Geophysical Research Abstracts
Vol. 14, EGU2012-2366, 2012
EGU General Assembly 2012

Post pyrolysis trapping of molecular hydrogen improves precision for δD(CH4) analysis

M. Bock, J. Schmitt, R. Schneider, and H. Fischer

Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland (bock@climate.unibe.ch)

Methane (CH4) is the third most important greenhouse gas after water vapour and carbon dioxide (CO_2). Since the industrial revolution the mixing ratio of CH4 in the atmosphere rose to $\sim$1800 ppb, a value never reached within the last 800 000 years. This CH4 increase can only be assessed compared to its natural changes in the past. Firn air and air enclosures in polar ice cores represent the only direct paleoatmospheric archive. The latter show that atmospheric CH4 concentrations changed in concert with northern hemisphere temperature during both glacial/interglacial transitions as well as rapid climate changes (Dansgaard-Oeschger events). Since the different sources of atmospheric methane exhibit distinct carbon and hydrogen isotopic composition (δ13CH4 and δD(CH4)) reconstructions of these parameters on ice cores allow to constrain individual CH4 source/sink changes. δD(CH4) also reflects water cycle changes as hydrogen of precipitation is traced into methane produced from wetland/thermokarst/permafrost systems (Bock et al. 2010, Science).

Here we present an updated high precision on line gas chromatography pyrolysis isotope ratio monitoring mass spectrometry technique (GC/P/irmMS) for analysis of δD(CH4) extracted from ice cores. It is based on earlier developments (Bock et al. 2010, RCM) and is improved concerning sample size and precision. The main achievement is post pyrolysis trapping (PPT) of molecular hydrogen after the high temperature conversion of methane leading to a better signal to noise ratio. Air from only 350 g of ice with CH4 concentrations as low as 350 ppb can now be measured with a precision of $\sim$2‰Ṡuch ice samples contain only approximately 30 mL of air and less than 1 nmol CH4.

The new method was applied on ice samples from the EDML and EDC ice cores (European Project for Ice Coring in Antarctica, Dronning Maud Land, Dome Concordia). We present the first δD(CH4) records covering the penultimate termination and interglacial from EDML and for MIS 11 (marine isotope stage) as recorded in the EDC core.

References:

Bock, M.; Schmitt, J.; Möller, L.; Spahni, R.; Blunier, T. & Fischer, H. (2010), 'Hydrogen Isotopes Preclude Marine Hydrate CH4 Emissions at the Onset of Dansgaard-Oeschger Events', Science 328(5986), 1686—1689.

Bock, M.; Schmitt, J.; Behrens, M.; Möller, L.; Schneider, R.; Sapart, C. & Fischer, H. (2010), 'A gas chromatography/pyrolysis/isotope ratio mass spectrometry system for high-precision δD measurements of atmospheric methane extracted from ice cores', Rapid Communications in Mass Spectrometry 24(5), 621—633.