC). Model sensitivity experiments suggest that the prerequisite for the most frequent climate instability with bipolar seesaw pattern during the late Pleistocene is associated with reduced atmospheric CO2 concentration via global cooling and sea ice formation in the North Atlantic, in addition to extended Northern Hemisphere ice sheets.

Keywords: Dome Fuji ice core, Paleoclimate, CO2, Abrupt Climate change, Atlantic meridional overturning circulation

#### Stability of AMOC and bipolar seesaw under different background climatic condition

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Millennial climate changes known as D-O cycles and AIM recorded in ice cores in both Hemispheres show a higher amplitude in the middle-level of a glacial cycle than in the interglacial state or severe glacial state. Here we investigate the stability of AMOC and climate by analyzing several sensitivity experiments using a coupled atmosphere and ocean GCM (MIROC4m). The stability under different climates are compared; modern climate state with the pre-industrial condition, middle glacial climate state and full glacial condition, mainly differing in the ice sheet configuration and the amount of Greenhouse Gases. The results under middle glacial condition show the largest cooling/warming response in North Atlantic and a reasonable bipolar warming/cooling signal, which are consistent to ice core data and deep-sea data. We show the stability diagram of AMOC in the model under different background conditions and discuss the implication on the mechanism of abrupt climate changes in the past.

Keywords: climate, climate model, paleoclimate

#### Importance of the sea ice-surface wind feedback on simulating the LGM AMOC

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Simulating and understanding the dynamics of the glacial Atlantic meridional overturning circulation (AMOC) is one of the main challenges in the paleoclimate community. However, most climate models in the Paleoclimate Model Intercomparison Project cannot reproduce a weak AMOC in their simulations of the last glacial maximum (LGM). Previous studies show that a stronger glacial surface wind over the northern North Atlantic induced by the Laurentide ice sheet is causing this model-data discrepancy. They suggest that a weaker wind over the northern North Atlantic may be important in simulating the weak LGM AMOC. Dome F members (2017) recently succeed in simulating a weak LGM AMOC in their simulations using a coupled model MIROC, and show that the surface wind over the northern North Atlantic is substantially reduced compare to previous LGM simulations. Differences in the sea ice extent over the northern North Atlantic are suggested to be the cause of the weaker surface wind, though the impact of the sea ice extent on the surface wind remains elusive. In addition, it remains unclear that whether the weakening of the surface wind plays a role in simulating the weak LGM AMOC. Therefore, in this study, we first investigate the role of sea ice expansion on the weakening of the surface wind, and then we explore the impact of the weakening of the surface wind on the LGM AMOC. For this purpose, simulations results from MIROC4m are utilized (Dome F members, 2017). To clarify the impact of changes in sea ice and associated changes in diabatic heating on the surface wind, sensitivity experiments are conducted with an atmospheric general circulation model and a linear baroclinic model. Additional experiments are conducted with the coupled model MIROC, which we modified the surface wind stress over the northern North Atlantic to assess the impact of weakening of the surface wind on the LGM AMOC. Results show that expansion of sea ice substantially weakens the surface wind over the northern North Atlantic. Analysis and experiments with linear baroclinic model shows that two processes are crucial in reducing the surface wind; the suppression of atmosphere-ocean heat exchange and the increase in the stability of the boundary layer over the sea ice due to an intense surface cooling. Additional experiments with MIROC show that the weakening of the surface wind due to the expansion of sea ice plays a role in maintaining the weak AMOC in the LGM simulation.

Keywords: LGM, AMOC, surface wind

#### Atmospheric CH<sub>4</sub> concentration during the Holocene reconstructed from the NEEM (Greenland) and Dome Fuji (East Antarctica) ice cores

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Methane ( $\mathrm{CH_4}$ ) is an important greenhouse gas, whose atmospheric concentration has been increasing due to human activities for the last few centuries. Orbital-scale variations of atmospheric  $\mathrm{CH_4}$  correlate with climatic precession, because the size of wetlands and their  $\mathrm{CH_4}$  production rate respond to Northern Hemisphere (NH) summer insolation, through the variations in temperature and rainfall on NH landmasses. The correlation between  $\mathrm{CH_4}$  concentration and NH summer insolation held for the last three interglacial periods, but the relationship collapsed during the latter half of the Holocene. NH summer insolation kept decreasing whereas the atmospheric  $\mathrm{CH_4}$  concentration increased since  $^{\sim}5$  kyr BP. Several explanations have been proposed for this trend, such as peat growth in circum-Arctic region  $^{1}$ , emission from tropical wetlands due to increasing rainfall in the Southern Hemisphere (SH) $^{2,3}$  and agricultural activity  $^{4}$ , and the exact mechanisms have been under continuing debate.

Inter polar difference (IPD) of  $\mathrm{CH_4}$  concentrations have provided important constraint on the evolution of  $\mathrm{CH_4}$  source distribution and its relationship with climate  $^{2,5,6,7}$ . However, time resolution and analytical precision of previous studies have not always been adequate to investigate precise IPD. In addition, reconstruction of accurate  $\mathrm{CH_4}$  variation is difficult during most of the Holocene from Greenland ice cores, because the depths for this time period often corresponds to poor quality ice (brittle zone). To reconstruct the  $\mathrm{CH_4}$  IPD during the Holocene, we have been measuring  $\mathrm{CH_4}$  concentrations in the NEEM (Greenland) and Dome Fuji (DF) (Antarctica) ice cores. Accurate  $\mathrm{CH_4}$  reconstruction from the Holocene NEEM ice core is challenging because of the brittle zone. We indeed found high  $\mathrm{CH_4}$  spikes in the brittle zone, thus we investigated them by measuring additional 3–5 samples from the neighboring depths (within  $^{\sim}50$  cm,  $^{\sim}5$  years) and checking the reproducibility, and then rejected the data which is more than 15 ppb higher than their means. Reproducibility after removing the outliers are  $\pm 2.5$  and  $\pm 1.7$  ppb for the NEEM and DF ice cores, respectively.

We investigate the integrity of our Holocene CH<sub>4</sub> data. The CH<sub>4</sub> variations of the NEEM core, including centennial to millennial variations in the brittle zone, agree well with the GISP2 data (recent high-precision data by the Oregon State University group) (ref.7 and unpublished data). For Antarctica, the variations of CH<sub>4</sub> concentration of the DF core also agree well with those of the WAIS divide core from West Antarctica (ref.7 & 8 and unpublished data), after considering centennial-scale smoothing effect on the DF record caused by slow gas trapping. These comparisons suggest that our new records, as well as the most recent records by other groups, provide reliable reconstruction of the past atmospheric CH<sub>4</sub> variations over the entire Holocene.

IPD are deduced from two different combinations of cores: the NEEM and DF cores, and the NEEM and WAIS Divide cores. For this analyses, the gas time scales of the NEEM and DF cores are placed on the WAIS Divide ice core chronology by pattern matching of the CH<sub>4</sub> records. IPD from both NEEM/DF combination and NEEM/WAIS combination increased from the early Holocene to mid Holocene, and then

decreased toward the late Holocene. We employ a simple 3-box model  $^{2,6}$  to deduce  $CH_4$  emissions from different latitudinal bands at 1000-yr intervals. The model calculates the emissions in the low-latitude box (30°S-30°N) and northern box (30-90°N), while small emission from southern box (90-30°S) is kept constant. The model results show that northern emission decreased, while low-latitude emission increased during the last half of the Holocene. This suggests significant contribution from the low-latitude sources to the atmospheric  $CH_4$  increase since  $^{\sim}5$  ka. A recent model study suggests that  $CH_4$  emission from the SH tropics may have increased due to SH summer insolation rise  $^{7}$ . Several terrestrial proxies suggest increased rainfall in the tropical regions in South America during the latter half of the Holocene  $^{9}$ , probably in response to the increase in SH summer insolation. Although we cannot reject the anthropogenic hypothesis at this stage and more investigations are needed, our results are consistent with the hypothesis that tropical SH emission was responsible for the  $CH_4$  rise during the latter half of the Holocene.

1)Blunier et al., 1995. 2)Chappellaz et al., 1997. 3)Singarayer et al., 2011. 4)Ruddiman & Thomson., 2001. 5)Nakazawa et al., 1993. 6)Brook et al., 1996. 7)Mitchell et al., 2013. 8)WAIS Divide Project Members, 2014. 9)Prado et al., 2013.

Keywords: Ice core, Methane, Holocene, Greenland, Antarctica

### Increasing insolation and greenhouse gas concentration trigger Bø Iling-Allerød warming

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During the last deglaciation, a major global warming was punctuated by several abrupt climate changes, likely related to Atlantic Meridional Overturning Curculation (AMOC) (Clark et al. 2012). Transient deglaciation experiments from the Last Glacial Maximum have been conducted by applying time-dependent insolation, greenhouse gas concentrations, and glacial meltwater forcing (Liu et al. 2009). They have showed that reduction in glacial meltwater discharge rate into North Atlantic induces abrupt recovery of AMOC, warming of Greenland and cooling of Antarctica (bipolar response) during the period of Bølling-Allerød (BA, ~14.6 ka).

We conduct a transient simulation from the Last Glacial Maximum to BA using an atmosphere-ocean coupled general circulation model (AOGCM) MIROC 4m (an IPCC-class Japanese community model). The model is initialized with the 21ka, and we change insolation, greenhouse gas concentrations and meltwater fluxes following the protocol of PMIP4 (Ivanovic et al. 2016). Glacial meltwater is derived from ice sheet reconstruction (ICE6g, Peltier et al. 2015). We assume the glacial meltwater due to ice sheet loss is uniformly applied to the area of 50-70N North Atlantic Ocean. We conduct additional experiments branched from 16 ka, where 50-80% of ICE6g meltwater fluxes are applied without reducing the meltwater fluxes before the BA.

The model results show that abrupt resumption of AMOC and warming of Greenland occurred at around the period of BA even under hosing of 0.06 Sv. Transition from cold stadial mode to warm interstadial mode occurs in about 100 years, which is consistent with reconstructions (Buizert et al. 2014). The result implies that increasing summer insolation and greenhouse gas concentration trigger abrupt AMOC recovery and warming in the Northern Hemisphere, and large fluctuation of meltwater due to ice sheet melting may not be necessary.

#### Toward understanding the climate change in the Pleistocene: Reproduction of the dominant 40-kyr periodicity in the early Pleistocene using an ice-sheet model

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The climate change in the Pleistocene is characterized by glacial-interglacial cycles that have a dominant periodicity at tens of thousands of years. Milankovitch theory suggests that variation of Earth's orbital parameters changes the way the sunlight enters the Earth and the northern hemisphere high-latitude summer insolation that have a dominant periodicity at 20-kyr causes the glacial-interglacial cycles. In contrast to this periodicity, however, the dominant periodicity of the climate change in the early Pleistocene was 40-kyr. Various hypotheses are proposed but it has not yet been fully understood. One reason is that the 40-kyr cycles have not been reproduced using a realistic 3-D model with realistic input. Our aim is to reproduce the 40-kyr cycles using a 3-D ice-sheet model with realistic input and to reveal the role of each orbital parameter by comparing the result with records of proxy. We used an ice-sheet model for Integrated Earth system Studies (IcIES; Abe-Ouchi et al., 2013), coupled with climate parameterization according to the results of a global climate model MIROC. The input is variability of insolation and atmospheric CO<sub>2</sub> concentration and the output is time evolution of ice-sheet distribution over the northern hemisphere.

We conducted experiments for two 40-kyr cycles. One is from MIS-49 to 47 and the other is MIS-45 to 43. These cycles are chosen as a representative of 40-kyr cycles that has a long and stable interglacial and that has a relatively short interglacial and long glacial respectively.

As a result, 40-kyr cycles are reproduced and the shape of the variation is similar to the proxy record. This is because the surface temperature exceeds a threshold that the North American ice-sheet starts deglaciating once in a 40-kyr cycle. Phase analysis of this result suggests that the difference in the shape of these cycles is explained by lead-lag relationship between obliquity and precession. For a long interglacial period, the peak of climatic precession precedes that of obliquity, and vice versa for a short interglacial period.

In summary, climatic precession decides a timing of a deglaciation because of the large influence on insolation and obliquity has a role as a pacemaker of 40-kyr cycles because of an existence of a threshold of an ice-sheet deglaciation. These are the role of the orbital parameters in the early Pleistocene. We would also analyse several sensitivity experiments under different basal conditions, and those coupled with the temperature anomaly calculated by using atmosphere-ocean-vegetation GCM MIROC-LPJ (O' ishi and Abe-Ouchi, 2011).

Keywords: Pleistocene, glacial-interglacial cycles

### High glacial dust amount worked to warm the polar regions at the Last Glacial Maximum: a modelling study using MIROC-ESM

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Aerosol and its impacts on climate is one of uncertain factors on future climate projection. One of the aerosol species, mineral dust aerosol (dust) can be investigated with the past climate changes. Especially, need of more investigation of the feedback of dust and vegetation under the different climatic condition compared to present day is repeatedly mentioned in the paleoclimate chapter of Intergovermental Panel on Climate Change 5<sup>th</sup> Assessment Report. Last Glacial Maximum (LGM, c.a. 21,000 years before present) is known with the enhancement of dust, globally but especially over the high latitude regions from the ice core and sediment core proxy data (Winkler et al. 2008, Lamy et al. 2014). It has been difficult to reproduce dust amount over the high latitudes with General Circulation Models (GCMs) at LGM and the effect of dust on high latitudes has not been cleared. The previous works used atmospheric part of GCM or Earth System Model (ESM) (Mahowald et al. 2006, Takemura et al. 2009, Albani et al. 2012, Hopcroft et al. 2015). For the first time, using an ESM, MIROC-ESM (Watanabe et al. 2011), we tested the impact of enhanced dust on LGM climate with adding glaciogenic dust (Mahowald et al. 2006) (hereafter, called LGMglac) on a standard LGM simulation following the Paleoclimate Modelling Intercomparison Project phase 3 (PMIP3) protocol (Sueyoshi et al. 2013). The resulting deposition distribution of dust in LGMglac matched better to the latest global dust data archives (Kohfeld et al. 2013, Albani et al. 2014). The experiment LGM is the identical with the one for PMIP3. LGMglac deviated from the LGM in a spin-up stage and the corresponding period with the LGM experiment is taken for the analyses. We have found that the high LGM dust amount warms the northern high latitudes and the surrounding of the Antarctica. Sensitivity experiments using atmospheric part of MIROC-ESM suggested that both of radiative forcing and the aging of snow and ice albedo by dust are important for the LGMglac-LGM warming in the northern hemisphere. One the other hand, over the Antarctica, the positive radiative forcing at surface plays a role for the warming with additional dust but the effect on the surface temperature of the high glacial dust amount is a little at the borehole sites over the high plateau of the Antarctica.

Keywords: Dust, LGM

#### On the migration of Dome Fuji summit of East Antarctica over glacial - interglacial periods

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Dome Fuji in East Antarctica is one of candidate areas for finding sites of "Oldest Ice" that has age beyond  $10^6$  years. In the Japanese Antarctic research program, this area was surveyed for long years since 1980's, focusing on glaciological study and ice core study. Two deep ice cores were drilled, once in 1990's and another in 2000's. For identification of proper sites for the oldest ice, we need to examine information of surface, internal and bottom conditions of the ice sheet. We are currently compiling data of radar sounding historically in this area. Main results are as follows. Strain pattern accumulated within the ice sheet was examined. The data was explainable if we assume that the dome summit was located somewhere in the southern direction from the present dome position in the past. In addition, snow deposition after the last glacial maximum (LGM) has steep spatial gradient; northern side has more accumulation rate. Contour map of the LGM surface of the ice sheet had highest summit in ~60 km south of present Dome Fuji, where we call the area as New Dome Fuji (NDF). We will show latest output of the data analysis.

Keywords: Antarctica, ice sheet, ice core

On the possibility of radiometric dating on the "oldest ice" using cosmogenic  $^{26}$ Al/ $^{10}$ Be ratio: Insights from the Dome Fuji second deep (DF2) ice core

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Deep ice core records have been playing a crucial role in paleooclimatology. However, there are no records that have reached over ca. 800 ka. To overcome this problem, several research groups are planning to recover the "oldest ice" (~1.5 Ma) from near the bases of ice-sheets overlying inland Antarctica (see e.g. Schiermeier, 2016). Nevertheless, it may be not an easy task to obtain an accurate chronology from such deepest parts of ice cores, because layer inclination and/or folding may prevent us to construct accurate stable-isotope chronologies, which usually rely on normal stratigraphy.

Cosmogenic  $^{26}$ Al and  $^{10}$ Be are produced by interactions of comic rays with specific elements in the atmosphere. Because the atmospheric production is similar between  $^{26}$ Al and  $^{10}$ Be, an exponential decrease of the  $^{26}$ Al/ $^{10}$ Be ratio with time, in ordinary cases, should represents the difference of the decay constants of the nuclides ( $T_{1/2}$  of the  $^{26}$ Al/ $^{10}$ Be ratio is 1.45 Myr). In this presentation, we show the profiles of the  $^{26}$ Al/ $^{10}$ Be ratios of certain stratigraphic intervals of the Dome Fuji second deep (DF2) ice core, plotted against the latest age model for this core (Dome Fuji ice core project members, 2017). By investigating these data, we discuss about the possibility of the radiometric dating on the "oldest ice" of an age of up to 1.5 Ma.

#### High resolution analyses of the Dome Fuji deep ice-core using a Continuous Flow Analysis (CFA) System

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We have been developing a Continuous Flow Analysis (CFA) system at the National Institute of Polar Research, Japan for high resolution analyses of ice cores, especially the deep ice core drilled at Dome Fuji, Antarctica. The CFA system consists of a melting unit and a detection unit. The detection unit consists of two parts, one for melt water analyses and the other for gas (currently methane) analyses. The melt water is analyzed for stable isotopes of water, electric conductivity, solid particles, black carbon and elements (currently Na, K, Mg, Ca, Al and Fe). Part of the melt water is collected in sample vials with fraction collectors. Here we report the results of various tests to evaluate the CFA system. We also present the first results obtained from the Dome Fuji deep ice-core.

Keywords: CFA analyses, Deep ice core, Dome Fuji, Antarctica

#### High-resolution measurements of methane concentration in the Dome Fuji ice core using Continuous Flow Analysis (CFA) system

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At National Institute Polar Research, we have developed a continuous flow analysis (CFA) system for ice core analyses, and started the measurement of the second Dome Fuji ice core. With the CFA system, we continuously melt ice core and analyze it for various species, such as water isotopes, chemical composition, dust and black carbon. We can also extract air and analyze it for methane concentration.

An advantage of the CFA system for measuring methane from ice cores is that it can generate very high-resolution data. The detail fluctuation is expected to provide new insights into the past climate variations. It would also be possible to use the methane data for correctly matching the chronology of different ice cores. For example, Buizert et al., (2015) measured methane concentration in the WAIS Divide core from Antarctica using their CFA system and matched it with a temperature proxy (d<sup>18</sup>O) in the NGRIP core from Greenland. The high-resolution matching enabled them to deduce a centennial lag of Antarctic temperature maxima and minima behind abrupt temperature changes in Greenland. For ice cores from low-accumulation sites, such as the Dome Fuji ice core, the age difference between ice and gas is large and uncertain. The CFA methane analyses may contribute to better estimate of the age difference by comparisons with the ice and gas records from high-accumulation ice cores.

For the CFA gas analyses, a membrane degassing unit is used for extracting gas from ice-core melt. However, the gas extraction is incomplete, and thus the data must be corrected for the fractionation. The sign and magnitude of this effect can be estimated by introducing standard gases with known methane concentrations into ultrapure water, and extract and measure the gas through the CFA system. For our system, the methane concentration of the extracted standard gases through the CFA system is lower than the true value by several %.

The second Dome Fuji ice core will be analyzed by CFA from surface to 2400 m (~300 ka), and the first measurement campaign from the early Holocene to the Last Glacial Maximum has started. So far, we have completed the measurement from 300 to 314 m (7.5 to 8.0 ka). The methane concentrations after the gas extraction correction agree with the values obtained with our established, discrete measurement system within 1 %. At the presentation, we report the details of the CFA gas extraction and analyses, and the methane record from the Dome Fuji ice core measurements.

Keywords: icecore, greenhouse gas, paleoclimatology, Antarctica

#### Preliminary report on the ice core drilling in Pamir-Arai Mountains, Central Asia in 2016

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In order to reconstruct local climate change in the western area of the Asian high mountain region, three ice cores were recovered from an ice cap in Pamir-Arai Mountains in Kyrgyz Republic, Central Asia in summer of 2016. The drilling site was located at 5300 m asl on a small ice cap in 20 km west from Mt. Lenin. The first drilling was stopped at 7 m in depth due to appearance of melt water in the firn layers. The second drilling was stopped at 12 m in depth due to crevasse. The third core was successfully reached to the bottom of the ice cap. The depth was 37 m. The borehole temperature was -6.3C at the bottom. Results show that the snow was melt and refrozen at this elevation and the quality of the core was not as good as expected.

Keywords: central asia, ice core, Pamir

Preliminary Modelling of the vegatation-climate, wet area and past methane emission by a general circulation model and a dynamical global vegetation model

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Past time series of methane concentration in the atmosphere is reconstructed from ice core. Generation and emission of methane depend on temperature, wetness and amount of soil organic carbon which reflects climate change and vegetation change. Hence past methane information is useful for validation of paleoclimate modelling. In the present study, we predict some typical past climate (mid-Holocene, the Last Glacial Maximum, the Last interglacial and mid-Glacial) by a general circulation model MIROC and corresponding past vegetation by a dynamical global vegetation model LPJ-DGVM. Furthermore, by introducing a formulation based on Cao et al. 1996, we try to predict the distribution of past methane emission and its total global amount.

Keywords: paleoclimate, vegetation, methane

#### Response of oceanic carbon cycle during Heinrich events

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Paleoproxy indicate that a substantial weakening of the Atlantic Meridional Overturning Circulation (AMOC) during Heinrich events was often accompanied by a notable atmospheric  $\mathrm{CO}_2$  increase. However, previous modeling studies show conflicting atmospheric  $\mathrm{CO}_2$  responses to an AMOC shutdown. In this study, we investigate the response of ocean carbon cycle to weakening AMOC using freshwater experiment conducted with a coupled atmosphere-ocean general circulation model MIROC and offline ocean biogeochemical model. The weakening of AMOC under mid-Glacial condition leads to an oceanic carbon reservoir decrease and to a 4 ppmv atmospheric  $\mathrm{CO}_2$  increase, which is smaller than the ice core date of 15 ppmv  $\mathrm{CO}_2$  rise. The weakening of the North Atlantic leads to a loss of DIC in the North Atlantic intermediate and deepwaters, resulting in  $\mathrm{CO}_2$  outgassing into the atmosphere. In contrast, the greater mixing in the Southern Ocean enhances biological pump and thus increases  $\mathrm{CO}_2$  uptake from the atmosphere. Because thse two process cancel each other out, our simulation underestimates the observed atmosphric  $\mathrm{CO}_2$  increase. We also discuss the potential mechanisms which cause the additional  $\mathrm{CO}_2$  increase of 10ppmv in this presentation.

Keywords: Heinrch events, Carbon cycle

### Precise dating of cosmic ray events in the 17th century found by the analysis of beryllium-10 content in Antarctic ice core

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The records of beryllium-10 content in ice cores from Greenland and Antarctica have indicated five events of cosmic ray flux enhancement around the Maunder Minimum from the late 17th century to the early 18th century. These events are suggested to have occurred associated with the change in the heliospheric environment due to the disappearance of sunspots. In order to determine absolute ages of these events, we conducted high precision measurements of carbon-14 in tree rings. Although the peaks in carbon-14 content is strongly attenuated in carbon cycle, they have been detected by the measurement with 0.1% precision.

Keywords: Ice core, Cosmogenic nuclide, Solar activity

### Seasonal scale dating of a shallow ice core from Greenland using oxygen isotope matching between data and simulation

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A precise age scale based on annual layer counting is essential for investigating past environmental changes from ice core records. However, the uncertain seasonal cycle (i.e., non-sinusoidal pattern) of oxygen isotope ( $\delta^{18}$ O) records causes inevitable errors in the dating. Here, we propose a dating method based on matching the  $\delta$  <sup>18</sup>O variations between ice-core records and records simulated by isotope-enabled climate models. We applied this method to a new  $\delta^{18}$ O record from an ice core obtained from a dome site in southeast Greenland. The close similarity between the  $\,\delta^{\,\,18}$ O records from the ice core and models enabled correlation and the production of a precise age scale, whose accuracy was ±2 months. A missing  $\delta^{18}$ O minimum in the 1995/1996 winter is an example of the uncertain  $\delta^{18}$ O seasonal cycle, which hampers annual layer counting. Our analysis suggests that the missing  $\delta^{18}$ O minimum was likely caused by a combination of warm air temperature, weak moisture transport, and cool ocean temperature. Based on the age scale, the average accumulation rate from 1960 to 2014 was reconstructed as 1.02 m yr<sup>-1</sup>. The annual accumulation rate increases with a slope of 3.6 (mm year<sup>-1</sup>), which is mainly caused by the increase in the autumn accumulation rate (2.6 mm year<sup>-1</sup>), which is likely linked to the enhanced hydrological cycle caused by the decrease in Arctic sea ice area. On a seasonal time-scale, our reconstructed accumulation suggests that the ERA re-analysis data overestimates the seasonality in this southeast dome region.

Keywords: Greenland, ice core, seasonal scale dating, oxygen isotope, air temperature, annual accumulation rate

# A 60-year record of atmospheric sulfate and nitrate depositions preserved in the high-accumulation dome ice core, South East Greenland

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Southeastern Greenland has a dome whose elevation is higher than 3000 m a.s.l. with high accumulation rate (about 1 m yr<sup>-1</sup>) in water equivalent, which is suitable conditions for reconstructing past environmental changes with a high-time resolution. In this study, we measured major ion fluxes in 90 m ice core drilled from the SE-Dome region in 2015, and obtained records of annual ion fluxes from 1957 to 2014. High average  $NO_3^-$  flux (68.9 mg m<sup>-2</sup> yr<sup>-1</sup>) with low  $\delta^{15}N$  value in the SE-Dome ice core suggests negligible effect of the post depositional  $NO_3^-$  loss. Thus, the SE-Dome region is one of the best locations for reconstructing nitrate fluxes. Decreasing trend of non-sea-salt (nss)  $SO_4^{-2}^-$  flux from 1970 to 2010 follows well that of anthropogenic SOx emission from North America, suggesting that the  $SO_4^{-2}^-$  flux in SE-Dome ice core mainly records anthropogenic emission of SOx from North America. In contrast, the decadal trend of  $NO_3^-$  flux in SE-Dome ice core differs from the decreasing trend of anthropogenic NOx emission in North America. The exact cause of the apparent non-linear relationship remains unclear but a formation of ammonium nitrate particles enhanced by SOx reduction appears to be an important mechanism as suggested by excess ammonium flux over sulfate. Our  $NO_3^-$  flux record is similar to other ice cores in Greenland high elevation sites on 5-yr running average, suggesting that  $NO_3^-$  concentrations records from these ice cores are reliable.

Keywords: Greenland, ice core, sulfate ion, nitrate ion, Anthropogenic emission

#### The triple isotopic composition of oxygen for sulfate and nitrate in surface snow in a latudinal transect in East Antarcica

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The isotopic compositions of sulfate ( $SO_4^{2-}$ ) and nitrate ( $NO_3^{-}$ ) reflect their sources and oxidation pathways. In particular, triple oxygen isotope compositions ( $\Delta^{17}O$ ) are potential tool to reconstruct how the oxidants work in past and present atmosphere. Antarctica is an ideal place to investigate the past proxy, because the ice core preserves in past hundred thousands Earth's history. However, recently we found the annual mean  $\Delta^{17}O$  values for atmospheric  $SO_4^{2-}$  at coastal Antarctica is not matched with the  $\Delta^{17}O$  values preserved in the inland Antarctic ice core records. In addition, the lack of observation, spatial variations of  $\Delta^{17}O$  values are limitedly reported.

In order to test spatial variation of isotopic compositions, especially for the difference in  $\Delta^{17}$ O values between coastal site and inland site, here we present latitudinal variation of  $\Delta^{17}$ O value and conventional isotopic compositions ( $\delta^{34}$ S,  $\delta^{15}$ N, and  $\delta^{18}$ O) of  $SO_4^{2-}$  and  $NO_3^-$  in surface snow in eastern Dronning Maud Land, East Antarctica. Snow samples were collected from the surface at low- and high-elevation sites during the 54th and 57 th Japanese Antarctic Research, respectively.  $\Delta^{17}$ O values of non-sea-salt (nss)- $SO_4^{2-}$  at the East Antarctica ranges from 2.2 to 3.3%, and the  $\Delta^{17}$ O value of nss- $SO_4^{2-}$  for coastal site was lower than those for inland site. Thus, this result suggest that oxidizing chemistry for biogenic sulfur is different among coastal and inland sites, although small sulfur isotopic variations are observed and source of sulfur is biogenic and homogeneous. For the isotopic compositions of  $NO_3^-$ , considerably increasing values of  $\delta^{15}$ N of  $NO_3^-$  are observed from coastal to inland sites. The  $\delta^{18}$ O and  $\Delta^{17}$ O of  $NO_3^-$  values, on the other hand, decreases with increasing of  $\delta^{15}$ N values, indicating the secondary formation of  $NO_3^-$ . Thus, spatial variations of isotopic compositions of  $NO_3^-$  reflect the post-depositional processes on the East Antarctic snow.

Keywords: stable isotope, triple oxygen isotopes, sulfate, nitrate

## A year-round observation of sulfur stable isotopic compositions of atmospheric sulfate at Dumont d' Urville, coastal Antarctica

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Sulfur stable isotopic compositions ( $^{34}$ S/ $^{32}$ S,  $^{33}$ S/ $^{32}$ S and  $^{36}$ S/ $^{32}$ S) of sulfate in the Antarctic snow and ice cores have been used to investigate the contribution of its sources such as marine biogenic activity and volcanic emissions, as well as its formation pathways (e.g., Patris et al., 2000; Uemura et al., 2016; Baroni et al., 2007). However, temporal variability of those signatures in the present Antarctic atmosphere has never been examined. Here we report a year-round observation of sulfur isotopic compositions of sulfate in aerosol samples collected at Dumont d' Urville ( $66^{\circ}40^{\circ}$  S,  $140^{\circ}01^{\circ}$  E), coastal Antarctica, throughout the year 2011. In summer months,  $^{34}$ S/ $^{32}$ S ratios were similar to the values observed in dimethyl sulfide (DMS) produced by marine biota (Amrani et al., 2013; Oduro et al., 2012), in contrast to  $^{34}$ S depletion during winter, which suggest the contribution of other sources or unknown processes. Throughout the year,  $^{33}$ S/ $^{32}$ S and  $^{36}$ S/ $^{32}$ S ratios suggested no significant contribution of reactions causing mass independent fractionation.

Keywords: Stable isotope, Antarctica, Sulfate

#### Stable isotope analysis of pollen grains for terrestrial paleoclimate reconstruction revisited

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Pollen grains in terrestrial sediments are used for estimating paleoenvironmental change through Quaternary period because of their well preservation. Stable isotopic composition of pollen has also been proposed as paleoclimate indicators such as temperature and humidity while the validity of this approach has been questioned. In this study, isotopic compositions of pollen obtained from several tree species in Japan were analysed for reevaluating the potential as paleoclimate indicator.

Keywords: stable isotopes, pollen, paleoclimate

#### Variation trend of <sup>17</sup>O-excess in an Arctic ice core

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Ice cores obtained from glaciers and ice sheets are important archives for reconstructing changes in the paleoclimate. The most important climate changes, such as the variation in temperature, precipitation, and the hydrological cycle, are reconstructed from stable water isotope ratios ( $\delta^{18}$ O,  $\delta$  D, and a second-order parameter, the d-excess, defined as d-excess =  $\delta$  D -8  $\delta^{18}$ O) measured in ice cores. With the improvment of water isotope analyzers, the ability to measure  $\delta^{17}$ O in water with high precision provided another second-order parameter, the  $^{17}$ O-excess, defined as  $^{17}$ O-excess = In ( $\delta^{17}$ O+1) -0.528 In( $\delta^{18}$ O+1). Previous studies reported that  $^{17}$ O-excess in polar snow is mainly controlled by the relative humidity in the water vapor source region, therefore expected as a new proxy of past climate change. However, at the present, there are few studies of  $^{17}$ O-excess in ice core, and therefore an undrestanding of variation factor of that is incomplete.

In this study, we analyzed  $\delta^{17}$ O and  $^{17}$ O-excess in an ice core which was drilled in Alaska. We also discussed the variation factors of those associated with environmental change.

Keywords: ice core, Arctic region, 170-excess

### SEM observation of insoluble particles in an ice core drilled from Grigoriev Ice core, Tien Shan Mountains.

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Ice cores usually contain insoluble particles, such as volcanic ash, pollen and mineral particles, which have been blown on glaciers by wind. Volcanic ash has been used to identify the age of layers and mineral dusts are used as proxies of land surface or climate. Ice cores drilled from mountain glaciers in mid or low latitude areas contain abundant mineral dust. Although the abundance of mineral particles is often quantified with a particle analyzer, the morphology and elemental composition of each particle has not been studied well. In this study, we analyzed mineral particles in the ice core drilled from Grigoriev Ice Cap in Tien Shan in Central Asia, with a scanning electrical microscope (SEM) and classified them based on their elemental compositions analyzed with EDS.

The size of mineral particles in the ice core ranged up to 30  $\mu$ m in diameter, but was mostly smaller than 10  $\mu$ m. Based on the elemental composition, 60 - 90% of analyzed particles were Si or Al-rich particles. They are likely to be quartz or feldspar derived from desert surrounding the glacier. The remaining particles were Mg, Fe, or Ca-rich particles. Their abundance varied among the different layers. The variation may be due to different provenance of the particles.

### Shallow ice cores from the western Cwm of the Khumbu Glacier of Mt. Everest in Himalayas drilled in 1980

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Two shallow ice cores have been drilled on the Western Cwm of Khumbu Glacier of Mt. Everest in winter of 1980 by the Japanese winter climbing expedition of Mt. Everest led by a famous climber, Naomi Uemura. The cores were successfully transported in frozen state to a cold room of National Institute of Polar Research in Japan. Since then, the ice cores have just been stored for a long time -without any analysis. In 2016, we recognized the cores and decided to restart the analysis. In this study, we reported the description of stratigraphy and results of stable isotope and soluble ion analyses. The ice cores were analyzed Core1 drilled at 6100 m a.s.l. and 8.83 m in length, and Core2 drilled at 6400 m a.s.l. and 4.06 m in length. The visual stratigraphy of the cores revealed that the two cores have a distinct stratigraphy. Core1 showed that 98% of the length were the granular snow and 2% were the refrozen ice layer. A dust layer was observed at a depth of around 7.3m. In contrast, In Core2 showed that, 15% of the length were the granular snow and 85% were the ice layer. The sand and gravel layers was observed frequently in the core, in particular at a depth of 0.40~0.60 m, 1.2m, 3.4~4.0 m. The results suggest that Core1 consists of continuous snow layers without significant melt, while Core2 consists of abundant refrozen ice layers and affected by avalanche snow from the south wall of Mt. Everest. The mean Hydrogen and oxygen isotope ratios were -126.4 and -17.6 permil for Core1, -163.3 and -21.5 permil for Core2. The lower isotope ratio for Core2 is probably due to the snow of lower isotopes supplied from the high elevation of the south wall by avalanche. The soluble ion composition were also distinctive between the two cores. Core1 was dominated by Na<sup>+</sup> and Cl<sup>-</sup> while Core2 was dominated by Ca<sup>2+</sup>. The difference was also due to debris supplied from the wall and effect of melt and refrozen of the snow.

Keywords: Shallow icecore, Snow chemistry, Himalayas, Mountain Glacier