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 ((NH4)2SO4) with high hygroscopicity (Pilinis et al, 1989). On the other hand, it is reported that calcite (CaCO3) in mineral particles reacts with sulfuric acid (H2SO4) during atmospheric transportation and forms gypsum (CaSO4·2H2O) (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 CaCO3 in mineral dust with H2SO4 causes suppression of forming (NH4)2SO4 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 CaSO4·2H2O in mineral dust, or identification of the neutralization process of CaCO3, 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 CaSO4·2H2O 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 Iizuka et al. (2009, 2012). Calcium-bearing particles in the trapped particles were identified by micro X-ray Fluorescence (μ-XRF) mapping. Subsequently, calcium species of the particles were determined by micro X-ray absorption fine structure (μ-XAFS) spectroscopy.

As a result of the calcium speciation, CaSO4·2H2O fraction to total calcium in 1971, 1978, and 1987 were lower than CaCO3 fraction. In contrast, CaSO4·2H2O fraction in 1995 and 2004 were higher than CaCO3 fraction. It is considered that chemical reaction of CaCO3 in mineral dust with H2SO4 was more active in recent 20 years. On the other hand, sulfate ion (SO42−) concentration in ice core decreased from late 1970s. The trend of SO42− was consistent with emission record of SO2 in industrial countries at the time,
however, emission amount of SO$_2$ 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$_2$SO$_4$ in China. These results suggested that suppression of (NH$_4$)$_2$SO$_4$ formation in the Northern hemisphere was associated with the neutralization reactions of CaCO$_3$ with H$_2$SO$_4$ in East Asia.

キーワード：エアロゾル、アイスコア、雲凝結核、中和反応、カルシウム化学種同定、X線吸収微細構造(XAFS)
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$^{-1}$) 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.

キーワード：安定同位体、硝酸

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\textsubscript{3}- 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\textsubscript{3}- mass fraction f of pit samples on each depths were evaluated using measured d15N values, assuming initial d15N value(-10 permil), NO\textsubscript{3}- concentrations, and atmosphere–snow fractionation constant $^{15}\varepsilon$ (-60 permil) for $\delta^{15}$N 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\textsubscript{2}, however, wasn’t detected from snow surface and in the atmosphere.
South 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 compared 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.

キーワード：LGM、AMOC、地表風
Keywords: LGM, AMOC, surface wind
Atmospheric CH$_4$ concentration during the Holocene reconstructed from the NEEM (Greenland) and Dome Fuji (East Antarctica) ice cores

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Methane (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 CH$_4$ correlate with climatic precession, because the size of wetlands and their CH$_4$ production rate respond to Northern Hemisphere (NH) summer insolation, through the variations in temperature and rainfall on NH landmasses. The correlation between 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 CH$_4$ concentration increased since ~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 CH$_4$ concentrations have provided important constraint on the evolution of 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 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 CH$_4$ IPD during the Holocene, we have been measuring CH$_4$ concentrations in the NEEM (Greenland) and Dome Fuji (DF) (Antarctica) ice cores. Accurate CH$_4$ reconstruction from the Holocene NEEM ice core is challenging because of the brittle zone. We indeed found high CH$_4$ spikes in the brittle zone, thus we investigated them by measuring additional 3–5 samples from the neighboring depths (within ~50 cm, ~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 ±2.5 and ±1.7 ppb for the NEEM and DF ice cores, respectively.

We investigate the integrity of our Holocene CH$_4$ data. The CH$_4$ 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$_4$ 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$_4$
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$_4$ 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 ~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.

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.
Increasing insolation and greenhouse gas concentration trigger Bølling-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 Circulation (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.
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$_2$ 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).
High glacial dust amount worked to warm the polar regions at the Last Glacial Maximum: a modelling study using MIROC-ESM

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 5th 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.
On the migration of Dome Fuji summit of East Antarctica over glacial - interglacial periods

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South Dome Fuji near is a candidate site for the drilling of Oldest Ice (more than 1 million years old), and has been observed in research for ice core and snow environment in the 1980s. In the 1990s and 2000s, two deep ice cores were obtained. For the Oldest Ice drilling candidate site, detailed observations and analysis of ice bed surface, internal, and bottom environments are required. We summarize the data collected by Japan and analyze the three-dimensional structure of the ice bed. The results indicate that past Dome Fuji was located about 60 km south of the current Dome Fuji under the ice. The results were presented in the latest state of data analysis.
Deep ice core records have been playing a crucial role in paleoclimatology. 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 cosmic 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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国立極地研究所ではアイスコアを高時間分解能で連続分析するため、連続融解分析（Continuous Flow Analysis、略してCFA）システムを開発した。本システムはアイスコアの融解ユニットと分析ユニットから構成される。分析ユニットは大きく分けて、アイスコアの融解水を分析する装置と、アイスコアに含まれる空気成分を分析する装置で構成される。現在、前者として電気伝導度計、レーザー式水同位体比アナライザー、ICP質量分析計、固体微粒子分析計、ブラックカーボン分析装置を用いており、後者としてはレーザー式メタンガス分析装置を用いている。また、融解水の一部はフラクションコレクターにより、自動的にサンプル瓶に注入される。国立極地研では、このCFAシステムを用いて南極ドームふじ深層コアの分析を開始した。本発表では、融解水を用いた分析について報告する。まず、本システムの性能を評価するために実施した様々なテストについて紹介し、次に、初期的な分析結果について報告する。

キーワード：CFA分析、深層氷床コア、南極ドームふじ

Keywords: CFA analyses, Deep ice core, Dome Fuji, Antarctica
連続融解システムによるドームふじ氷床コア中のメタン濃度の高分解能測定

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

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国立極地研究所では、氷床コアの連続融解分析（CFA）システムが開発され、ドームふじ氷床コアの測定が開始された。CFAシステムでは連続的に氷床コアを融解し同時に様々な測定をするため、多くの情報を得ることが可能となる。融解水に含まれる成分（水同位体、化学成分、ダスト、ブラックカーボン等）の測定だけでなく、氷床コア中に保存された過去の大気を抽出しメタンの濃度を測定することができる。

CFAシステムを用いるメリットは、従来の測定に比べて圧倒的に高い分解能のデータを得ることにある。メタンの詳細な変動データによって、これまでの手法では見ることのできなかった新たな古環境変動が見出される可能性がある。また、複数のコアの年代をより正確に合わせて比較することが可能となる。例えば、Buizertら(2015)は、CFAによって得られた南極WAIS Divide氷床コアのメタン濃度データとグリーンランドNGRIPコアの酸素同位体比データ（気温の指標）を対比させることにより、両コアの気温変動のタイミングを正確に比較した結果、南極の気温の変曲点（極大、極小）がグリーンランドの急激な気温変化に約200年遅れることを見出した。ドームふじコアのような低涵養度の地点のコアでは、空気の年代決定に不可欠となる氷と空気の年代差の誤差が大きいが、これが他のコアとの比較によって正確に推定できるようになる可能性がある。

CFAにおいて、氷の融解水からの気体の抽出には、通常脱気装置に用いられるような薄膜を使用する。しかし、溶存気体の抽出は完全には行えないため、そのことによる測定対象成分の分別効果を補正する必要がある。その量を、超純水に濃度既知の標準ガスを混入させて実際のアイスコア試料と同様に抽出する実験によって見積もった結果、メタン濃度の場合には真の値に比べて数%低めに測定されることが示された。第2期ドームふじコアのCFA分析は、最終的には表面から2400m（約30万年前）にかけて行われるものであり、現在、主に最終退氷期を対象とした分析を開始したところである。予稿投稿時点で300〜314m（ガス年代：約7500〜8000年前）の測定が行われた。気体抽出時の分別を補正したCFA分析値と、氷床コアを個別に分析する従来の測定方法による値との差は約1%以下であり、補正が正しく行われていることが判明した。当時は、CFAの気体分析部と標準ガスを用いたキャリプレーションの詳細に加え、ドームふじコアからのメタンのCFAによる復元結果を報告する。

キーワード：アイスコア、温室効果ガス、古気候学、南極
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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Central Asia, ice core, Pamir

中央アジア山岳域の西端に位置するパミール高原は、アジアモンスーンよりも偏西風の影響を強く受ける中央アジアの中でも特別な気候条件をもつ地域である。パミール高原には数多く氷河が存在し、その融解水は下流部乾燥域の人間社会を支え、最終的にアラル海に注ぐ。この地域の水資源変動の将来予測のためにも、パミール山域の過去の気候変動の復元は重要である。2016年8月に中央アジア・キルギス共和国パミールアライ山域でアイスコアを掘削した。掘削した氷河は、レーニン峰（7134m）から西へ約20km離れた標高約5300mの氷帽頂上である。3本のアイスコアを掘削し、1本目は約7mで水が現れ、2本目は約12mでクレバスに達し、3本目は約37mで底部岩盤に達した。底部に達した3本目のコアは、平均密度は847 kg m⁻³で、15m以深はほぼ再凍結氷であった。掘削高温度の測定の結果は、底部で-6.3℃であった。以上の結果は、パミール山域では5300mの標高でも氷河表面は融解再凍結が起こること、また掘削したアイスコアは過去環境復元の目的としては限定的な試料であることを示している。アイスコアは今後、同位体、化学分析等が進められる予定である。

キーワード：中央アジア、アイスコア、パミール
Keywords: central asia, ice core, Pamir
Preliminary Modelling of the vegetation-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.

キーワード：古気候、植生、メタン
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 CO₂ increase. However, previous modeling studies show conflicting atmospheric CO₂ 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 CO₂ increase, which is smaller than the ice core date of 15 ppmv CO₂ rise. The weakening of the North Atlantic leads to a loss of DIC in the North Atlantic intermediate and deepwaters, resulting in CO₂ outgassing into the atmosphere. In contrast, the greater mixing in the Southern Ocean enhances biological pump and thus increases CO₂ uptake from the atmosphere. Because these two process cancel each other out, our simulation underestimates the observed atmospheric CO₂ increase. We also discuss the potential mechanisms which cause the additional CO₂ increase of 10 ppmv in this presentation.

Keywords: Heinrich 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.

キーワード：氷床コア、宇宙線生成核種、太陽活動
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 $\delta^{18}O$ 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$^{-1}$. The annual accumulation rate increases with a slope of 3.6 (mm year$^{-1}$), which is mainly caused by the increase in the autumn accumulation rate (2.6 mm year$^{-1}$), 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$^{-1}$) 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$^{-2}$ yr$^{-1}$) 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.

キーワード：グリーンランド、アイスコア、硫酸イオン、硝酸イオン、人為起源排出量
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 latitudinal transect in East Antarctica

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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 57th 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.

キーワード：安定同位体、三酸素同位体組成、硫酸、硝酸
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 (34S/32S, 33S/32S and 36S/32S) 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°40’S, 140°01’E), coastal Antarctica, throughout the year 2011. In summer months, 34S/32S 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 34S depletion during winter, which suggest the contribution of other sources or unknown processes. Throughout the year, 33S/32S and 36S/32S ratios suggested no significant contribution of reactions causing mass independent fractionation.

キーワード：安定同位体、南極、硫酸
Keywords: Stable isotope, Antarctica, Sulfate
花粉の安定同位体比分析による陸域古気候復元の可能性の検証
Stable isotope analysis of pollen grains for terrestrial paleoclimate reconstruction revisited

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堆積物に残存する花粉化石は、その保存の良さから主に第四紀の古環境復元に利用されてきた。近年、気温や湿度の指標として花粉の安定同位体比を使用するアプローチが提案されているが、その妥当性には議論がある。本発表では、日本各地で採取された樹木花粉の安定同位体比と各種環境指標との関連を再検証した結果について報告する。

キーワード：安定同位体、花粉、古気候
Keywords: stable isotopes, pollen, paleoclimate
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 (δ\textsuperscript{18}O, δD, and a second-order parameter, the d-excess, defined as d-excess = δD - 8δ\textsuperscript{18}O) measured in ice cores.

With the improvement of water isotope analyzers, the ability to measure δ\textsuperscript{17}O in water with high precision provided another second-order parameter, the 17O-excess, defined as 17O-excess = ln(δ\textsuperscript{17}O+1) - 0.528 ln(δ\textsuperscript{18}O+1). Previous studies reported that 17O-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 17O-excess in ice core, and therefore an understanding of variation factor of that is incomplete.

In this study, we analyzed δ\textsuperscript{17}O and 17O-excess in an ice core which was drilled in Alaska. We also discussed the variation factors of those associated with environmental change.
天山山脈グリゴレア氷帽アイスコア中の固体粒子のSEM観察

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

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アイスコアには大気を介して氷河に飛ばされてきた火山灰や花粉、鉱物粒子など様々な固体粒子物質が保存されている。アイスコアの固体粒子は、年代決定や地表面環境のプロキシーとして広く利用されている。例えば、極域のアイスコアでは、火山灰粒子のSEM-EDS分析から起源となる火山を特定し層の絶対年代の決定に利用されている。一方、低緯度山岳域の氷河のアイスコアでは、極域に比べ高濃度の鉱物粒子が含まれており、その濃度は砂塵嵐や気候の乾燥度のプロキシーとして利用されている。一般に、固体粒子濃度は、パーティクルカウンター等で機械的に定量されることが多く、含まれる粒子の形態、種類等に注目した分析は少ない。固体粒子の鉱物種や化学成分等の分析によって、その粒子の起源を特定し、過去のより詳しい地表面環境や大気循環を明らかにする可能性がある。そこで、本研究では、中央アジア・天山山脈グレゴリア氷帽で掘削されたアイスコア中の固体粒子についてSEM-EDS分析を行った結果を報告する。

分析に使用したアイスコアは、2007年にグリゴレア氷帽（4600m）の頂上部で掘削された全長約87mのコアである。年代決定は、花粉濃度および放射性炭素同位体によって行われ、底部は約13000年前であることが明らかになっている。年代の異なる層を選択し、含まれる固体粒子を電子顕微鏡（JSM-6010PULUS/LA, 日本電子）で観察した。低真空モードで観察し、各粒子のEDSによる元素分析を行った。観察された鉱物粒子は直径数μmから30μmの範囲で、特に10μm以下の粒子が多く観察された。観察された鉱物粒子についてEDXによる元素分析を行い構成元素による粒子の分類を行った。その結果、年代に関係なくどの層でもSiまたはAlが主成分のタイプである鉱物粒子が、分析数の60-90%を占めた。これらは主に砂漠に由来する石英や斜長石などの珪酸塩鉱物と考えられる。一方、残りの鉱物粒子はMgやFe、Caを比較的豊富に含む粒子であった。これらのタイプは年代によって含有率が異なった。この含有率の違いは、鉱物粒子の供給源の違いを示している可能性がある。
1980年ヒマラヤ山脈エベレスト・クンブ氷河ウエスターンクームで掘削された浅層アイスコア解析

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

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1980年12月、植村直己隊長率いるヒマラヤ山脈エベレスト冬季登山隊によってクンブ氷河の涵養域ウエスターンクーム（標高6100-6400 m）にて、2本のアイスコアが掘削された。掘削されたコアは、冷凍されたまま日本に輸送され、国立極地研究所の低温室に保管された。このアイスコアは冷凍のまま保存されているヒマラヤの氷資料として非常に貴重なものである。アイスコアはそのまま長く間隔なく保管されていたが、2016年になってコアの再確認が行われ、千葉大学で解析が行われることになった。2本のアイスコアについて、層位観察、コア長、密度の測定、さらに水素・酸素安定同位体比と主要化学成分濃度の分析を行い、アイスコアの基礎的特徴を明らかにすることを目的とした。コアの層位観察の結果、Core1とCore2では大きく層位が異なった。Core1は全層位の98%がザラメ層で、2%が氷板層、ダスト層は唯一深さ7.3 m付近で観察された。一方、Core2は全層位の15%がザラメ層で、85%が氷板層であった。さらに砂や礫を含む層が多く見られ、特に深さ0.40~0.60 m、1.2 m、3.4~4.0 mに顕著な層があった。以上の結果は、Core1は比較的融解の少ない連続的なコアであるのに対し、Core2は融解が激しく、さらにエベレスト南壁からの雪崩の影響を大きく受けていることを示唆している。アイスコア中の水素・酸素同位体比を分析した結果、Core1はそれぞれ平均で-126.4 ‰、-17.6 ‰、Core2はそれぞれ平均で-163.3 ‰、-21.5 ‰であった。わずか300 mの標高差で大きく同位体比に差がついたのは、Core2には南壁上部の同位体比の小さい雪が雪崩によって供給されているためと考えられる。アイスコア中の主要化学成分も2つのコアに差があった。Core1は、Cl⁻とNa⁺が全体の60%以上を占めたのに対し、Core2は、Ca²⁺が平均72%を占めていた。これは、Core2に含まれる南壁からのデブリ、および融解再凍結の影響と考えられる。

キーワード：浅層アイスコア、雪氷化学、ヒマラヤ、山岳氷河
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