

*Mariusz-Orion JEDRYSEK*¹

THE ORIGIN OF C-ISOTOPE SIGNATURE IN CARBONATES
FROM FRESHWATER LAKE SEDIMENTS

Abstract: It is demonstrated that microbial oxidation of organic compounds (including methane), in freshwater sediments, may result in precipitation of carbonates, which may become an important geochemical archive of paleoenvironmental variations. Most probably low $\delta^{13}\text{C}$ value in calcite in eutrophic systems results from an advanced oxidation of organic compounds in turbulent or/and sulphate-rich conditions. Likewise, high $\delta^{13}\text{C}$ value in calcite from organic-rich sediments may evidence low red-ox potential of the freshwater system. More advanced studies might help to calibrate a new tool for paleoenvironmental reconstructions.

Key words: sediments, calcite, organic compounds, sulphate, stable isotopes, lake

INTRODUCTION

Autochthonous components of freshwater sediments (mostly organic matter, carbonates and clay minerals) are potentially important geochemical archive of paleoenvironmental variations. However, sources and processes, which control chemistry of lakes, can not be distinguished by chemical analyses alone, and must be coupled with stable isotopic data. Due to dissimilatory reduction of sulphate dissolved in freshwater, it is a major substrate for microbial sequestration of organic compounds (e.g. Böttcher and Thamdrup 2001) including methane (Hornibrook et al.2000). In this process, autochthonous calcite (sometimes other carbonates) may precipitate, and isotope record in that calcite may provide important environmental information (Jędrysek 1995, 1999). Nevertheless, the knowledge concerning origin and isotope evolution, of organic matter and calcite in lakes, is surprisingly poor and arise many questions. To answer these questions, concentration and stable isotope measurements in dissolved sulphate (water column), bubble methane and calcite (freshwater sediments) have been carried out in 24 lakes, 2 ponds and 4 rivers in Poland (Fig. 1, 2).

MATERIALS AND METHODS

The main criteria in selection of lakes for sampling was to obtain high variety of samples due to trophic state, anthropogenic impact, depth and altitude. Details on precise locality and limnologic characteristics of lakes sampled and experimental procedures is described elsewhere (Jędrysek 1997, Jedrysek et al. 2002).

¹ *Lab.Isotope Geol&Geoec., Dept. App. Geol.&Geochem., Univ., Wrocław, Cybulskiego 30, 50-205 Wrocław, POLAND, www.ing.uni.wroc.pl/~isotope morion@ing.uni.wroc.pl*

RESULTS AND DISCUSSION

For all the lakes studied, two general sources of sulphate can be assumed: (1) anthropogenic and (2) biogenic. However, the lakewater analysed widely ranges in the $\delta^{18}\text{O}(\text{SO}_4^{2-})$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})$ values, as compared to atmospheric precipitation and biogenic sources (Jędrysek et al. 2002) and often show higher sulphur, or sulphur and oxygen isotope signatures, respectively (Fig. 1).

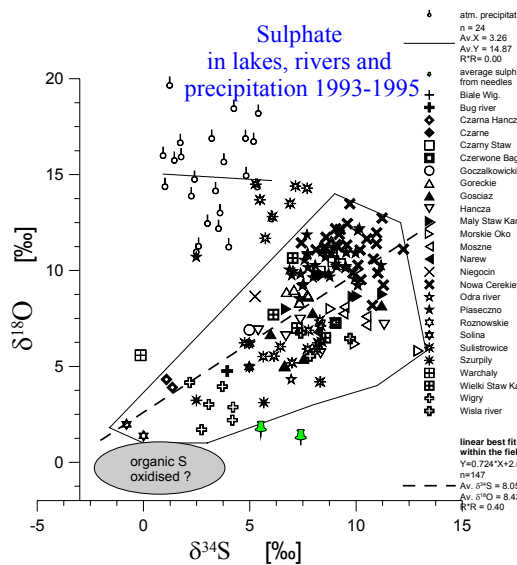


Fig. 1 Sulphur and oxygen isotope ratios in sulphate dissolved in freshwater systems.

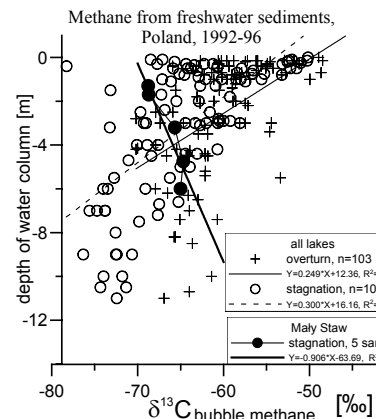


Fig. 2 $\delta^{13}\text{C}(\text{CH}_4)$ value and depth of the water column in selected lakes in Poland.

It can be postulated that the isotope signature of sulphate dissolved in lakewater can evolve due to microbial reduction and eutrophic lakes have high $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ values compared to clean oligotrophic or mesotrophic lakes. Dissimilatory reduction of sulphate requires substrates to be oxidised and methanogenic bacteria are usually outcompeted for organic substrates (methane precursors) by sulphate-reducing bacteria. Likewise, methane can be also oxidised (e.g. Lojen S. et al. 1999). Organic compounds are ^{13}C -depleted and moreover oxidation involve isotope effect (^{12}C bonding are broken preferentially). Consequently, ^{13}C -depleted DIC (dissolved inorganic carbon) is formed. This process is of variable importance and magnitude at individual environments, therefore, shallow-water methane, and that formed during seasonal overturn, are enriched in ^{13}C isotope as compared to these collected at depth or during stagnation (Fig. 2). The lower $\delta^{13}\text{C}$ values at depths can be controlled by variations in temperature and in increasing role of $\text{CO}_2\text{-H}_2$ methanogenic pathway due to deficit of acetate (Jędrysek 1999). On the other hand, the limiting factor for oxidation at depths is deficit of sulphate. However, during seasonal overturn, especially at a greater depth below the point of light penetration, sulphate reducers consume

(oxidise) most of the hydrogen. This became the limiting factor for CO₂ pathway of methanogenesis – thus the δ¹³C value increases due to the relative increase in the importance of the acetate pathway.

The importance of red-ox processes in Mały Staw Lake is supported by C-isotope ratios in bubble methane which shows the opposite trend (Fig. 2). Negative correlation observed between δ¹³C(CH₄) value and depth of the water column may be the result of the strong contamination by the SO₄²⁻, exceeding the biological buffering abilities of lake Mały Staw. However, it can be postulated that frequent turbulences of the water, which results in homogenisation of lakewater (both with respect chemical and physical parameters) were responsible for the opposite trend in δ¹³C value of methane resulted from oxidation.

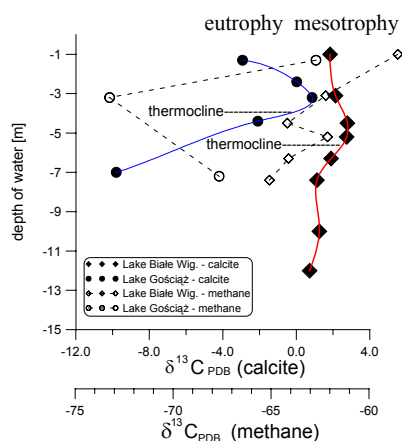


Fig. 3. δ¹³C value and depth of the water column in methane and calcite form selected lakes in Poland.

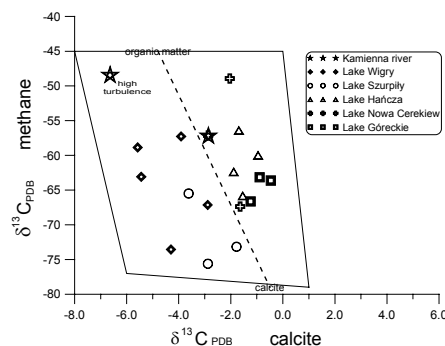


Fig. 4. δ¹³C value of calcite and methane form selected lakes in Poland.

In freshwater lakes, calcite can precipitate from the water column (δ¹³C value is controlled dominantly by activity of phytoplankton) or from porewater in the sediments. In the second case, it can be expected that oxidation of methane and methane precursors (even more efficient than oxidation of methane) supersaturates, the porewater in sediments and the water the depth, with bicarbonate. This in turn may result in precipitation of ¹³C-depleted calcite (or other carbonates). In fact, mesotrophic lakes show higher δ¹³C values in methane have also higher δ¹³C values in calcite found in that methanogenic sediments (Fig. 3). This is probably due to: (i) lower methanogenic activity – thus acetate fermentation is relatively high as compared to CO₂ pathway, and (ii) advanced dissimilatory microbial reduction of methane precursors – the residual organic compounds become ¹³C-enriched. It is difficult to judge which mechanism is more important. However, highly turbulent environment in the upstream of Kamienna river (Wigierski Nat. Park) show the highest δ¹³C value of methane and lowermost δ¹³C value in calcite. This suggests that nearly entire calcite formed due to oxidation of methane/methane precursors. However, in the eutrophic lakes (Góreckie, Nowa

Cerekiew, Fig. 4) with low red-ox potential, methane oxidation do not occur (but acetate pathway dominates) and the nearly entire calcite forms due to precipitation from the water column.

CONCLUSIONS

1. Sulphate and availability of organic compounds are the most important factors controlling isotope signature of sulphate, methane and carbonates in freshwater systems.

2. Future studies might help to calibrate a new tool to precisely reconstruct environmental variations, especially: (i) trophic state and advance in microbial red-ox processes, (ii) individual biological buffering potential and limnological character (depth, turbulence, seasonal overturn *etc*), (iii) ecological conditions and methanogenic potential (iv) climatic variations.

3. Probably, dark organic-rich layers form at the end of summer stagnations and the light carbonate-rich layers form during seasonal overturns. Occasional formation of winter dark (allochthonous material) layer and spring (oxidation) layers makes number of layers and ¹⁴C-dating not comparable.

ACKNOWLEDGMENTS: This study was supported from the State Committee for Scientific Research grants, University of Wrocław S and W grants, and IAI.

REFERENCES

- BÖTTCHER M.E., THAMDRUP B., 2001: Anaerobic sulfide oxidation and stable isotope fractionation associated with bacterial sulphur disproportionation in the presence of MnO₂. *Geochim.Cosmochim Acta*, 65: 1573-1581.
- HORNIBROOK E.R.C., LONGSTAFFE F.J., FYFE W.S., 2000: Factors influencing stable isotope ratios in CH₄ and CO₂ within subenvironments of freshwater wetlands: Implications for delta-signatures of emissions. *Isot. Envir. Health S* 36: 151-176.
- JĘDRYSEK M.O., 1995: Carbon isotope evidence for diurnal variations in methanogenesis in freshwater lake sediments. *Geochim. Cosmochim. Acta* 59: 557-561.
- JĘDRYSEK M. O., 1997: Spatial and temporal variations in carbon isotope ratio of early-diagenetic methane from freshwater sediments: methanogenic pathways. *Acta Universitatis Wratislaviensis - Prace Geologiczno-Mineralogiczne*, 63: 1-110.
- JĘDRYSEK M.O., 1999: Spatial and temporal patterns in diurnal variations of carbon isotope ratios of early-diagenetic methane from freshwater sediments. *Chem. Geol.* 159: 241-262.
- JĘDRYSEK M.O., KAŁUŻNY A., HOEFS J., 2002: S and O isotope ratios in spruce needles as a tracer of atmospheric pollution. *Jour.Gephysical Research – Atmospheres*, 107(D18): ACH5-1 – ACH5-12.
- LOJEN S., OGRINC N., DOLENEC T., 1999: Decomposition of sedimentary organic matter and methane formation in the recent sediment of Lake Bled (Slovenia). *Chem. Geol.* 159: 223-240.