Geophysical Research Abstracts
Vol. 16, EGU2014-8218, 2014
EGU General Assembly 2014

Atmospheric methane isotope records during MIS 4

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The long-term $\delta^{13}CH_4$record has led to a new paradigm in our thinking of the biogeochemistry of atmospheric CH_4 (Möller et al. 2013). Throughout the last glacial period, abrupt D/O CH_4changes appear to be decoupled from $\delta^{13}CH_4$, while for δD_{CH4} we are still missing the big picture. The lack of a clear long-term relationship between loading changes and the isotopic composition of atmospheric CH_4suggests multiple sources/sinks were responsible for the observed changes and/or that the characteristic isotope value for some of these sources may have changed over time.

During the early part of MIS 4, we observed a $\sim$4‰ increase in $\delta^{13}CH_4$during a period when CH_4changes were less than 50 ppb. We measured 12 ice core samples from the NEEM core for δD_{CH4} covering DO 8 and the MIS 5-4 transition. These new δD_{CH4} data compliment previously published δD_{CH4} data from EDML covering the same period (Möller et al. 2013). Replicate analyses of NEEM ice from DO 8 agreed with previously measured samples from NGRIP (Bock et al., 2010). External precision of the analyses based on replicate air standards run throughout each analytical day were $\pm$1.8‰These data were overlain on previously measured $\delta^{13}CH_4$data from the Vostok and EDML ice cores from the same periods. The $\delta^{13}CH_4$data for the MIS4 start at $\sim$ -48‰ around 75ka and increase to -44‰ at 65ka and then decrease to -46‰ by 59ka. In contrast, NEEM δD_{CH4} values start at -90‰ at 70ka and decrease to -97‰ at 64ka before increasing to -92‰ by 59ka. These two records appear to be roughly in phase with one another but opposite in the sign of their changes. Comparison between NEEM and EDML δD_{CH4} data for MIS4 suggest the interpolar δD_{CH4} difference increases somewhat during the $\delta^{13}CH_4$transition.

We plan to discuss these records in terms of constraints on the biogeochemistry of atmospheric methane during MIS 4.

Bock, M., J. Schmitt, L. Möller, R. Spahni, T. Blunier and H. Fischer (2010). "Hydrogen Isotopes Preclude Marine Hydrate CH4 Emissions at the Onset of Dansgaard-Oeschger Events." Science **328**(5986): 1686-1689, 10.1126/science.1187651.

Möller, L., T. Sowers, M. Bock, R. Spahni, M. Behrens, J. Schmitt, H. Miller and H. Fischer (2013). "Independent variations of CH_4 emissions and isotopic composition over the past 160,000 years." Nature Geoscience10.1038/ngeo1922.