

Detection and formation processes of Na₂SO₄ salt particles in a Dome Fuji Holocene ice as short-term paleoclimate proxies.

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Ice core research is widely conducted to reconstruct regional and global paleoclimates. Ice cores drilled from the inland regions of polar ice sheets are particularly important for reconstructing climates up to several hundred thousand years ago, a time period that includes several glacial cycles. In the interior of Antarctica, long-term paleoclimate studies have been done for Dome Fuji ice core by using ion proxies. However, analyses of short-term climatic fluctuations in the ice core have not been done. This is mainly because owing to the low annual snowfall rates the annual layers are too thin to obtain sufficient sample for ionic analyses. Furthermore, in this region post-depositional processes are expected to have a larger influence on the variations of chemical concentrations and on the oxygen/hydrogen isotope ratio than is observed in other regions of Antarctica. The post-depositional processes include 1) sublimation, condensation, and volatilization in surface snow and 2) molecular diffusion in firn or ice.

We found by using Raman spectrometer that most of the soluble impurities in the Dome Fuji ice core were present as salt inclusions within ice grains. Because solid inclusions hardly diffuse in ice, depth profiles of soluble ions comprising the salt inclusions are considered to be preserved in the deep ice as reliable climate proxies. We found that the sizes of salt inclusions, several micrometers, are about the same in the whole ice core, indicating that there was neither growth nor active formation of the inclusions in the ice matrix. We found that the inclusions were primarily Na₂SO₄·10H₂O and MgSO₄·12H₂O in the Holocene ice, whereas CaSO₄·2H₂O and others in the LGM ice. By using SEM-EDS, we found that the major elements of micro particles in the Holocene ice are pair of Na and S, and pair of Mg and S. On the other hand, S is frequently detected with Ca in the LGM ice. These results from SEM-EDS strongly support the existing of the above salt inclusions in ice. We suggested from 2-mm resolution ion profiles that almost all of the Na⁺, Mg²⁺, and SO₄²⁻ existed as salts of Na₂SO₄ and MgSO₄ in the Holocene ice, but almost all of the Na⁺ existed as salts of NaCl in the LGM. These results from ion profiles suggest that the salt inclusions are critical compounds if we reconstruct the past environment by using ion proxies.

The formation of the Na₂SO₄·10H₂O and MgSO₄·12H₂O salts in the Holocene ice starts by chemical reactions of NaCl and H₂SO₄ during transport through the atmosphere, and is mostly completed within the firn. We concluded the probable formation processes of Na₂SO₄·10H₂O and MgSO₄·12H₂O salts that 1) some NaCl particles and liquid H₂SO₄ putted on outside of snow crystal have already reacted to Na₂SO₄ particles during transport through the atmosphere, 2) the other NaCl particles and liquid H₂SO₄ existed in inside of snow crystal are exposed and deposited on the firn surface by sublimation, and then 3) the surface diffusion of liquid H₂SO₄ creates Na₂SO₄ particles within firn.

The formation processes of the salts of Na₂SO₄·10H₂O and MgSO₄·12H₂O within firn indicates a low mobility of Na⁺ and Mg²⁺ in the Holocene ice, and is trusted for reconstructing the past Holocene environment with millimeter resolution, which corresponds to several months in the Holocene.