Concentration and carbon stable isotope patterns of methane and DIC in deep peatlands – Implications for the microbial methanogenic pathways and gas transport

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Abstract

This study reports the results of a field study from October 1999 to August 2001 at the Etang de la Gruère (EGr) Bog in the Swiss Jura Mountains. Pore water samples were obtained in situ using diffusion chambers ("peepers") down to a depth of almost 6 m. Methane concentration of up to ca. 0.5 mM in the upper catotelm are comparable to those reported from shallow peat at other locations. Values continue to increase to almost 2.4 mM in the deep layers. The DIC concentration also generally increases with depth from ca. 1 mM in 0.5 m depth to up to 12 mM in 5 m depth. While DIC became less depleted in ^{13}C with depth (ca. -22 ‰ vs. VPDB in the upper to ca. +9 ‰ in the lower catotelm), δ^{13}C values for pore water methane at EGr showed no straight trend with depth. Methane was isotopically light with $\delta^{13}C\text{-}CH_4$ values ranging from ca. -69 to -58 ‰ vs. the VPDB standard. The results indicate that CO_2-reduction represents a “background” microbial process, while the intensity of acetate splitting is much more variable depending mainly on temperature and the availability of acetate as metabolic substrate.

Significant seasonal variations can be inferred from concentration and isotope data for pore water methane in particular. These variations can be explained by the seasonal and depth-related change of the methane producing pathways: CO_2 reduction (lowest $\delta^{13}C\text{-}CH_4$ and high fractionation between CH_4 and CO_2) versus acetate splitting (higher $\delta^{13}C\text{-}CH_4$ and moderate $CH_4\text{-}CO_2$ fractionation). Transport processes such as pore water advection, molecular diffusion, and ebullition have a major impact on the concentration of the chemical species in depth/time space.

A numerical model adapted to the observations made at EGr indicates that gas transport by bubble formation is by far (maybe over 70 times) more efficient than diffusive transport. The discrepancies between model and field results underline the importance of the seasonality of labile organic precursor availability and over-saturation effects.

Kinetic Effects on Calcium Isotope (δ^{44}Ca) Fractionation in Calcium carbonate

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The calcium isotope ratios (δ^{44}Ca) of *Orbulina universa* and of inorganically precipitated aragonite are positively correlated to temperature. The slopes of 0.019 and 0.015 ‰ $°C^{-1}$ are a factor of 13 and 16 times smaller than the previously determined temperature dependence of 0.24 ‰ $°C^{-1}$ measured on *Globigerinoides sacculifer* (Nägler et al., 2000). The observed δ^{44}Ca fractionation is positively correlated to temperature. This fractionation is opposite to the oxygen isotopic fractionation (δ^{18}O) which is inversely correlated to temperature in calcium carbonate ($CaCO_3$). This difference in sign is explained by a model that takes into account that Ca^{2+} ions, forming ionic bonds, are affected by kinetic fractionation only whereas covalently bound atoms like oxygen are also affected by equilibrium fractionation. From thermodynamic considerations it can be shown that the slope of the enrichment factor $\alpha(T)$ is mass dependent. However, the calculated mass for *O. universa* and the inorganic precipitates is about 640 amu (atomic mass units) which is not compatible with the expected ion mass for ^{40}Ca and ^{44}Ca. To reconcile this discrepancy we propose that Ca diffusion and Ca isotope fractionation at liquid/solid transitions involves the transport of Ca^{2+}-aquocomplexes ($Ca[(H_2O)_6]_n^{2+}$) rather than pure Ca^{2+} ion diffusion. From our measurements we calculate that such a Ca^{2+}-aquocomplex correlates to a hydration number of up to 33 water molecules ($Ca[(H_2O)_6]_{4-6}^{2+}$) although alternative complexation with other anions cannot be ruled out. The strong temperature dependence of δ^{44}Ca in *G. sacculifer* but weak temperature dependence in *O. universa* suggests considerable differences in their calcification mechanisms.

References

Nägler T., Eisenhauer A., Müller A., Hemleben C., and Kramers J. (2000) The δ^{44}Ca-temperature calibration on fossil and cultured Globigerinoides sacculifer: New tool for reconstruction of past sea surface temperatures. *Geochemistry, Geophysics, Geosystems* 1(2000GC000091)