Geophysical Research Abstracts
Vol. 17, EGU2015-11406, 2015
EGU General Assembly 2015


# Automated $CO_2$ extraction from air for clumped isotope analysis in the atmo- and biosphere

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The conventional stable isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in atmospheric $CO_2$ are a powerful tool for unraveling the global carbon cycle. In recent years, it has been suggested that the abundance of the very rare isotopologue $^{13}C^{18}O^{16}O$ on m/z 47 might be a promising tracer to complement conventional stable isotope analysis of atmospheric $CO_2$ [Affek and Eiler, 2006; Affek et al. 2007; Eiler and Schauble, 2004; Yeung et al., 2009]. Here we present an automated analytical system that is designed for clumped isotope analysis of atmo- and biospheric $CO_2$.

The carbon dioxide gas is quantitatively extracted from about 1.5L of air (ATP). The automated stainless steel extraction and purification line consists of three main components: (i) a drying unit (a magnesium perchlorate unit and a cryogenic water trap), (ii) two $CO_2$ traps cooled with liquid nitrogen [Werner et al., 2001] and (iii) a GC column packed with Porapak Q that can be cooled with liquid nitrogen to -30ºC during purification and heated up to 230ºC in-between two extraction runs. After $CO_2$ extraction and purification, the $CO_2$ is automatically transferred to the mass spectrometer. Mass spectrometric analysis of the $^{13}C^{18}O^{16}O$ abundance is carried out in dual inlet mode on a MAT 253 mass spectrometer. Each analysis generally consists of 80 change-over-cycles. Three additional Faraday cups were added to the mass spectrometer for simultaneous analysis of the mass-to-charge ratios 44, 45, 46, 47, 48 and 49. The reproducibility for $\delta^{13}C$, $\delta^{18}O$ and $\Delta_{47}$ for repeated $CO_2$ extractions from air is in the range of 0.11‰ (SD), 0.18‰ (SD) and 0.02 (SD)‰ respectively.

This automated $CO_2$ extraction and purification system will be used to analyse the clumped isotopic signature in atmospheric $CO_2$ (tall tower, Cabauw, Netherlands) and to study the clumped isotopic fractionation during photosynthesis (leaf chamber experiments) and soil respiration.

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