



The stable isotopic composition of carbon monoxide from Greenland firn samples collected at NEEM

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CO plays an important role in tropospheric chemistry. Precise measurement of its isotopic composition from the past is useful in constraining individual source and sink processes and thus its global cycle. High volume air samples from the NEEM 2009 S2 borehole were measured for mixing ratio, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO on a continuous-flow isotope ratio mass spectrometric (CF-IRMS) system. This system extracts the CO from the air sample (100 mL-200 mL of air required), converts the CO to CO_2 using Schütze reagent and transfers the CO_2 (derived from CO) via an open-split to the IRMS for isotope analysis. A single, automated, measurement is performed in 15 minutes, so multiple measurements can be combined to improve precision. Each firn air sample was measured 10 times.

The top 30 m of the firn show a pronounced signal from the seasonal cycle for the CO mole fractions and the isotope signatures. Below this seasonal feature, CO mole fractions are relatively constant at $\sim 125 \text{ nmol mol}^{-1}$ in the top 60 m of the firn column, followed by a peak up to $150 \text{ nmol mol}^{-1}$ at 69.4 m and a drop to $139 \text{ nmol mol}^{-1}$ at 73.6 m. The peak in CO mole fractions coincides with a peak in $\delta^{18}\text{O}$ of 10.5 ‰ (at 66.8 m), up from $\sim 9.4 \text{ ‰}$ in younger air above that is not affected by seasonal changes. A $\delta^{13}\text{C}$ maximum of -25.4 ‰ appears higher up in the firn than the CO mole fraction and $\delta^{18}\text{O}$ peaks, at a depth of about 60 m, corresponding to younger air. After the maximum (i.e. in the firn column above the peak), $\delta^{13}\text{C}$ values decrease by about 1 ‰

The signals are qualitatively similar to the ones published in Wang et al. (2012) but also show differences that will be investigated by firn modeling.

References:

Wang, Z., Chappellaz, J., Martinerie, P., Park, K., Petrenko, V., Witrant, E., Emmons, L.K., Blunier, T., Breninkmeijer, C.A.M. & Mak, J. E. (2012). The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950: implications for the CO budget. *Atmos. Chem. Phys.* 12, 4365-4377.