

## Chemical compositions of non-volatile particles in NEEM (Greenland) ice core over the last 100,000 years

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The polar ice cores provide us with information of past atmospheric aerosols. Soluble aerosols in polar ice cores are well discussed by using proxies of ion concentration/flux, however, there are few studies about chemical compositions of soluble aerosols in ice cores. Using a sublimation method, we show differences in the compositions of non-volatile aerosols over the last 100,000 years in the NEEM ice core, which was drilled during 2008-2012 on the northwest ridge line of Greenland ice sheet (77° 27' N, 51° 03' W).

A total of 86 samples were distributed from NEEM ice core sections from 220 to 2195 m, which covers from late Holocene to Dansgaard-Oeschger event 24. Non-volatile particles were extracted from the ice by sublimation system [Iizuka et al., 2009]. Constituent elements of each non-volatile particle were measured by a scanning electron microscope and energy dispersive X-ray spectroscopy. We made a classification of non-volatile particles into insoluble dust, soluble sulfate salts and soluble chloride salts as following; if Si found in a particle, we regard the particle as dust (Silicates); if S found, we regard the particle as sulfate; if Cl found, we regard the particle as chloride salt. For the sulfate salt, we did further classification that a particle containing Ca and S are assumed as CaSO<sub>4</sub>, Na and S are Na<sub>2</sub>SO<sub>4</sub>, Mg and S are MgSO<sub>4</sub>, K and S are K<sub>2</sub>SO<sub>4</sub>, the residual sulfate particles are "the other sulfate salt (other-S)". In the same way, for chloride salts, we assumed NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, KCl and the other chloride salt (other-Cl).

The number ratio of soluble salts to total particles is 9±6 % during Dansgaard-Oeschger (DO) events. In Last Glacial Maximum (LGM), the ratio decreased in 3±2%. In Bolling-Allerod (BA), ratio of soluble salts slightly increased (10±5%). In Younger Dryas (YD), the ratio decreased again (6±3%). After Holocene, the ratio increased (16±10 %). In summary, more than 90 % of particles contain insoluble dust during the cold stages. These ratios suggest that during cold periods, insoluble dust concentration is higher contribution to total non-volatile particles than that in warm periods.

We examined chemical characteristics of non-volatile particles by dividing into 7 climatic stages (Late Holocene; LH, Early Holocene; EH, YD, BA, LGM, DO events-warm; DO-W and DO events-cold; DO-C). The 7 stages can be sorted into 2 types; interglacial-type (LH, EH and BA) and glacial-type (YD, LGM, DO-W and DO-C). For the interglacial-type, number of Na-containing particles is larger than that of Ca-containing particles (Na:Ca = 4:3). On the other hand, for the glacial-type, number of Ca-containing particles is larger than that of Na-containing particles (Na:Ca = 5:9). Ca-containing particles is suggested to mainly come from terrestrial materials and Na-containing particles is mainly from sea-salt [Steffense et al., 1997]. Our results of the ratio of Ca and Na particles may be explained by not only absolute concentration of dust and sea-salt but also relative valance of those concentrations. In the three interglacial-type, the ratio of other-S and other-Cl, those are sulfate and chloride salts without Na, Mg, K, nor Ca, during the LH are relatively higher than the other stages. Since NH<sub>4</sub><sup>+</sup> concentration increased due to increasing of vegetation area and biological activity by warming in LH [Fuhrer and Legrand, 1997], other-S and Cl might be ammonium sulfate and ammonium chloride, respectively. Focusing on Ca-particles more in detail in the four glacial-type, number of Ca-containing particles without S and Cl is higher in LGM (11%) and DO-C (12%) than that in YD (6%) and DO-W (7%). Since the X-ray spectroscopy cannot detect carbon, the Ca-containing particles may be CaCO<sub>3</sub> in the LGM and DO-C because CaCO<sub>3</sub> was founded during the LGM by single particle measurement in the GRIP (Greenland) ice core [Sakurai et al., 2009].

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## Modelling the climate and the terrestrial carbon cycle for the last millennia

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Climate-induced changes in the terrestrial biosphere and the ocean modulate the release and uptake of carbon dioxide and this, in turn, alters atmospheric composition and influences the climate. This is known as the climate-carbon cycle feedback. The Coupled Carbon Cycle Climate Model Intercomparison Project (C4MIP), using models of the ?terrestrial and ocean carbon cycles inside ocean-atmosphere general circulation models, has shown that the carbon cycle-climate feedback appears to be positive BUT there is great uncertainty about the magnitude. It is important to know the magnitude of this feedback because it affects the amount of carbon dioxide that can be emitted in the future in order to stabilize the concentration of CO<sub>2</sub> at a given level. There are projects attempting to reduce these uncertainties through systematic evaluation of carbon cycle models against observations of the contemporary carbon cycle. An alternative approach is to use knowledge about past variations in climate and CO<sub>2</sub> to provide additional constraints. Here we therefore work on the last millennium (LM) climate-carbon modeling and examine the factors that contribute to atmospheric CO<sub>2</sub> change. Ice core is the only proxy that provides the CO<sub>2</sub> content in detail for the last millennium and it shows up to 10ppm change around the Little Ice Age and during the LM. Several LM experiments by AOGCM are used to drive the terrestrial carbon cycle model LPJ. We investigate the role of external forcing of climate such as volcano and solar forcing as well as that of internal variability of climate in an unforced experiment of decadal to centennial time scale. We show that the CO<sub>2</sub> changes in the same order of magnitude in the unforced experiment as in the forced experiment.