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## SUMMARY

Diagenetic pathways, including organic matter (OM) oxidation and fermentation to methane (CH<sub>4</sub>) as well as [CH₄] (mM)  $[CO_2] (mM)$ Water lethanotrophy + OM oxidation Methanogenesis  $R_{net}$  (10<sup>-13</sup> mol cm<sup>-3</sup> s<sup>-1</sup>)  $R_{net}$  (10<sup>-13</sup> mol cm<sup>-3</sup> s<sup>-1</sup>) Figure 3: Measured (symbols) and modelled (blue line) concentration profiles the carbon isotopic signature ( $\delta^{13}C$ ) of end-products: Sediment diagenetic pathways nfluence as well as net reaction rate ( $\mathbf{R}_{net}$ ) profiles (red line) of CH<sub>4</sub> and CO<sub>2</sub>. **forganic matter** (OM) **oxidation**,  $\{\delta^{13}C \text{ of } CO_2 \& CH_4\}$  $\alpha_{\rm Hydro} = 1.075^{[1]}$  $\alpha_{AOM} = 1.005^{[4]}$ \ methanogenesis & methanotrophy ( and varies between and varies between In particular, the  $\delta^{13}C$  of CH<sub>4</sub> is largely affected as a result of the contrasted isotopic separation factor ( $\epsilon$ ) of **10**<sup>[4]</sup> and **1.031**<sup>[4]</sup> **1.050**<sup>[2]</sup> and **1.095**<sup>[2]</sup> Bacterial Methane Formation and Consumption ε<sub>Acet</sub> ~ -21‰ c = 90 / 80 / $\varepsilon_{c}=40$  $CH_3COOH \rightarrow CH_4 + CO_2$ **ε<sub>Hydro</sub> ~ -75‰** CH<sub>4</sub>, CO<sub>2</sub> (from Conrad et al., 2014) The precise quantification of diagenetic pathways is diffi-\_\_\_\_\_  $\delta^{13}$ C-methane (‰) δ<sup>13</sup>C modelling tool to quantify **Figure 1:** Combination plot of  $\delta^{13}$ C of CH<sub>4</sub> and CO<sub>2</sub> (from Whiticar, 1999) Scen 70% 30% \_\_\_\_\_ 52°  $\frown$ L. Tantaré  $\sqrt{}$ 0 500 m \_. Tantaré ★ 🦉 Ottawa USA 🖂 🕷 Montréa

methanotrophy, are processes that modify the carbon isotopic composition ( $\delta^{13}$ C) of sediment CH<sub>4</sub> and CO<sub>2</sub>. To unravel diagenetic pathways in the sediments of an oligotrophic lake, we determined high-resolution vertical profiles of dissolved CH<sub>4</sub> and CO<sub>2</sub>, as well as their  $\delta^{13}$ C. The concentration profiles of CH<sub>4</sub> and CO<sub>2</sub> were modeled, using a one-dimensional transport-reaction equation, to constrain the depth-intervals where these species are produced or consumed in the first 25 cm of the sedimentary column, and to estimate their net production/consumption rates ( $\mathbf{R}_{net}$ ) in each of the zones (Fig. 3). The comparison of CH<sub>4</sub> and CO<sub>2</sub>  $\mathbf{R}_{net}$  enables us to constrain, in each zone, rates for each diagenetic pathway. Then, fitting the measured  $\delta^{13}$ C profiles with those simulated by a steady-state transport-reaction model allows us to clarify the relative contribution of acetoclasty and hydrogenotrophy (Figs. 4-5). The model takes into account the constrained rates and established isotope fractionation factors for all the above-mentioned processes. We conclude, after a sensitivity analysis on fractionation factors and several possible scenarios, that nearly 100% of CH<sub>4</sub> was produced by hydrogenotrophy following the non-fractionating fermentation of OM, represented by  $C_6H_{12}O_2$ , to  $CO_2$  and  $H_2$ . INTRODUCTION both methanogenic pathways: Acetoclasty **Hydrogenotrophy**  $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ cult given the complexity of early diagenesis. We often obtain only a rough idea of the methanogenic pathway as the relative contribution of diagenetic pathways. MATERIALS & METHODS Sediment porewater of Lake Tantaré (Fig. 2A) were sampled by in situ dialysis (Fig. 2B) in October 2014. • We measured  $CH_4$  and  $CO_2$  concentrations. • The  $\delta^{13}$ C of CH<sub>4</sub> and CO<sub>2</sub> was measured using a gaschromatograph coupled to a

shown on Fig. 1. In order to fill this gap, we present here a





combustion interface and to an isotop ratio mass spectrometer (GC-C-IRMS).



**B** - picture of a dialyser.

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## CARBON ISOTOPE SIGNATURE OF CH4 AND CO2 AS A TOOL AGENETIC PATHWAYS IN LAKE SEDIMENTS TO UNRAVEL DI

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#### RESULTS & DIS **JSSION**





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Reactions	Equation	Reaction rate
OM oxidation	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	Romx
Methanotrophy	$CH_4 + Oxidant \rightarrow CO_2 + Reductant$	R <sup>Mt</sup>
OM fermentation	$C_xH_yO_z + ?H_2O \rightarrow ?CH_3COOH + ?CO_2 + ?H_2$	Romf
Acetoclasty	$CH_3COOH \rightarrow CH_4 + CO_2$	RAcet
Hydrogenotrophy	$\mathbf{CO}_2 + \mathbf{4H}_2 \rightarrow \mathbf{CH}_4 + \mathbf{2H}_2\mathbf{O}$	R <sup>Hydro</sup>

**Table 1:** Reactions during early diagenesis.

From Table 1, we can write:

 $\mathbf{R}^{\mathrm{CH}_{4}} = \mathbf{R}^{\mathrm{Acet}} + \mathbf{R}^{\mathrm{Hydro}} - \mathbf{R}^{\mathrm{N}}$ It and  $R_{not}^{CO_2} = R^{Acet} - R^{Hydro} + R^{Mt} + R^{OMx} + R^{O}$ 

In the zone of methanogenesis (dark blue on Fig. 3), R = 109 and 51 (in fmol cm<sup>-3</sup> s<sup>-1</sup>) indicate that, at least, some CH<sub>4</sub> is produced by hydrogenotrophy. Assuming that R<sup>OMx</sup> and R<sup>Mt</sup> are negligible in this zone, there are several possible scenarios varying between methanogenesis being :

#### 100% hydrogenotrophic:

 $R^{Hydro} = 109 R^{Acet} = 0 R^{OMf} =$ 

~30% hydrogenotrophic:

 $R^{Hydro} = 29$   $R^{Acet} = 80$   $R^{OMf} = 0$ 

Using a modified diagenesis equation (see section MODELLING), and **blue** lines are calcu-  $\delta^{13}$ C profiles of CH<sub>4</sub> and CO<sub>2</sub> were simulated, and parameters lated with default and were calibrated to fit the measured profiles. Four scenarios were tested values, respectively. tested (Fig. 4) considering probable values for isotope fractionation factors and rates of diagenetic pathways comprised within a range of possible values. The best fit is Scenario 1 where methanogenesis is 100% hydrogenotrophic (Fig. 5).

> In this scenario, the simplistic model molecule CH<sub>2</sub>O is no longer suitable to represent OM fermenting into CH<sub>4</sub>. Based on our approach, the new model molecule and the net reaction for methanogenesis are given by:

## $C_6H_{12}O_2 + 2H_2O \rightarrow 4CH_4 + 2CO_2$



**<u>Figure 5</u>**: Measured (symbols) and modelled (blue line)  $\delta^{13}$ C profiles of CH<sub>4</sub> and  $CO_2$  as well as estimated rates for each reaction in each zone (in fmol cm<sup>-3</sup> s<sup>-1</sup>)

# MODELLING CONCENTRATION AND $\delta^{13}$ C PROFILES

Inverse modelling of porewater profiles (Berg et al., 1998):

Assuming steady state conditions and neglecting advection and bioturbation, the diagenetic equation is:



Eq. 1 is resolved via a numerical procedure to: Constrain the depth intervals where solutes are produced or consumed • Obtain the **net reaction rate (R**<sub>net</sub>) in each zone (**red line** in Fig. 3)

Similar to Eq. 1, the diagenesis equation for the solute containing the heavy isotop is:

 $\alpha = \frac{1}{1}$ 

and the fractionation factor  $\alpha$  is given by:

Combining Eq. 2 and 3 we obtain:

 $\frac{\partial \mathbf{x}}{\partial \mathbf{x}} \left( \frac{\boldsymbol{\varphi} \mathbf{D}_{\mathbf{S}}}{\partial \mathbf{x}} \right)$ Eq. 4 is resolved via a MATLAB<sup>®</sup> function to obtain a modelled  $\delta^{13}C$ profile (blue & red lines in Figs. 4-5). Inverse modelling Literature

## CONCLUSIONS

The application of a steady-state reactive-transport model following the inverse modelling of porewater concentration profiles of  $CH_4$  and  $CO_2$  (Fig. 3) allowed us to:

**9C**\*/

- fit the simulated profiles with those measured by calibrating isotope fractionation factors and estimated rates for each diagenetic pathway (Figs. 4-5).
- quantify the contribution of each diagenetic pathway including methanogenesis (hydrogenotrophy and acetoclasty), methanotrophy, as well as OM oxidation and fermentation (Fig. 5).

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CENTRE

the porewater concentration,  $C_w$  is the bottom water concentration, x is the depth,  $\phi$  is the porosity,  $D_s$  is the diffusivity, and  $R_{net}$  is the bio-irrigation coefficient.

Equation 1 Diagenesis equation for a solute

### <u>Modelling $\delta^{13}$ C profiles of CH<sub>4</sub> and CO<sub>2</sub> (from Alperin et al., 1988):</u>

$$\frac{\partial}{\partial x} \left( \varphi D_s \frac{\partial C^*}{\partial x} \right) + R^* = 0$$
 where C<sup>\*</sup> and R<sup>\*</sup> are the porewater concentration and the net reaction rate of the solute containing the heavy isotop.  
Equation 2 Diagenesis equation for the « heavy solute »

 $\mathbf{R}/\mathbf{C}_{\mathbf{r}}$  where the index "**r**" is for reacting species

 $\mathbf{K}^{*}/\mathbf{C}_{\mathbf{r}}$  Equation 3 Expression of the fractionation factor  $\boldsymbol{\alpha}$ 

uation 4 Model for the estimation of  $\delta^{13}$ C

δ<sup>13</sup>C of reacting species

• simulate the  $\delta^{13}$ C profiles of CH<sub>4</sub> and CO<sub>2</sub> contained in the sediment of Lake Tantaré (Figs. 4-5).

• refine the stoichiometry of OM which ferments into  $CH_4$  and, consequently

• precise the net reaction of methanogenesis :  $C_6H_{12}O_2 + 2H_2O \rightarrow 4CH_4 + 2CO_2$ 





<sup>1]</sup>Conrad, R., Claus, P., Chidthaisong, A., Lu, Y., Fernandez Scavino, A., Liu, Y., Angel, R., Galand, P. E., Casper, P., Guerin, F. & Enrich-Prast, A. (2014) Stable carbon isotope biogeochemistry of propionate and acetate in methanogenic soils and lake sediments. Organic Geochemistry 73, 1-7.

<sup>2]</sup>Whiticar, M. J. (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chemical Geology 161, 291-314.

<sup>[3]</sup>Berg, P., Risgaard-Petersen, N. & Rysgaard, S. (1998) Interpretation of measured concentration profiles in sediment pore water. Limnology and Oceanography 43, 1500-1510. <sup>[4]</sup>Alperin, M. J., Reeburgh, W. S. & Whiticar, M. J. (1988) Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation. Global Biogeochemical Cycles 2(3), 279-288.