

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 CaSO₄, Na and S are Na₂SO₄, Mg and S are MgSO₄, K and S are K₂SO₄, the residual sulfate particles are "the other sulfate salt (other-S)". In the same way, for chloride salts, we assumed NaCl, CaCl₂, MgCl₂, 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 NH₄⁺ 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 CaCO₃ in the LGM and DO-C because CaCO₃ was founded during the LGM by single particle measurement in the GRIP (Greenland) ice core [Sakurai et al., 2009].

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