Continuous measurements of methane mixing ratio from ice cores: method development at NIPR and initial test with the Mizuho ice-core

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Ice cores offer the unique possibility to study the history of the past atmospheric greenhouse gases. Since the 1950s, scientists have developed a variety of techniques to extract the trapped air from individual ice core samples, and to measure the mixing ratio of greenhouse gases such as carbon dioxide, methane and nitrous oxide, in the extracted air. These discrete measurements have become highly accurate and reproducible, but are both time-consuming and labor-intensive.

Recent technical developments of gas continuous measurement by spectroscopy, combined with an efficient method of separation of the gas-water stream, allowed successful continuous methane measurements along the NEEM (refs. 1,2,3) and the WAIS DIVIDE (as explained by Rhodes et al., AGU meeting, fall 2012) deep ice-cores.

Here we present the development of a method for continuous measurements of methane mixing ratios from ice cores at the National Institute of Polar Research, following previous works (refs. 1, 2, and 3). This method is based on a melting device of the continuous flow analysis (CFA) system, which provides a continuous stream of melt water and air bubbles. Water and air are separated in two steps. After a first separation in a sealed main degassing unit to provide a bubble-free water stream for impurities, dust, and stable water isotopes analysis, the overflow containing the bubbles passes through a gas-permeable membrane. Analysis of methane mixing ratios in the air stream is performed by a cavity ring down laser spectrometer (Picarro G2301 customized by manufacturer for low-pressure operation).

We present the first results of continuous methane mixing ratio as well as stable water isotopes, which were obtained by melting five consecutive bags of the Mizuho ice core (East Antarctica, $77^{\circ}42$ 'S, 44° 20'E, 2230 m.a.s.l., annual accumulation rate:4 to 6 cm ice equivalent, see ref.4). The depths of the corresponding bags are between 421.3 and 423.75 meters. In this presentation, we will discuss the behavior of our system mostly in terms of continuous gas extraction and methane measurement as well as the performance of the water isotope measurements with the modified water-gas separation unit.

References

J. Chappellaz, C. Stowasser, T. Blunier, D. Baslev-Clausen, E. J. Brook, R. Dallmayr, X. Faïn, J. E. Lee, L. E. Mitchell, O. Pascual, D. Romanini, J. Rosen, S. Schüpbach, "High-resolution glacial and deglacial record of atmospheric methane by continuous-flow and laser spectrometer analysis along the NEEM ice core", Climate of the Past, 9, 2579-2593, 2013
Stowasser, C., Buizert, C., Gkinis, V., Chappellaz, J., Schüpbach, S., Bigler, M., Faïn, X., Sperlich, P., Baumgartner, M., Schilt, A., and Blunier, T.: Continuous measurements of methane mixing ratios from ice cores, Atmos. Meas. Tech., 5, 999-1013.

(3) Rhodes et al, "Continuous methane measurements from a late Holocene Greenland ice core : Atmospheric and in-situ signals" Earth and Planetary Science Letters. 2013, 368, 9–19

(4) Watanabe, O., Fujii, Y. and Motoyama, H. (1992) Results of Analyses of Mizuho 700m Ice Core, East Antarctica, Part. 1 δ18O, Microparticles, ECM(Acidity), pH, Major Ions. JARE Data Report, 181 (Glaciology 20), 1-79.