Kinetic isotope effect in the atmospheric reaction of the methane clumped isotopologue $^{13}CH_3D$ with OH and Cl

L. M. T. JOELSSON[1], R. FORECAST[1], S. ONO[2] AND M. S. JOHNSON[1*]

[1]Copenhagen Center for Atmospheric Research, CCAR, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
[2]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
[*]Corresponding author msj@kiku.dk

Methane, as the long lived greenhouse gas with the second largest radiative forcing [1], has a significant impact on Earth's climate. Atmospheric methane abundance has undergone a critical growth from pre-industrial levels of 400-700 ppb to above 1750 ppb around year 2000, where the growth seemed to level out [1]. The recent trend, however, shows renewed growth [2]. The causes for these changes are not well known. Methane has an array of natural and anthropogenic sources. The study of clumped isotopes has proven useful for determining sources of atmospheric gases, since the formation temperature give each source contains a characteristic distribution of stable isotopes. Removal processes such as oxidation often prefer one isotopologue over another and thus shift the isotopic composition of atmospheric samples relative to the source. By characterizing the kinetic isotope effects of the sink reactions, the composition of the source can be determined.

Oxidation of methane by OH and Cl was studied experimentally in the photochemical reactor at Copenhagen Center for Atmospheric Research [5]. OH was formed from photolysis of ozone in the UV region and subsequent reaction with H_2O. Cl_2 was photolysed to obtain Cl radicals. A synthesised sample of pure $^{13}CH_3D$ was used along with natural abundance CH_4. Under the course of reaction several infrared spectra were recorded with a Bruker IFS 66v/s Fourier Transform Infrared spectrometer. The spectra were analysed using the non-linear least squares algorithm MALT [6].The kinetic isotope effect α was obtain from the data points by linear regression as:

$$\alpha=\log([^{13}CH_3D]_{t=0}/[^{13}CH_3D]_t)/\log([^{12}CH_4]_{t=0}/[^{12}CH_4]_t)$$

We present the first results of this study.

[1] Solomon *et al*, (2007) Fourth Assessment Report of the IPCC. [2] NOAA Earth System Research Laboratory, http://www.esrl.noaa.gov/gmd/obop/mlo/ 2013-04-12 [4] Nilsson *et al*. (2009), *Atmos. Enviro*. **43** 3029–3033. [5] Griffith (1996), *Appl. Spectrosc*. **50** 59-70

Response of the biological pump to elevated ocean temperatures during the Eocene

E.H. JOHN*[1], P.N. PEARSON[1], B. WADE[2], H. K. COXALL[3], G.L. FOSTER[4], J. WILSON[1] AND A. RIDGWELL[5]

[1]School of Earth and Ocean Sciences, Cardiff University, CF10 3AT, johneh@cf.ac.uk (* presenting author)
[2]Earth Sciences, University College London, WC1E 6BT
[3]Department of Geological Sciences. Stockholm University, Svante Arrhenius väg 8, SE-106 91 Stockholm, Sweden
[4]Ocean and Earth Science, National Oceanography Centre Southampton, SO14 3ZH
[5]School of Geographical Sciences, University of Bristol, BS8 1SS.

The sensitivity of biological processes to changes in temperature is described in terms of Q_{10}, the fractional increase in metabolic rate per 10°C increase in temperature [1]. This value is greater in heterotrophs than autotrophs (e.g. [2,3]). Consequently, faster bacterial respiration rates in a warmer ocean may result in more efficient remineralisation of organic matter at shallower sinking depths with major implications for carbon and nutrient cycling. We find support for this in a series of reconstructed carbon isotope depth profiles based on well-preserved planktonic foraminifera assemblages from Tanzania and Mexico from the warm Eocene epoch. Our results suggest relatively sharp $\delta^{13}C$ gradients in the upper water column which supports hypotheses that invoke high metabolic rates in a warm Eocene ocean leading to more efficient recycling of organic matter and reduced burial rates of organic carbon [4]. We examined these ideas using a GENIE model that incorporates temperature sensitivities of primary producers and respiring bacteria, i.e. different Q_{10} values.

[1] Arrhenius (1889) *Zeit. für Physik. Chem.* **4**, 226-248; [2] López-Urrutia *et al*. (2006) *Proc. Nat. Acad. Sci. USA*. **103**, 8739–8744; [3] Regaudie-de-Gioux & Duarte (2012) *Glob. Biogeochem. Cy*. 26, GB1015; [4] Olivarez Lyle & Lyle (2006) *Paleoceanography* 21, PA2007.

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.10