Identification of annual layers in polar region ice cores by seasonal variations in chemical concentrations

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Measurement of many elements at ppt level was achieved with ICP-MS, consuming about 0.1 ml of polar ice melt. Contamination was prevented by the use of ceramic knives, a class 10 clean bench, and plastic vials. Sample consumption was reduced with a microflow nebulizer in ICP-MS. Cold plasma technique overcame interference from Ar and its compositions. A15-m polar ice core was analyzed. Elemental concentrations and stable isotope ratios were measured at intervals of 2 cm and 4 cm, respectively. Both showed periodical changes with the period of 40-50 cm in length. Seasonal variations in concentrations were recognized based on the correspondence to temperature changes indicated by isotope ratio variation. Peaks on chemical profiles were clearer than those for stable isotope ratios.

Many researches have demonstrated that polar region ice cores are valuable archives of the past climatic changes. Ice core samples have unique features. The stable isotope ratio analysis of oxygen or hydrogen indicates the changes in temperature that is essential for climate researches. The analytical resolution in time scale is relatively high (up to decadal or annual) compared to other material cores. However, chemical analysis is difficult in general because of the extremely low concentration of materials in ice sheets in polar region, which is very far from the material sources.

We developed a method to reveal detailed climate variation recorded in ice cores by measuring low concentration elements with inductively coupled plasma mass spectrometry (ICP-MS). The objectives are to enhance the analytical resolution in time scale from decadal to annual or seasonal, and to make use of low concentration elements as signals for environmental change. In order to cut down the sample consumption and prevent possible contamination during sample operation, we improved the procedure of sample preparation, preliminary treatment and ICP-MS devices. As a result, measurement at ppt level was achieved by ICP-MS for many elements, consuming about 0.1 ml of ice melt. The primary factors are as follows: 1. Prevention of contamination: Ceramic knives are used to cut ice cores in a class 100 clean bench in a –20-deg. C low-temperature room. All of vials are made of plastics. Preliminary treatments were done in the class 10 clean bench installed in the class 1000 clean room. 2. A new type of microflow nebulizer was introduced to reduce the sample consumption drastically for ICP-MS operation. 3. Shielded torch system under cold plasma condition was used to overcome the spectral interference from the plasma gas on $39K$ ($38ArH$), $40Ca$ ($40Ar$) and $56Fe$ ($40Ar16O$).

We applied this method to 15-m ice core drilled at the dome of Devon Ice Cap on Devon Island, Canadian Arctic (75.3 deg. N, 82.3 deg. W). The ice core had a diameter of 10 cm, and was cut into small sections with a length of 2 cm. Elements measured were Na, Mg, Al, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and U. The concentrations ranged from 1 ppt level (e.g., U) to 10 ppb level (e.g., Na). Periodical changes in concentration were recognized for all of elements measured, with the most outstanding period of 40-50 cm in length of the core. Each of elements showed the similar period lengths and positions of peaks on concentration profiles. For comparison, stable isotope ratio of oxygen and hydrogen was measured for the same ice core. The ice core was cut into small sections with a length of 4 cm for isotope analysis. Periodical changes were also recognized for stable isotope ratio, with the period of 40-50 cm in length of the core. This change reflects the seasonal variation in temperature.

Concentrations of many elements showed seasonal variations. Periodical changes were recognized and the patterns of change were similar in both of chemical concentration and stable isotope ratio profiles. Peaks on profiles for chemical concentrations of the most of elements were clearer than those for stable isotope ratios. Therefore, the changes in elemental concentrations gave helpful information when the changes in stable isotope ratios were not clear. Measurement of elements at low concentration and stable isotope ratios should be done together for reliable identification of annual layers in ice cores.