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Interactive comment on "Mineralization of organic matter in boreal lake sediments: Rates, pathways and nature of the fermenting substrates" *by* François Clayer et al.

Anonymous Referee #3

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In this paper, Clayer et al. found the average carbon oxidation state (COS) is negative COS values by modelling solute pore-water profiles. They concluded that carbohydrates do not adequately represent the fermenting OM and that the COS should be included in the formulation of OM fermentation in models. It is an interesting work and the results can guide new biogeochemical model for OM degradation.

However, the manuscript needs substantial improvement of the presentation before it can be recommended for publication. The main issues is the lack of the OM and mobile labile information. There are no data for the deposition/sedimentation rate of OM, the chemical composition of OM (C,H,O,N,S,P,..), d13C distribution of OM et al.

The results of COS from modelling solute pore-water profiles have not been validated. Even in the solute model there are too many fitting parameters and the conclusion is not convincing.

Here are some details:

1. Reactions: Since the reactions the precipitation of siderite (r7) and sulfide oxidation by iron oxides (r8) were taken into account, the pyrite formation by Fe2+ and H2S should be considered,too. The hydrogen H2 in eq.(r8) is usually consumed easily by sulphate reducer bacteria rather than CO2 reduction. The authors used general oxidant instead of O2,Fe(III) and SO4, which could have different oxidation rates, especially for CH4 oxidation (r5).

2. Rate calculation: The reaction rate were calculated by computer code PROFILE. This rates obtained from PROFILE were very rough. It is better to use reaction-transport model to calculate the rate by considering OM deposition and degradation.

3. The bioirrigation term was shown in the equation (2) but the bioirrigation depth and coefficient were not clear. How does the bioirrigation affect COS estimatation was also not clear. General once bioirrigation is strong, bioturbation should be considered, too. The solid phase (OM, iron oxides) in the bioturbation zone is well mixed, which strongly affect OM degradation.

4. I don't understand why the acetoclastic methanogenesis was absent here. Generally acetoclastic methanogenesis dominates in lake sediment and hydrogenotrophic methanogenesis in sea sediment. The two pathways generate different d13C-CH4 and d13-DIC pattern. Diffusion and birrigation will also change this pattern. The authors should prove it.

5. The chemical composition of individual molecules in OM pools can be detected from various state-of-the-art instrumentation including GC-MS, LC-MS/MS, HPLC-MS, NMR, Orbitrap MS, and Fourier transform ion cyclotron resonance (FTICR-MS). By

combining a suite of previously developed thermodynamic theories (Kleerebezem and Van Loosdrecht, 2010; LaRowe and Van Cappellen, 2011), one can calculate COS. If the results are consistent, the paper method is more convincing.

6. d13C-CH4 in Lake Tantaré Basin A (Fig.3) is very negative (-107.0). Is there some explanation?

ref:

Kleerebezem, R., and Van Loosdrecht, M.C.M. (2010). A Generalized Method for Thermodynamic State Analysis of Environmental Systems. Critical Reviews in Environmental Science and Technology 40, 1-54.

Larowe, D.E., and Van Cappellen, P. (2011). Degradation of natural organic matter: A thermodynamic analysis. Geochimica Et Cosmochimica Acta 75, 2030-2042.

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