Continuous methane measurement by a Continuous Flow Analysis system

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A Continuous Flow Analysis (CFA) system can continuously measure multiple components contained in ice cores. The CFA system provides high-resolution data more efficiently than traditional discrete measurements, and thus it has become a common way to obtain detailed paleoclimatic data from ice cores. The CFA system at National Institute Polar Research (NIPR) has been developed to measure major elements, water isotopes, dust, black carbon, and methane in polar ice cores. Here, we present the technique for methane measurements using the NIPR CFA system.

Ice core samples were cut into 3.5 x 3.5 x 50 cm sticks. The ice sticks were melted on a clean metal plate heated at 15 °C, which is placed in a freezer at -20 ° C. The melt rate is about 3 cm/min, and when the remaining ice stick became 10-cm long, the next ice stick was placed above the previous one, making continuous melting of multiple ice sticks. The meltwater with air bubbles was led to a "debubbler" unit, where bubble-free meltwater was separated from air bubbles, and the bubble-free water was led to several instruments for measuring the water sample (Figure 1). For the methane measurement, the air-water mixture from the debubbler was led to a gas-permeable membrane tube ("degasser tube" in Fig. 1) to extract the bubble air and dissolved air. The extracted air was passed through a dryer (Nafion) to remove water vapor. Finally, the methane mixing ratio of the dried gas was measured by a cavity ringdown spectrometer (Picarro G2301), which was customized to operate at low cavity pressure (40 torr).

The methane concentration measured by the CFA system is altered from the original value in the ice sheet by three factors: (1) incomplete extraction of gases dissolved in the meltwater, (2) smoothing due to mixing in dead volumes in the sample line and cavity of the spectrometer, and (3) contamination by the intrusion of laboratory air from the slight gap between the ice sticks. The effects (1) and (2) were evaluated using a "test line" (Fig. 1) that can mix ultrapure gas-free water and a standard gas with the same flow rates as those from the ice-core samples. The effect (1) was evaluated to be 5 - 8 % by measuring three standard gases mixed with gas-free water. After correcting for the effect (1), the ice-core CFA data was still slightly lower (by 2%) than the data from high-accuracy discrete measurements (our unpublished data). Moreover, gaps in methane concentrations were sometimes observed at the boundaries between the consecutive measurement dates, indicating some inconsistency in daily calibrations. As for the effect (2), we evaluated the effective depth resolution as ~5cm. To try reducing the effect by minimizing the dead volumes, we tested two different degassing devices (tube-type and box-type membrane) and compared the response time by switching between different standard gases. The box-type degasser showed similar or longer response time than the tube-type degasser (the difference is dependent on the flow direction and mounting angle of the box-type degasser). The contaminated data by the effect (3) typically appeared as asymmetric positive CH_4 anomaly for ~210 s (by up to a few tens of ppb), resulting in data rejection for ~10 cm after each gap. Spatial resolution was estimated to be 5cm.

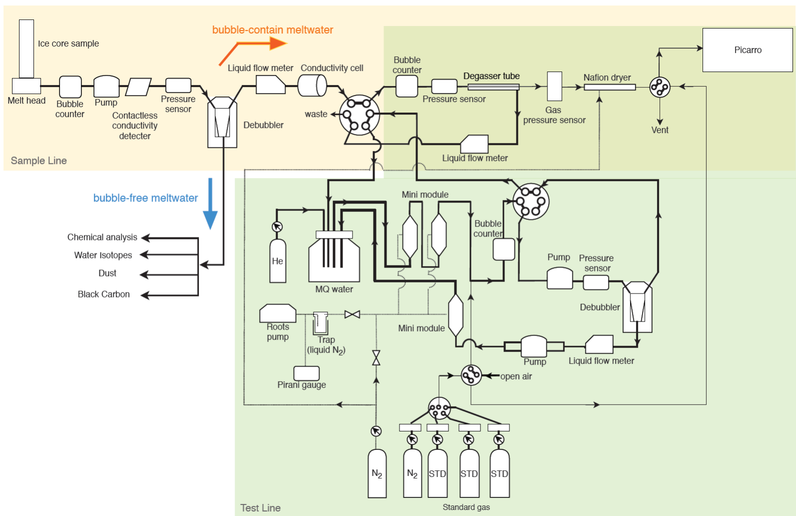

Figure 1. Schematic of methane measurement line of NIPR CFA system.