

UV light induces methane emission from plant biomass: Mechanism and isotope studies

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Methane is the second most important greenhouse gas (GHG) in the atmosphere, which has increased in the last century mainly due to human activity. Recent findings have demonstrated that plants can be a source of methane. New experiments show that dry and fresh leafs and other plant matter, as well as several structural plant components, emit methane upon irradiation with UV light and heating. We have determined the carbon and hydrogen isotopic composition of the produced methane in an experimental setup where plant matter is irradiated with UV light in a quartz reactor. CH₄ concentrations, emission rates and isotopic compositions are determined by measurements using an optical absorption technique (cavity ring-down spectroscopy), gas chromatography and continuous flow isotope ratio mass spectrometry. We will present the source isotope signatures of the methane emitted from a range of natural plant materials, as well as a preliminary study on the possible reaction pathway involved in the formation of aerobic methane. If this source from plants is indeed significant, this has to be included in the global isotope budget.

Another important finding is the role of water in determining the δD values of the methane released; we will show how this relation can be quantified. Finally a consideration on a global scale will be provided.

Li isotopes in foraminifera: A new proxy for past ocean dissolved inorganic carbon?

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Past ocean pH and pCO₂ are critical parameters for establishing relationships between Earth climate and carbon cycle. For the Miocene-Pleistocene period, two main proxies have been used: carbon isotopes of di-unsaturated alkenones extracted from sea cores, and boron isotope signatures of marine carbonates [1, 2]. Both techniques lead to self-consistent palaeoceanic pH or pCO₂ estimates, but are associated with large uncertainties. Moreover, the paleovariations calculated from boron isotope measurements are a matter of debate. Additional proxies are therefore needed.

Based on an *in situ* analytical technique recently developed [3], we analysed a series of foraminifera - *Amphistegina* - cultured under various conditions (in pH, T and Dissolved Inorganic Carbon). We show that the lithium isotope signature of the foraminifera correlates with the DIC ($r^2 = 0.93$). Conversely, there is no dependency of Li isotope signature on pH or T. A simple model of biomineralization in which growth rate is a key parameter can fit the whole dataset, including published values for other foraminifera species [4, 5]. This strongly suggests that the DIC- $\delta^7\text{Li}$ correlation highlighted by the cultured *Amphistegina* can also be applied to other species.

These results, combined with the published oceanic Li and B isotope paleovariations [2, 4, 5], allow us to estimate the ocean DIC and pCO₂ evolution for the past 18Ma. The similarity with the pCO₂ curve given by carbon isotopes measured in di-unsaturated alkenones is striking. This supports the use of Li isotopes as a new proxy and adds support to the existing data. It also suggests, in contrast with the common view, a less significant role of river input on the variation of the ocean Li isotope composition, at least for the period considered.

[1] Pagani *et al.* (2005) *Science* **309**, 600-603. [2] Pearson & Palmer (2000) *Nature* **406**, 695-699. [3] Vigier *et al.* (2007) *G-cubed* **8**, Q01003 [4] Hall *et al.* (2005) *Mar. Geology* **217**, 255-265 [5] Hathorne & James (2006) *EPSL* **246**, 393-406.