SULPHATE REDUCTION — METHANE OXIDATION: A POTENTIAL ROLE OF THIS PROCESS IN THE ORIGIN OF C ISOTOPE ENVIRONMENTAL RECORD IN FRESHWATER CARBONATES

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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 palaeoenvironmental variations. Most probably low ^{13}C value in calcite in eutrophic systems results from an advanced oxidation of organic compounds in turbulent or/and sulphate-rich conditions. Likewise, high ^{13}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 palaeoenvironmental reconstructions. Oxidation of methane and organic matter results in significant isotope effects in sulphates dissolved in water. Therefore, to better understand the origin of carbon isotope signal in carbonates, 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.

Dissolved sulphate is a major compound of freshwater systems and sulphur, being an important bioelement, controls many processes in lakes therefore quality of water (e.g. microbial sequestration of organic compounds, inhibitor of methane ebullitive flux). The highest concentration of sulphate has been detected in rivers (85.47 SO_4^{2-} mg/l) and an artificial lake (70.3 SO_4^{2-} mg/l) located in the extremely SO_4^{2-}-polluted region called the "Black Triangle". The lowest concentration of sulphate are found in dystrophic and mountain lakes (from 0.5 to about 3 mg/l SO_4^{2-}). The lowest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values occur in unpolluted lakes in Eastern Poland (–0.94 and 1.38‰, respectively). The highest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values are found in polluted lakes in western Poland and dystrophic lakes (12.95 and 16.15‰, respectively). It is proposed that $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values in lakes represent a good tool to asses and quantify anthropogenic impact by acid precipitation and to monitor variations in the trophic state and redox processes controlled by biodegradation of organic compounds in sediments and water column. In contrast to clean lakes, an increase of the value with increasing depth of the $\delta^{13}C(CH_4)$ water column, in a strongly SO_4^{2-} contaminated lake, is observed. This is probably due to a loss of biological buffering potential of the lake accompanied by an active oxidation of methane precursors.

Key words: freshwater, carbon, oxygen, sulphur, methane, carbonates, sulphates, isotopes, anthropogenic impact.

Abstrakt. W pracy wykazano, że węglany jeziorne powstałe w wyniku mikrobiologicznego utleniania związków organicznych (w tym metanu), przy redukcji jonów siarczanowych, mogą stanowić ważny geochemiczny zapis zmian środowiskowych. Najprawdopodobniej niskie wartości [13]C w kalcycie, w rzekach i jeziorach eutroficznych wynikają z silnego utleniania związków organicznych w warunkach turbulencji i/lub podwyższonych stężeń siarczanu. Podobnie, wysokie wartości [13]C w kalcycie, zawartym w osadach słodkowodnych bogatych w materię organiczną, mogą wskazywać na niski potencjał redox. Na podstawie tego typu badania wydaje się możliwe wykalibrowanie nowego narzędzia do rekonstrukcji palaeośrodowiskowych. Z drugiej strony, utlenianie metanu (związków organicznych) może powodować wzbogacenie rezydualnego jonu siarczanowego w ciężkie izotopy tlenu i siarki. Dlatego, aby lepiej zrozumieć sygnał izotopowy w węglanach jeziornych, wykonano badania stężenia i badania izotopowe siarczanu kolumny wodnej oraz badania metanu i kalcytu w osadach 24 jezior, 2 stawów i 4 rzek w Polsce.

Rozpuszczony jon siarczanowy jest jednym z głównych składników rozpuszczonych w wodach jeziornych, a siarka, jako istotny biopierwiastek, wpływa na procesy zachodzące w jeziorach, w tym na jakość wód (mikrobiologiczny rozkład związków organicznych, inhibitor metanogenezy). Najwyższe stężenie jonu siarczanowego stwierdzono w rzekach (85,47 SO_4^{2-} mg/l) i sztucznym jeziorze (70,3 SO_4^{2-} mg/l) w regionie silnego zanieczyszczenia (tzw. „Czarny Trójkąt") w Polsce

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południowo-zachodniej. Najniższe stężenie siarczanu stwierdzono w jeziorach dystroficznych i oligotroficznych — górskich (od 0,5 do 3 mg/l SO_4^{2-}). Najniższe wartości $\delta^{34}S(SO_4^{2-})$ i $\delta^{18}O(SO_4^{2-})$ występują w niezanieczyszczonych jeziorach wschodniej Polski (–0,94 i 1,38‰). Najwyższe wartości $\delta^{34}S(SO_4^{2-})$ i $\delta^{18}O(SO_4^{2-})$ stwierdzono w Polsce zachodniej i jeziorach dystroficznych (12,95 i 16,15‰). Wykazano, że $\delta^{34}S(SO_4^{2-})$ i $\delta^{18}O(SO_4^{2-})$ jezior mogą być dobrym narzędziem do ilościowej charakterystyki antropopresji (kwaśne opady) oraz do monitorowania zmian trofii i procesów redoks związanych z biodegradacją związków organicznych w osadach i kolumnie wodnej. W przeciwieństwie do czystych jezior, jeziora silnie zanieczyszczone jonem siarczanowym wykazują wzrost wartości $\delta^{13}C(CH_4)$ wraz ze wzrostem głębokości kolumny wodnej. Może to być wskaźnikiem utraty przez jezioro mikrobiologicznej zdolności buforującej.

Słowa kluczowe: woda słodka, węgiel, tlen, siarka, metan, węglany, siarczany, izotopy, antropopresja.

INTRODUCTION

Autochtonous components of freshwater sediments (mostly organic matter, carbonates and clay minerals) are potentially important geochemical archive of palaeoenvironmental 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 including methane (Hornibrook *et al.*, 2000; Böttcher, Thamdrup, 2001). In this process, autochtonous 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. Oxidation of methane and organic matter results in significant isotope effects in sulphates dissolved in water. Therefore, to better understand the origin of carbon isotope signal in carbonates, 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.

Sulphate dissolved in water is one of the most abundant and important chemical compound of freshwater systems and it is the major source of sulphur for biota and a major substrate for microbial sequestration of organic compounds (including organic contaminants, heavy metals) and earlydiagenetic methane. Sources and processes, which control chemistry of lakes, can not be distinguished by chemical analyses alone, and must be coupled with stable isotopic data. Numerous observations show that various origin inputs of sulphate (evaporites, anthropogenic, endogenic, biogenic *etc*) can be traced in river systems (e.g. Trembaczowski, 1990, 1994 a; Trembaczowski, Halas, 1993; Robinson, Bottrell, 1997; Cortecci *et al.*, 2002). However, from isotopic point of view river and lake systems differ significantly (e.g. due to dissimilatory SO_4^{2-} reduction which can change both concentration and isotope signatures of lakewater sulphate). Nevertheless, the knowledge concerning origin and isotope evolution of SO_4^{2-} in lakes is surprisingly poor.

SULPHATE IN LAKES — THE PROBLEM OF CONTAMINATION

Sulphur deposition has been generally the most important acidifying contaminant for the global hydrosphere, pedosphere and biosphere in the last 100–150 years. Anthropogenic SO_4^{2-} contamination has considerably changed most aquatic freshwater environments, especially in the last decades in Europe. Even with the decline of acid rain since the mid-70's (Mylona, 1996; Hovmand, 1999; Jędrysek, 2000), Europe is still one of the world's largest acid rain regions, and the so called "Black Triangle" (the region of SE Germany, NW Czech Republic and SW Poland — Fig. 1) still remains the most heavily contaminated region in Europe (Dore *et al.*, 1999; Jędrysek *et al.*, 2002). The effect of acid rain contamination is strongly enhanced in mountainous regions of the "Black Triangle", (especially Izera Mts. and Karkonosze Mts. which are the western part of Sudety Mts.). Over the last 25 years, the acid rain was dominated by sulphate ions formed from burning of sulphide-rich lignite in the western part of the "Black Triangle". Due to western-dominated wind directions, a large portion of the pollution produced in western Europe in the last two centuries was deposited in the Sudety Mts. region in addition to the "Black Triangle" SO_4^{2-} source. In 1990 the annual average pH in wet precipitation was 3.57, and the lowest noted pH in bulk rain-water was 2.08 in the western region. The lowest noted acid building roof-flow (water flowing down from roofs of buildings) reached 1.56 (Baron, Sobik, 1995; Dore *et al.*, 1999). In the "Black Triangle" area the acid rain $\delta^{18}O(SO_4^{2-})$ values varied from 11.22 to 19.65‰ and $\delta^{34}S(SO_4^{2-})$ values varied form 0.92 to 6.02‰ (Jedrysek, 2000).

A large portion of the contaminant sulphate is deposited in lakes and strongly affects vital (especially microbial) processes. Biospheric uptake of sulphur in gaseous and dissolved form can be readily ascertained if the sulphur isotope composition of the natural and anthropogenic sources differ significantly (Jędrysek *et al.,* 1991; Krouse *et al.,* 1991 b). In general, the stable isotope composition of sulphur compounds of industrial origin contained in the atmosphere, biosphere and hydrosphere may differ from natural analogues

Fig. 1. Locations of lakes, rivers and pond sampled in Poland

Sampling points are described in Jędrysek (1995, 1997 a, b, 1999). For "Black Triangle" definition see Introduction and Jędrysek *et al.* (2002).

List of sampled lakes, ponds and rivers: 1: Antonin Lake, 2: Bełchatów–Słok Lake, 3: Białe Wigierskie Lake, 4: Borki Village, 5: Bug River: 6: Chocianów Lake, 7: Czarna Hańcza River, 8: Czarne Lake, 9: Goczałkowice Lake, 10: Gopło Lake, 11: Gościąż Lake, 12: Gościąż Stream, 13: Góreckie Lake, 14: Hańcza Lake, 15: Kamionka River, 16: Krobielice Stream, 17: Łosice Pond, 18: Łukie Lake, 19: Mały Staw Lake, 20: Mniszek Stream, 21: Moszne Lake, 22: Narew River, 23: Ner River (Dąbie), 24: Niegocin Lake, 25: Niesłysz Lake, 26: Nowa Cerekiew Lake, 27: Nowa Cerekiew Pond, 28: Odra River (Brochów), 29: Odra River (Wrocław), 30: Opoczno Pond, 31: Otmuchów Lake, 32: Otok Lake, 33: Piaseczno Lake, 34: Polesie Lake, 35: Rożnowskie Lake, 36: Skrzynka Lake, 37: Solina Lake, 38: Sulistrowiczki Lake, 39: Szurpiły Lake, 40: Warchały Lake, 41: Warta River (Osjaków), 42: Wądołek Lake, 43: Wigry Lake, 44: Wisła River (Płock), 45: Wisła River (Puławy), 46: Wielki Staw Lake, 47: Morskie Oko Lake, 48: Czarny Staw Lake.

Not all sampling spots are listed in the Table 1[1] as some of them concern methane sampling only.

(e.g. Trembaczowski, 1990, 1994 a, b; Krouse *et al.,* 1991 b; Newman *et al.,* 1991; Staniaszek, 1992; Mayer *et al.,* 1993; Krouse, 1994; Robinson, Bottrell, 1997, Moncaster *et al.*, 2000). Therefore, the primary aim of this study was to find isotope relations of inorganic sulphur dissolved in water in lakes and in atmospheric precipitation. Although, it may be expected that reduction processes are the most important sink for the SO_4^{2-} in lakes, little is known on the relevant mechanisms of the contaminant sulphate cycling. This paper is especially focused on oxygen and sulphur isotopic characteristics of sulphate ion and provides some new view of its origin and interaction with methane/methane precursors in lakes, especially in the light of individual buffering potential of the lake.

REDUCTION OF THE DISSOLVED SULPHATE

In contrast to marine environments (e.g. Cappenberg, 1974; Martens, Berner, 1974; Reeburgh, 1980; Iversen, Blackburn, 1981; Hines, Buck, 1982; Devol, 1983; Alperin,

Reeburgh, 1984; Iverson, Jorgensen, 1985; Parkers *et al.,* 1989; Reeburgh *et al.,* 1993; Hoehler *et al.,* 1994; Blair, Aller, 1995; Habicht *et al.*, 1998) the reduction of sulphate in freshwater methanogenic sediments is poorly recognized (e.g. Martens, Berner, 1977; Rudd, Hamilton, 1978, Panganiban *et al.,* 1979, Iversen, Blackburn, 1981; Devol *et al.,* 1984; Iversen, Jorgensen, 1985). On the other hand, freshwater systems are the most impospheric methane whereas methanogens and sulrtant source for atmophate reducers are strongly combined them, may occupy the same environments and utilize the same substrates (Oremland *et al.,* 1987). Moreover, the sulphate reducers in lakes may utilize methane, especially when some sulphate-recalcitrant organic compounds (methyl amines, methanol, dimethylosulfides) keep methanogenesis active (Oremland, Polcin, 1982; Oremland *et al.,* 1982; King *et al.,* 1983; King, 1984 a, b; Kiene *et al.,* 1986; Kiene, Visscher, 1987). On the other hand, sulphate reducers usually outcompete methanogens for the most important substrates as hydrogen and acetate. This is due to higher yield of energy, during metabolism of acetate and hydrogen, by sulphate reducers than methanogens (see Wake *et al.,* 1977; Abram, Nedwell, 1978; Nedwell, Banat, 1981; Ingvorsen, Brock, 1982; Kristjanson *et al.,* 1982; Schonheit *et al.,* 1982; Robinson, Tiedje, 1984; Westermann, Ahring, 1987). Moreover, the first show higher affinity toward acetate and hydrogen than to the other organic compounds present in the sediment (Winfrey, Zeikus, 1977; Zehnder, 1978; Nedwell, Banat, 1981, Ingvorsen, Brock, 1982; Kristjansson *et al.,* 1982; Lovley *et al.,* 1982; Robinson, Tiedje, 1984; Lupton, Zeikus, 1985; Ward, Winfrey, 1985; Conrad *et al.,* 1987; Conrad, 1989, 1996; Parkers *et al.,* 1989; Scholten *et al.,* 2002). Therefore, the dissolved sulphate is the limiting factor controlling production of methane and, in the presence of sulphate the emission of methane from freshwater sediments may be suppressed by 80% (Henrichs, Reeburgh, 1987; Reeburgh, Alperin, 1988).

Reduction of sulphate and oxidation of methane or methane precursors is not always parallel or strictly combined with each other. In addition to sulphate reducers, small amounts of methane can be oxidized also by methanogens (Zehnder, Brock, 1979, 1980). Likewise, unrelated to methane, little known microbial processes may even control the sulphate reduction which in marine sediments can be 10 times more efficient than the rate of methane oxidation (Alperin, Reeburgh, 1985). All what can be told that is that the sulphate reduction are complex (e.g. Habicht *et al.*, 1998) and unknown processes and the knowledge on them in freshwater systems is still very limited (e.g. Lovley, Klug, 1986). Therefore, sulphur isotope microbial metabolism and red-ox processes with special reference to methane should be elucidated and a potential anthropogenic- and biosphere-driven effects can be described. Some help is provided by stable isotope analysis, as biospheric uptake of sulphur involves red-ox processes which are traced by S and O isotope effects. Dissimilatory sulphate reduction by

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[1] for Table 1 see the end of this article

sulphate-reducing bacteria, which seems to be the most important for sulphate budget in lakes, results in enrichment of ^{34}S and ^{18}O in the remaining sulphate pool due to lower bond strength of ^{32}S-O and S-^{16}O which are preferentially broken during reduction. (e.g. Harrison, Thode, 1958; Kaplan, Rittenberg, 1964; Mizutani & Rafter, 1973; Fritz *et al.,* 1989; Trembaczowski, Hałas, 1993; Stempvoort, Krouse 1994; Trembaczowski, 1994 a, 1995; Aggarwal *et al.*, 1997).

MATERIALS AND METHODS

LAKES SAMPLED

In general, 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. Names of the lakes sampled and their location are shown on the Fig. 1, however details on precise locality and limonologic characteristics of the lakes can be found elsewhere (Jędrysek 1995, 1997 a, b, 1999). Samples have been collected from the surface at various distances from the lake bank using boat, or by mean of scubadiving up to 30 m. Most samples were collected within an 18 day period in August/September 1993 (Tab. 1).

ANALYTICAL PROCEDURES

The water sampled was filtered and BaSO$_4$ was precipitated. The precipitated BaSO$_4$ was rinsed with distilled water, dried, weighed, powdered in an agate mortar, preheated at 550°C (2 minutes) and weighed again in order to calculate the concentration of sulphate (see Jędrysek, 2000 for more details).

For sulphur isotope analysis, 10 mg of BaSO$_4$ were mixed with 100 mg of V$_2$O$_5$ and 100 mg of pure quartz (Yanagishawa, Sakai, 1983). The mixture was placed at the bottom of quartz glass tubes together with preheated pure copper wire situated 2 cm above the reaction mixture, and attached to the vacuum preparation line. The tube was heated at 450°C for about 10 minutes to remove any volatile contaminants. Afterwards, the temperature was raised to 950°C (while the copper was at about 750°C) and kept for 25 minutes to complete the reaction. The obtained was frozen in a liquid nitrogen trap and then cryogenically cleaned using dry ice-ethanol mixture. Alternatively, the was obtained using NaPO$_3$ reagent (V$_2$O$_5$ yields the same results and both techniques has been used alternatively for calibration) as described by Hałas and Wołącewicz (1981). The sulphate was reacted under vacuum at 850°C with dry NaPO$_3$. and SO$_3$ were the gaseous products of this reaction. SO$_3$ was reduced to by passing the SO$_3$ over hot (*c.* 700°C) pure copper.

For oxygen isotope analysis it was necessary to obtain oxygen quantitatively as from BaSO$_4$. The was prepared according to the Mizutani and Rafter (1973) technique; the sulphate was reacted with pure graphite at 1400°C under vacuum. and some CO were produced by this reaction. Therefore, the CO had to be converted to CO$_2$ using a high voltage discharge between platinum electrodes.

Sulphur and oxygen isotope analyses were carried out using a Varian MAT CH7 mass spectrometer with a modified detection system, or substantially modified MI-1305 mass spectrometer (Hałas 1979, Hałas, Skorzyński 1980). The $\delta^{18}O(SO_4^{2-})$ and $\delta^{34}S(SO_4^{2-})$ values are given in permill (‰) units in reference to V-SMOW and CDT international standards, respectively. The precision (1σ) obtained for complete analysis of replicate aliquots of standards and samples, was generally better than 0.1‰ for both sulphur and oxygen isotope analysis.

RESULTS

The highest concentrations of sulphate were found in polluted rivers and polluted eutrophic lakes while the lowest ones — in dystrophic and oligotrophic lakes (Tab. 1). The highest concentrations of sulphate were measured in Odra River (85,47SO$_4^{2-}$ mg/l) and Wisła River (78,24 SO$_4^{2-}$ mg/l) and in an extremely polluted pond near Warchały (79,39 SO$_4^{2-}$ mg/l). In the case of lakes, the highest concentration of sulphate was detected in Sulistrowiczki artificial lake (70,3 SO$_4^{2-}$ mg/l) located in the E margin of the "Black Triangle" (Fig. 1; Jędrysek, 2000). The lowest concentration of sulphate was detected in Skrzynka Lake (0.5 SO$_4^{2-}$ mg/l) and mountain lakes (Czarny Staw, Morskie Oko, Wielki Staw, Mały Staw). In contrast to concentration of sulphate, there is a general pattern in the geographical distribution of sulphur and oxygen isotope composition in that sulphate. The lowest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values are found in lakes in eastern Poland with a minimal value in Solina Lake (–0.94 and 1.38‰ respectively). In general, the highest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values are found in lakes in western Poland with maximal values in Mały Staw Lake (12.95‰) and Sulistrowiczki Lake (14.50‰), respectively, both located in the east margin of the "Black Triangle" (Fig. 1). One exception to the general trend is that the highest $\delta^{18}O(SO_4^{2-})$ value analysed was found in the lake Wądołek Lake (Tab. 1), which is located in NE Poland, shows extremely dystrophic conditions.

DISCUSSION

CONTAMINANT ANTHROPOGENIC SULPHATE

Inasmuch as, for all the lakes studied, the contribution of oceanic (marine) sulphate is generally negligible and dissolution of evaporites (oceanic/marine) is in general not relevant due to geology of catchments of the lakes, (perhaps the lake Piaseczno is an exception — see Discussion — Sulphate formed by organisms...), two general sources of sulphate for lakes far form the seashore can be assumed: anthropogenic and biogenic (Jędrysek *et al.*, 2002). In this section the anthropogenic source will be discussed.

There are abundant quantitative data on dynamics of acid rain, at both local and global scale (e.g. Baron, Sobik, 1995; Mylona, 1996; Dore *et al*., 1999; Hovmand, 1999; Jędrysek, 2000). However, little is known about isotopic evolution of the acid rain sulphate deposited in freshwater aquifers. Lakes sulphate analysed falls into a restricted field and evolve along a positive $\delta^{34}S(SO_4^{2-})$ *vs* $\delta^{18}O(SO_4^{2-})$ correlation line (Fig. 2). The points above the field represent rains from downtown Wrocław (SW Poland, see Jędrysek 2000) and surface lakewater collected during or just after very heavy rains. The points below the field represents the terrestrial biogenic sulphate (see Discussion — Sulphate formed by organisms...).

Oxygen isotope signatures in sulphate are controlled by the origin of the oxygen and isotopic fractionation during oxidation of the substrate sulphur compounds. In natural exogenous conditions oxygen in sulphate dominantly comes from the atmospheric O_2 (also dissolved oxygen when oxidation takes place in water) and (including atmospheric moisture when oxidation takes place in the atmosphere), (e.g. Lloyd, 1968; Toran, Harris, 1989; Krouse *et al.,* 1991 a, b). However, the dominant source of sulphur in the atmospheric is a high-temperature oxidation of reduced sulphur (fossil fuel burning, sulphide-based metals smelting, *etc*.). The SO_2 and some SO_3 produced in this process are usually readily oxidised in the atmosphere to (Krouse *et al.,* 1991 a, b). Therefore, oxygen in the sulphate comes from the anthropogenic SO_2, and then likewise to the natural analogue, from the atmospheric O_2 and . However, oxygen in the anthropogenic SO_2 comes from atmospheric O_2 with the role of atmospheric moisture (H_2O) being negligible. Atmospheric oxygen is isotopically heavy (+23,5‰) and at the high temperature of SO_2 formation (fossil fuel burning or smelting) the fractionation factor α is expected to be close to 1. Accordingly, in the region under study, the anthropogenic sulphate has about 10‰ higher $\delta^{18}O$ value than its natural analogue (Jędrysek, 2000). Note that the isotopic composition of sulphate in the rain in downtown Wrocław shows no correlation in the oxygen and sulphur isotope system and the R^2 coefficient is 0.00 (Fig. 2). The R^2 correlation coefficient (0.4), in this field in the Fig. 2, is apparently a relatively low value. Nevertheless, the R is 0.63 which is remarkable when consider the large number of data points (n = 147) within the filed (Fig.2). Therefore, this correlation found in lakewater sulphate cannot be ignored.

The isotope signature of sulphate dissolved in lakewater can evolve due to microbial reduction, mixing with its natural analogues (geogenic, oceanic) or formation of sulphate (oxidation). Therefore, the mixing ratio of these three main sources of sulphate together with reduction of sulphate are the main factors controlling concentration and isotopic signature of the sulphate in lakes. It has been reported that in Wrocław downtown (SW Poland) the concentration of sulphate in the rain was highest during autumn of 1993 and 1994, and reached 47.64 and 58.67 mg/l SO_4^{2-}, respectively (Jędrysek, 2000). The weighted averages, relevant to the sampling period in lakes (mainly 1993) were $\delta^{18}O(SO_4^{2-}) = 14.41‰$ and $\delta^{34}S(SO_4^{2-}) = 1.76‰$. These values can be considered as rather stable because the subsequent continuos observations showed about 2‰ sudden and single-event (mid-1994) increase in the $\delta^{34}S(SO_4^{2-})$ value and less than 1‰ steady decrease in the $\delta^{34}S(SO_4^{2-})$ value (till 2001). This obviously has little importance for the comparative analysis of the data presented for lakes, but is evidence that probably no significant variations in the isotope ratios of rainwater sulphate can be expected to have taken place before sampling in the lakes (mainly 1993) — thus, the acid rain data (Jędrysek, 2000) plotted on Fig. 2 are representative and relevant to be compared with those for the lakes (Figs. 2, 3, 4). However, in many cases concentration of sulphate in lakewater is higher than concentration of sulphate in precipitation in respective lake catchments (concentration of sulphate in rainwater in eastern Poland was below 1 mg/l). Moreover, lakewater in general shows lower $\delta^{18}O(SO_4^{2-})$ valanges in the $\delta^{34}S(SO_4^{2-})$ values, as compared to atmospheric precipitation. Thus, other important source of sulphate in lakes has to be considered.
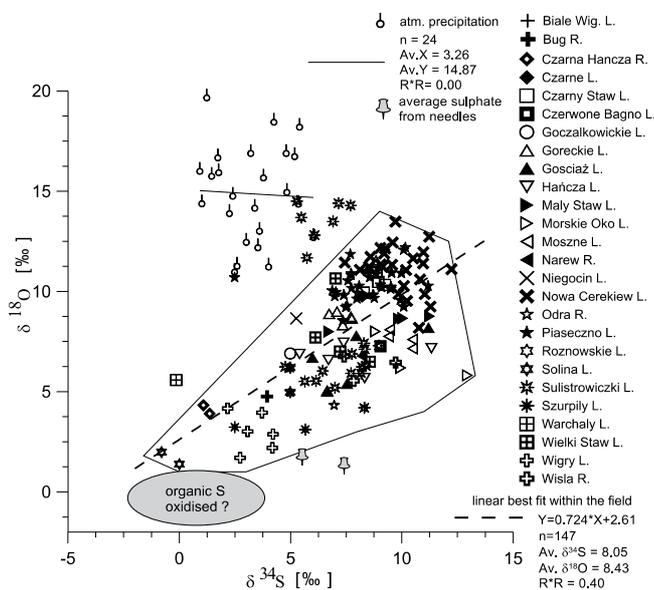

Fig. 2. Sulphur and oxygen isotope ratios in sulphate dissolved in lakes, rivers and precipitation 1993–1995

Sulphur and oxygen isotope variations in lake water may results from mixing of sulphate from two dominant sources (biogenic an anthropogenic), and from red-ox processes; the points out off the field represents rain from downtown Wrocław (SW Poland, see Jedrysek, 2000) and surficial lakewater collected during/after heavy rains as well as biogenic sulphate or spruce needles sulphate
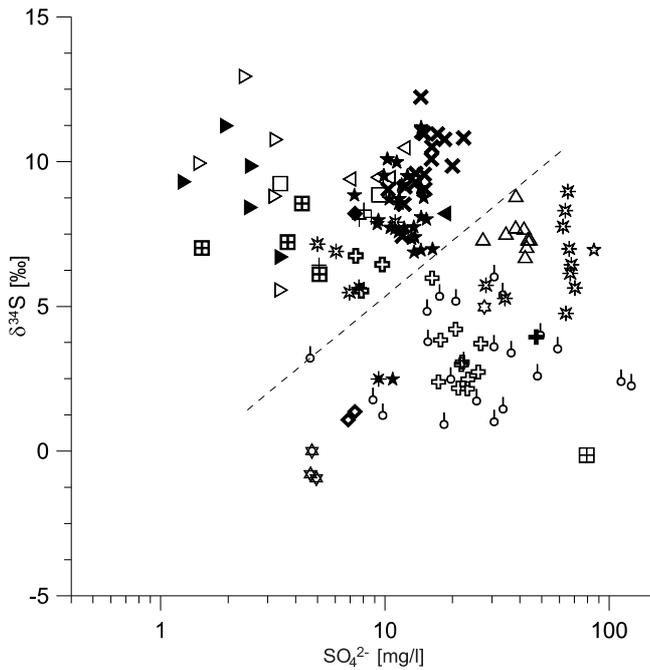
Fig. 3. Concentration of sulphate and sulphur isotope variations in sulphate dissolved in lakes, rivers and precipitation 1993–1995

For explanation see Fig. 2.
Points below the dotted line represents mostly oligotrophic and mesotrophic lakes. The points over the dotted line represent mostly lakes where advanced sulphate reduction takes place or oceanic origin of sulphate is present.
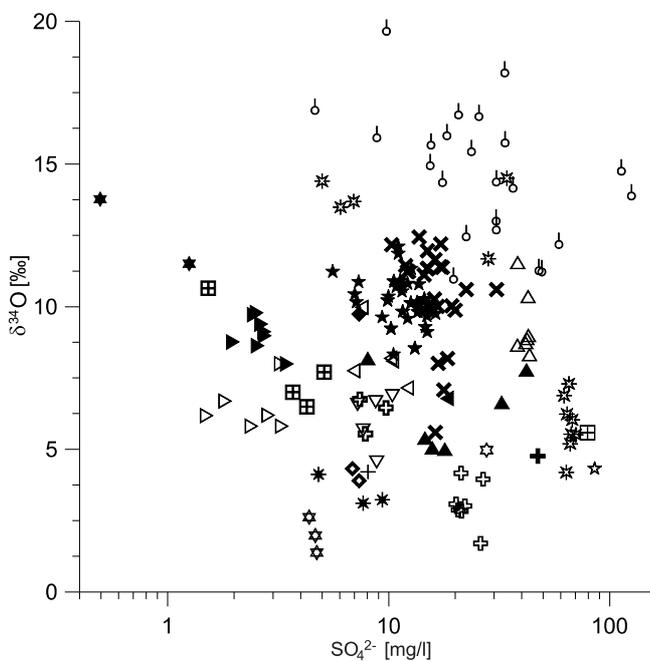

Fig. 4. Concentration of sulphate and oxygen isotope variations of dissolved sulphate lakes, rivers and precipitation

For explanation see Fig. 2

SULPHATE FORMED BY ORGANISMS — ALLOCHTONOUS AND AUTOCHTONOUS BIOGENIC SULPHATE

Two biogenic sources of sulphate in lakes, allochtonous and autochtonous, can be discriminated: 1 — allochtonous-terrestrial that formed by terrestrial organisms (macrophytes, oxidation in soil etc.) and 2 — autochtonous-aquatic that formed by aquatic organisms (aquatic sulphate) from oxidation of sulphur compounds in lakes (e.g. Krouse *et al.*, 1991 a, b). The $\delta^{18}O$ value of the atmospheric oxygen is rather stable and isotopically heavy, but $\delta^{18}O(H_2O)$ value of precipitation varies seasonally, roughly along the meteoric water line (Dansgaard, 1964), showing a maximum during summer. Likewise, evaporation from lakes causes a significant ^{18}O-enrichment (several permill) of the lakewater, while lakes at higher elevations or at higher latitudes shows lower $\delta^{18}O(H_2O)$ value accordingly to decreasing $\delta^{18}O(H_2O)$ value in meteoric precipitation (e.g. Różański *et al.*, 1993; Staśko, 1994). In fact, it has been shown that in precipitation, annual variations in the $\delta^{18}O(SO_4^{2-})$ value roughly corresponds to the annual variations in $\delta^{18}O(H_2O)$ (e.g. Lloyd, 1968; Longinelli, Cortecci, 1970; Trembaczowski, 1991, 1994 b).

On the other hand, dissimilatory reduction of sulphate, which is important process in lakes, results in decreasing of SO_4^{2-} concentration. Therefore, terrestrial biosphere assimilation of from the atmosphere and formation of also needs to be considered. Lakes are often surrounded by coniferous forests which, to a much larger degree than deciduous forests, assimilate SO_2 from the atmosphere and store it in their needles in the form of organic sulphur compounds and sulphate. The sulphate in needles is usually about 3.5 ‰ enriched in ^{34}S isotope compared to organic sulphur. Moreover, in SO_2-contaminated regions, conifers remove excessive sulphur in the form of H_2S, which results in additional ^{34}S and ^{18}O enrichment of the retained needle sulphate (Jędrysek *et al.*, 2002). Sulphur compounds are usually not retranslocated before needle shedding (Bringmark, 1977) and sulphate from shedded needles is easy mobilized by rainwater and transported through streamwater and groundwater to neighbouring lakes. Consequently, the lakes receive additional input of sulphate from coniferous forested catchments. Moreover, evaporation of lakes also slightly increases concentration of sulphate, but this effect is probably less important than the terrestrial biosphere input. In fact, in most mountainous lakes, surrounded dominantly by dwarf mountain pine and spruce, the concentration of the sulphate in lakewater was found to be higher than that in the local precipitation and the average concentration of sulphate on the surface of needles, inside needles and organic sulphur is 0.03, 0.01 and 0.1%, respectively (Jędrysek *et al.,* 2002; Kałużny, 2002). The total quantity of the litter from coniferous vegetation amounts from about 0.8 to 3.0 t/ha/year (e.g. Schall, 1991; Oleksyn *et al.,* 1999; Oleksyn — oral information) and the total quantity of the litter from shrub *Pinus mugo Turra* high mountain and subalpine belt of the Romanian Carpathians (1500–2200 m) amounts to 2.6 t/ha/year (Coldea, Plamada, 1978). Providing roughly that 20% of organic S in shedded needles is oxidised to sulphate and that practically all sulphate is removed from needles, the total output of SO_4^{2-} from shedded

needles to the ecosystem is more than 1 t/ha/year. That means that in a typical mountainous lake (small watershed, deep) surrounded by coniferous vegetation, the total input of SO_4^{2-} can be estimated to vary between 10 to 100 mg/l of lakewater per year. Hence, the SO_4^{2-} is dominantly of allochtonous biogenic origin and from isotopic mass balance point of view the SO_4^{2-} from precipitation is negligible, because concentration of SO_4^{2-} in precipitation is usually between much less than 1 mg/l and not higher than 10 mg/l. Consequently, coniferous areas may determine concentration of sulphate in freshwater systems (including groundwaters) and thereby control the oxidation of organic compounds in freshwater sediments and the water column in freshwater systems.

The above statement is in agreement with isotopic data. Although, sulphur isotope ratios in the needles (sulphate and organic sulphur) are generally similar to that in precipitation, the $\delta^{18}O(SO_4^{2-})$ value in needles is significantly lower than that in precipitation (Fig. 2). This is due to the fact, and in contrast to atmospheric sulphate (see above), the needle sulphate forms within the needles and the oxygen in it comes from ^{18}O-depleted water (in average $\delta^{18}O$ during vegetation season is from about -8 to $-12‰$). In addition, the low $\delta^{18}O(SO_4^{2-})$ value in needles is due to the fact that a large part of sulphate is formed in needles during winter, when the assimilation is active and local precipitation has the lowest values in the annual cycle. Likewise, it can be expected that sulphate, formed due to oxidation of shedded needles organic sulphur, may show slightly lower $\delta^{18}O(SO_4^{2-})$ value than the needle sulphate when the latter experience advanced reduction resulting in ^{34}S and ^{18}O isotope enrichment of the residual sulphate (Jędrysek et al., 2002).

The lake-born sulphate in lakes (aquatic sulphate) is the sulphate formed from oxidation of reduced sulphur compounds in lakes. Probably the enrichment in ^{18}O of lakewater due to evaporation may result several permill higher $\delta^{18}O(SO_4^{2-})$ value of the aquatic sulphate. However, in practice it rarely can be isotopically discriminated form the biogenic terrestrial sulphate. Consequently, $\delta^{18}O(SO_4^{2-})$ and $\delta^{34}S(SO_4^{2-})$ values, in majority of lakes, are controlled by mixing ratio between sulphate from precipitation and that of biogenic (allo- and autochtonous) origin (Fig. 2). These lakes are usually relatively clean and show mesotrophic character (e.g. Solina L., Wigry L.).

PRECIPITATION OF CARBONATES
— SULPHATE DISSIMILATORY REDUCTION
AND METHANOGENESIS

Understanding of the effects of anthropogenic acidification is important especially when studying problems of aquifers at industrial areas, mining waters discharge to freshwater environments, acidification of soils, evaluation and production of tap water, etc. It has been suggested that $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values and variations in $\delta^{13}C(CH_4)$ values in lakes are potentially a good tool to assess and quantify the anthropogenic impact induced by sulphuric acidification (including acid precipitation), and to monitor variations in the trophic level (Jędrysek, 1998). Further modification of the isotopic fingerprint by sulphate reduction in an anaerobic environment can result in a large range of concen-

tration of sulphate and sulphur and oxygen isotope ratios. Potential superimposition of bacterial sulphate reduction and re-oxidation of the H_2S (e.g. Böttcher, Thamdrup, 2001) complicates $\delta^{34}S(SO_4^{2-})$ and especially the $\delta^{18}O(SO_4^{2-})$ pictures because beside some common environmental parameters controlling S and O isotope ratios (e.g. source, SO_4^{2-} concentration, pH, temperature, carbon source, bacterial processes, etc.) the $\delta^{18}O(SO_4^{2-})$ variations depends on parameters which in general do not influence $\delta^{34}S(SO_4^{2-})$ value e.g. isotopic composition of atmospheric oxygen and water or concentration of dissolved oxygen. Nevertheless, a general isotopic picture composed of many waterbodies can be drown (Fig. 2) hence some driving mechanisms with respect to individual lakes is discussed below to find general rules controlling isotope composition and concentration of sulphate in lakes.

Eutrophic lakes have high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values compared to clean oligotrophic or mesotrophic lakes (Fig. 2). In general, the increase both in sulphur and oxygen isotope ratios most probably results from: 1 — bacterial reduction of the dissolved sulphate (e.g. Nowa Cerekiew Lake — manmade); 2 — presence of oceanic origin sulphate — when $\delta^{18}O(SO_4^{2-})$ values is less than 10‰ (e.g. Piaseczno L. that is feed by groundwater that is rich in oceanic origin sulphate). The lakes and rivers from NE (Czarna Hańcza R., Szurpiły L., Wigry L.), and SE Poland (Solina L.) represent mesotrophic conditions and receive the lowest amount of acid rain in Poland. Thus, they show the lowest isotopic values in the $\delta^{34}S$-$\delta^{18}O$ diagram (Fig. 2). In the same lakes, relatively high concentration of sulphate as compared to the low $\delta^{34}S$ value (Fig. 3) may apparently suggest that the sulphur in these systems originates mostly from acid rain or forms due to re-oxidation (oxidation of some reduced forms of sulphur). However, the low $\delta^{18}O$ value in the sulphate ion (Fig. 4) suggests the second case, namely that the sulphate in the lakes from NE Poland is dominantly of natural origin, despite that originally the sulphur is assimilated from anthropogenic atmospheric SO_2. The relatively high isotope signatures in the Hańcza Lake, when compared to other lakes in NE Poland, (Fig. 2) result, most probably, from advanced reduction of the sulphate. On the other hand, the relatively low $\delta^{18}O$ value suggests sulphide oxidation, in agreement with the concentration of sulphate (Fig. 4). This indicates that probably both processes take place in the Hańcza Lake. The advanced reduction may result from the fact that the lake is very deep (103 m) and narrow (width/depth ratio is only about 10). Thus, the reduction in the bottom zone may proceed simultaneously with an active oxidation in shallower zone.

All mountain lakes in the area under study show strictly oligotrophic parameters. However, these lakes (Morskie Oko and Czarny Staw in Tatra National Park; and Wielki Staw and Mały Staw in Karkonosze National Park) show relatively high isotope values, suggesting advanced microbial reduction of sulphate, especially when compared to the corresponding low sulphate concentrations (Figs. 3, 4). However, these high $\delta^{34}S(SO_4^{2-})$ values cannot be caused by microbial methane-based reduction, as among the mountain lakes, bubble methane is only observed in the Mały Staw Lake (Jędrysek, 1997 b). On the other hand, the $\delta^{18}O(SO_4^{2-})$ values in the mountain lakes are lower than the value in the acid rain in this region (see Jędrysek, 2000). This opposite trends in sulphur and oxygen iso-

tope ratios can be linked to sulphate reduction alone, and oxidation in the presence of ^{18}O depleted mountain water (see e.g. Dansgaard, 1964; Różański *et al.,* 1993; Staśko, 1994). An alternative explanation is that biogenic sulphate of terrestrial origin is the dominant source of sulphate in these mountainous lakes (see Discussion — Sulphate formed by organisms...). Likewise, a portion of sulphate in mountain lakes may be of oceanic origin (^{34}S-enriched oceanic spray), although the contribution from the sea-spray sulphate is probably extremely small.

A large number of data show that oxidation of methane due to sulphate reduction has variable importance and magnitude at individual marine environments (e.g. Devol, 1983; Alperin, Reeburgh, 1985; Iversen, Jorgensen, 1985). The lakes Mały Staw and Wielki Staw are located in the "Black Triangle" where sulphur stress was extremely high. Moreover, they have mountainous watershed, but in the case of the Mały Staw Lake a higher trophy than could be expected and the organic-rich methanogenic sediments has been observed (Jędrysek, 1997 b). The importance of red-ox processes in Mały Staw Lake is supported by C-isotope ratios in bubble methane. This is due to the fact that the mechanisms of methanogenesis and potential oxidation of methane are the main factors controlling concentration and carbon isotope ratio in methane (e.g. Brick, Moore, 1996; Marek *et al.,* 1996; Hornibrook *et al.,* 1997, 2000; Lojen *et al.,* 1997, 1999; Miyajima *et al.,* 1997; Whiticar, 1999). Sulphate is the main oxidant of methane and methane precursors (see Introduction — Reduction of the dissolved sulphate). It has reported earlier that most methanogenic lakes show significant decrease in the $\delta^{13}C$ value with increasing depth of water column (Jędrysek *et al.,* 1994; Jędrysek, 1997 b, 1999) and depth within sediments (Jędrysek *et al.,* 1994; Jędrysek, 1997 b). This can be related to the variations in temperature in methanogenic pathways including competing for substrates in the sulphate reduction — methane production system. However, in contrast to the other lakes (Jędrysek, 1997 b, 1998), the Mały Staw Lake shows the opposite trend (Fig. 5). Despite the relatively very low sulphate concentration, it was still higher than the individual biological ability of lakes to buffer the anthropogenic sulphate. Simply, the lakes shows pore activity of aquatic biosphere and the sulphate input can not be assimilated. Thus methane and the methane precursors (hydrogen) are oxidised both in the water column and within the sediments. This process could be important also in the Wielki Staw Lake (about 100 m above Mały Staw L.), where anthropogenic SO_2 impact was extremely high (Jędrysek *et al.,* 2002) and no bubble methane in organic-bearing sediments has been detected (Jędrysek, 1997 b). In this case the biological buffering potential of the lake (for SO_4^{2-}) has been exceeded. Probably, at a greater depth, below the point of light penetration, sulphate reducers consume most of the hydrogen which became the limiting factor for CO_2 pathway of methanogenesis (Jędrysek, 1997 b, 1998, 1999). In the lake Mały Staw, the role of hydrogen deficit probably increased with increasing depth of the water column, hence the $\delta^{13}C(CH_4)$ increased due to the relative increase in the importance of the acetate pathway. Consequently, $\delta^{13}C$ values of methane in the Mały Staw Lake increase with increasing depth.

It has been shown above that the lakewater sulphate is microbially reduced and the main substrates for methane as well as perhaps methane itself are oxidised. The system becomes more complicated as the acetate, methanol and hydrogen, produced *via* methane oxidation, subsequently are metabolised by microbes able to reduce selected electron acceptors, especially MnO_2 and SO_4^{2-} (Zehnder, Brock, 1979). On the other hand, sulphate reducers cannot grow *via* methane oxidation alone, as they need another electron donor for methane oxidation. It can be proposed that methane may be also oxidized in a metabolic reaction which does not require energy for growth. However, the advanced reduction of sulphate is supported by low concentration of sulphate and the extremely high $\delta^{34}S(SO_4^{2-})$ value detected in Mały Staw Lake (12.95‰) (Fig. 3). This is in agreement with the relatively low $\delta^{18}O(SO_4^{2-})$ value (Fig. 4) which can result from low $\delta^{18}O$ value water from local mountainous moisture/precipitation and substantial input of sulphate of both autochtonous and allochtonous biogenic origin.

However, it can be postulated that not necessary concentration of sulphate alone but also temperature (Westermann, 1993) and other physicochemical factors were responsible for the opposite trend in $\delta^{13}C$ value of methane. Namely, the Mały Staw Lake is a small and shallow (6.5 m) lake with a small retention capacity and a windy mountainous location (potentially frequent turbulences of the water). In fact, during sampling the author observed significant waving even clearly detectable at the maximal depth of the lake, and no clear thermocline has been observed. Therefore, it can be expected that the lake experiences frequent mixing which may result in homogenisation of lakewater (both with respect chemical and physical parameters) similar to seasonal turnover. Consequently, no vertical variation in red-ox processes should be expected. This obviously could result in a very stable $\delta^{13}C$ value of methane at all depths, but cannot explain increasing $\delta^{13}C(CH_4)$ with increasing depth of the water column. Future studies of the effects described here might help to calibrate a new tool to assess individual biological potential of lakes to assimilate pollutants and to express the ecological conditions of lakes in the form of a kind of isotope index (e.g. SOC — sulphur, oxygen, carbon).
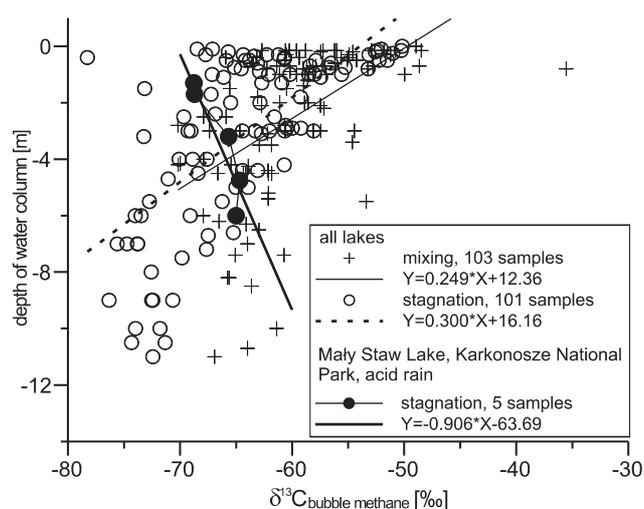

**Fig. 5. Methane from freshwater sediments
in selected lakes in Poland, 1992–1996**

During stagnation, the strongly acidified Lake Mały Staw shows an "oxidation" trend typical for seasonal overturn.
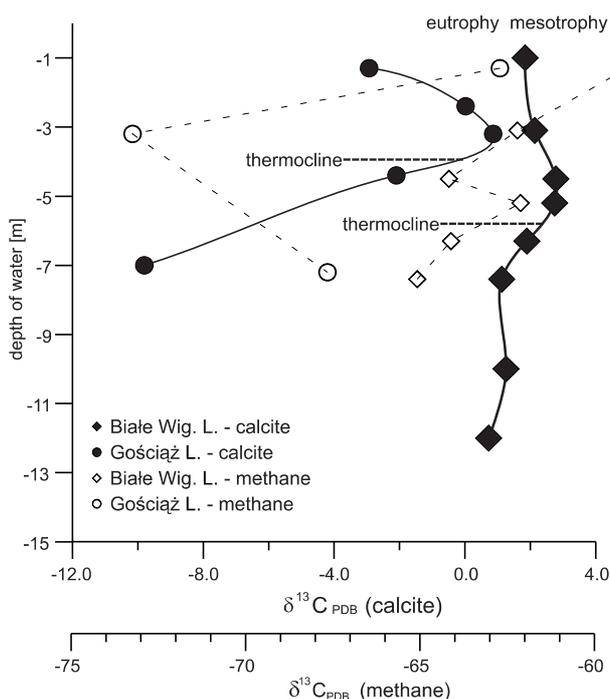
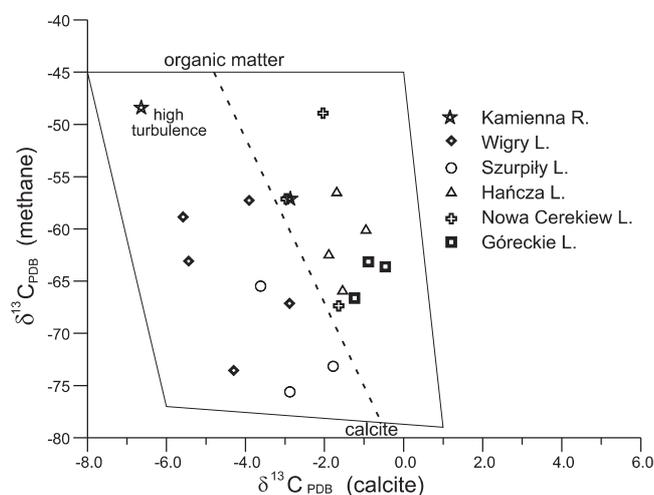Fig. 6. $\delta^{13}C$ value and depth of the water column in methane and calcite from selected lakes in Poland

Fig. 7. $\delta^{13}C$ value of calcite and methane from selected lakes in Poland

Organic compounds are ^{13}C-depleted and moreover oxidation involve isotope effect (^{12}C bonding are broken preferentially). Consequently, ^{13}C-depletd 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 $\delta^{13}C$ values at depths can be controlled by variations in temperature and in increasing role of CO_2-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 CO_2 pathway of methanogenesis — thus the $\delta^{13}C$ 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. 5). Negative correlation observed between $\delta^{13}C(CH_4)$ value and depth of the water column may be the result of the strong contamination by the , exceeding the biological buffering abilities of Mały Staw Lake. 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 $\delta^{13}C$ value of methane resulted from oxidation.

In freshwater lakes, calcite can precipitate from the water column ($\delta^{13}C$ 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 ^{13}C-depleted calcite (or other carbonates). In fact, mesotrophic lakes show higher $\delta^{13}C$ values in methane have also higher $\delta^{13}C$ values in calcite found in that methanogenic sediments (Figs. 6, 7). This is probably due to: lower methanogenic activity — thus acetate fermentation is relatively high as compared to CO_2 pathway, and advanced dissimilatory microbial reduction of methane precursors — the residual organic compounds become ^{13}C-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 $\delta^{13}C$ value of methane and lowermost $\delta^{13}C$ value in calcite (Fig. 7). This suggests that nearly entire calcite formed due to oxidation of methane/methane precursors. However, in the eutrophic lakes (Góreckie, Nowa Cerekiew) 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. Most lakes show narrow ranges of an individual $\delta^{34}S$ and $\delta^{18}O$ signal. Degraded eutrophic lakes have high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values while clean or oligotrophic lakes have low $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values.

2. In contrast to not contaminated lakes, higher carbon isotope ratios in methane at depths may result from strong

contamination with sulphate ion resulting oxidation of methane and methane precursors. In these lakes substantial portion of isotopically depleted carbonates may precipitate.

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 (allochtonous material) layer and spring (oxidation) white layers makes the number of layers and ^{14}C-dating not comparable. Counting of laminae can overestimate the age of the sediment.

4. Carbon isotope ratios in calcite from eutrophic lakes can better record environmental variations than low trophies lacustrine calcite.

Lower C isotope ratios in calcite — the higher tropic state, more nutrients, greater depth — out of the thermocline zone

5. Future studies might help to calibrate a new tool to precisely reconstruct environmental variations, especially:

— trophy state and advance in microbial red-ox processes,
— individual biological buffering potential and limnological character (depth, turbulence, seasonal overturn etc),
— ecological conditions and methanogenic potential,
— climatic variations.

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Table 1 31

T a b l e 1

Concentration and stable isotope ratios of sulphur and oxygen in sulphate dissolved in lakes and rivers in Poland

Lakes and rivers	Sampling date	Depth of sampling	Concentration of SO_4^{2-} [wt%]	$\delta^{34}S$ sulphate [‰] CDT	$\delta^{18}O$ sulphate [‰] SMOW
1	2	3	4	5	6
Białe Wig. Lake	1993.09.02	0.0	8.05	8.33	4.21
Białe Wig. Lake	1993.09.02	0.0	7.67	8.02	n. a.
Białe Wig. Lake	1993.09.02	−3.0	8.68	8.08	n. a.
Białe Wig. Lake	1993.09.02	−13.0	5.09	6.43	n. a.
Białe Wig. Lake	1993.09.02	−20.0	5.43	n. a.	n. a.
Bug River	1993.08.31	0.0	47.26	3.94	4.76
Czarna Hańcza River	1993.09.01	0.0	7.34	1.36	3.90
Czarna Hańcza River	1993.09.01	0.0	6.85	1.08	4.32
Czarne Lake	1993.09.25	2.0	7.35	8.21	9.74
Czarny Staw Lake	1993.08.25	?	3.44	n. a.	n. a.
Czarny Staw Lake	1993.08.25	?	n. a.	8.94	10.48
Czarny Staw Lake	1993.08.26	0.0	4.01	8.29	9.94
Czarny Staw Lake	1993.08.26	−9.0	9.41	8.86	10.95
Czarny Staw Lake	1993.08.26	−17.0	1.26	n. a.	9.98
Czarny Staw Lake	1993.08.31	0.0	3.42	9.24	10.33
Czerwone Bagno Lake	1993.09.05	−0.20	4.52	9.04	7.26
Goczałkowickie Lake	1993.08.23	0.0	34.26	4.98	6.90
Gopło Lake	1993.09.07	0.0	36.72	n. a.	7.96
Gościąż Lake	1993.09.07	0.0	n. a.	5.98	6.69
Gościąż Lake	1993.09.07	−3.0	14.61	7.53	5.39
Gościąż Lake	1993.09.07	−15.0	11.59	11.59	n. a.
Gościąż Lake	1993.09.07	−21.5	8.04	11.20	8.18
Gościąż Lake	1993.09.07	−5.9	17.97	6.64	5.00
Gościąż Lake	1993.09.07	0.0	32.48	n. a.	6.64
Gościąż Lake	1993.09.07	0.0	15.77	6.64	5.05
Gościąż Lake	1993.09.07	0.0	42.00	7.96	7.78
Góreckie Lake	1993.05.22	0.0	42.84	7.08	8.99
Góreckie Lake	1993.05.22	−1.0	42.19	6.73	8.88
Góreckie Lake	1993.05.22	−2.0	42.75	n. a.	10.36
Góreckie Lake	1993.05.22	−3.0	43.39	7.34	8.32
Góreckie Lake	1993.05.22	−4.0	38.27	7.75	8.65
Góreckie Lake	1993.05.22	−5.0	41.69	7.71	8.74
Góreckie Lake	1993.05.22	−7.0	38.37	8.84	11.55
Góreckie Lake	1993.09.08	0.0	44.31	7.34	n. a.
Góreckie Lake	1993.09.08	−3.2	34.65	7.54	n. a.
Góreckie Lake	1993.09.08	−7.0	27.37	7.34	n. a.
Hańcza Lake	1993.09.04	0.0	8.73	n. a.	6.66
Hańcza Lake	1993.09.04	−3.0	7.97	9.25	n. a.
Hańcza Lake	1993.09.04	−12.5	7.66	8.33	5.67
Hańcza Lake	1993.09.04	−18.0	10.39	5.40	6.87
Hańcza Lake	1993.09.04	−25.0	7.23	6.70	6.57
Hańcza Lake	1993.09.04	0.0	8.82	n. a.	4.55
Hańcza Lake	1993.09.04	?	n. a.	7.38	7.43
Mały Staw Lake (Kark.)	1993.08.21	0.0	3.29	10.77	5.81
Mały Staw Lake (Kark.)	1993.08.21	0.0	1.82	n. a.	6.69
Mały Staw Lake (Kark.)	1993.08.21	−1.0	2.85	n. a.	6.19
Mały Staw Lake (Kark.)	1993.08.21	−2.0	2.40	12.95	5.81
Mały Staw Lake (Kark.)	1993.08.21	?	3.25	8.81	8.00
Mały Staw Lake (Kark.)	1993.08.21	−4.5	1.50	9.95	6.18

1	2	3	4	5	6
Mały Staw Lake (Kark.)	1993.08.21	−6.0	3.45	5.57	n. a.
Morskie Oko Lake	1993.08.24	0.0	2.65	n. a.	9.39
Morskie Oko Lake	1993.08.24	−2.0	2.75	n. a.	8.98
Morskie Oko Lake	1993.08.24	−7.3	2.74	n. a.	9.12
Morskie Oko Lake	1993.08.24	−10.0	2.55	9.85	8.63
Morskie Oko Lake	1993.08.24	−20.0	1.97	11.24	8.76
Morskie Oko Lake	1993.08.24	−30.0	3.46	6.71	7.99
Morskie Oko Lake	1993.08.25	0.0	2.53	8.42	9.79
Morskie Oko Lake	1993.08.25	−5.0	2.45	n. a.	9.72
Morskie Oko Lake	1993.08.25	−11.0	1.28	9.31	n. a.
Moszne Lake	1993.05.02	0.0	12.65	11.28	7.39
Moszne Lake	1993.05.02	−0.5	12.14	10.48	7.15
Moszne Lake	1993.08.30	0.0	9.21	9.46	n. a.
Moszne Lake	1993.08.30	−0.4	10.40	9.45	8.09
Moszne Lake	1993.08.30	0.0	6.94	9.40	7.75
Moszne Lake	1994.02.11	0.0	7.54	n. a.	9.98
Narew River	1993.08.31	0.0	7.62	9.55	3.75
Narew River	1993.08.31	0.0	18.38	8.21	6.78
Niegocin Lake	1993.09.06	0.0	n. a.	6.39	8.21
Niegocin Lake	1993.09.06	0.0	n. a.	5.25	8.65
Nowa Cerekiew Lake	1993.05.29	0.0	30.76	n. a.	10.60
Nowa Cerekiew Lake	1993.05.29	0.0	12.17	8.53	11.23
Nowa Cerekiew Lake	1993.05.29	−1.0	13.73	9.28	n. a.
Nowa Cerekiew Lake	1993.05.29	−2.3	11.95	7.43	11.44
Nowa Cerekiew Lake	1993.05.29	−5.0	n. a.	9.25	12.14
Nowa Cerekiew Lake	1993.05.29	−9.0	n. a.	8.59	11.73
Nowa Cerekiew Lake	1993.05.29	0.0	10.32	9.04	12.17
Nowa Cerekiew Lake	1993.07.28	−2.0	14.97	9.56	11.33
Nowa Cerekiew Lake	1993.07.28	−6.0	15.06	9.05	11.35
Nowa Cerekiew Lake	1993.08.23	0.0	20.02	9.85	9.88
Nowa Cerekiew Lake	1993.08.23	−1.0	n. a.	10.23	9.52
Nowa Cerekiew Lake	1993.08.23	−4.0	n. a.	10.19	11.07
Nowa Cerekiew Lake	1993.10.29	0.0	12.31	9.13	11.23
Nowa Cerekiew Lake	1993.10.29	−3.0	n. a.	9.71	13.48
Nowa Cerekiew Lake	1993.10.29	−5.9	n. a.	8.12	11.08
Nowa Cerekiew Lake	1993.10.29	−9.0	n. a.	11.23	12.73
Nowa Cerekiew Lake	1994.03.07	0.0	14.59	11.03	9.87
Nowa Cerekiew Lake	1994.03.07	−1.7	16.68	n. a.	10.01
Nowa Cerekiew Lake	1994.03.07	−6.0	22.44	10.82	10.60
Nowa Cerekiew Lake	1994.03.07	−10.0	14.47	12.23	11.11
Nowa Cerekiew Lake	1994.03.07	0.0	19.32	n. a.	10.03
Nowa Cerekiew Lake	1994.06.24	−5.0	16.21	10.51	11.65
Nowa Cerekiew Lake	1994.06.24	−0.3	17.50	n. a.	11.38
Nowa Cerekiew Lake	1994.06.24	−5.2	13.75	9.59	12.44
Nowa Cerekiew Lake	1994.12.20	0.0	16.26	n. a.	5.59
Nowa Cerekiew Lake	1994.12.20	−5.0	16.79	n. a.	8.01
Nowa Cerekiew Lake	1994.12.20	−3.2	17.79	n. a.	7.08
Nowa Cerekiew Lake	1994.02.25	0.0	15.00	10.97	11.96
Nowa Cerekiew Lake	1994.02.25	−4.0	18.47	10.77	8.18
Nowa Cerekiew Lake	1994.02.25	0.0	17.15	10.96	11.40
Nowa Cerekiew Lake	1994.02.25	−4.0	16.13	10.09	10.27
Odra River	1992?	0.0	85.47	6.95	4.32

Table 1   33

1	2	3	4	5	6
Piaseczno Lake	1992.09.26	−1.5	14.96	n. a.	9.11
Piaseczno Lake	1992.09.26	−10.0	14.67	n. a.	9.28
Piaseczno Lake	1992.09.26	−5.0	7.14	n. a.	10.16
Piaseczno Lake	1992.09.26	0.0	13.72	n. a.	10.79
Piaseczno Lake	1992.09.28	0.0	9.97	n. a.	10.36
Piaseczno Lake	1992.09.26	−10.0	12.66	n. a.	11.33
Piaseczno Lake	1992.09.26	−20.0	12.19	n. a.	9.58
Piaseczno Lake	1992.09.26	−30.0	7.02	n. a.	10.44
Piaseczno Lake	1993.05.02	−3.0	11.07	7.69	11.86
Piaseczno Lake	1993.05.02	−6.0	11.88	9.20	n. a.
Piaseczno Lake	1993.05.02	−10.0	10.44	8.70	n. a.
Piaseczno Lake	1993.08.29	0.0	11.55	8.56	10.70
Piaseczno Lake	1993.08.29	0.0	10.56	7.72	10.89
Piaseczno Lake	1993.08.29	0.0	9.89	9.51	10.22
Piaseczno Lake	1993.08.30	0.0	11.29	9.98	10.91
Piaseczno Lake	1993.08.31	0.0	10.24	10.09	9.23
Piaseczno Lake	1993.08.31	0.0	10.52	n. a.	8.32
Piaseczno Lake	1993.08.31	0.0	13.15	7.34	8.54
Piaseczno Lake	1993.08.30	0.0	15.33	8.01	9.92
Piaseczno Lake	1993.08.30	−3.0	n. a.	7.53	9.28
Piaseczno Lake	1993.08.30	−10.0	14.48	6.94	n. a.
Piaseczno Lake	1993.08.30	−30.0	9.23	7.85	n. a.
Piaseczno Lake	1993.11.13	0.0	5.58	n. a.	11.23
Piaseczno Lake	1993.11.13	−3.0	16.33	6.98	9.75
Piaseczno Lake	1993.11.13	−5.0	7.30	8.84	10.87
Piaseczno Lake	1993.11.14	−10.0	13.46	7.74	10.16
Piaseczno Lake	1993.11.14	−20.0	9.34	7.98	9.63
Piaseczno Lake	1994.02.12	−1.0	12.61	9.50	10.13
Piaseczno Lake	1994.02.12	−1.0	14.52	8.08	10.27
Piaseczno Lake	1994.02.12	0.0	14.46	9.09	10.21
Piaseczno Lake	1994.02.13	−1.0	13.58	7.39	9.82
Piaseczno Lake	1994.02.13	−1.0	14.91	8.76	9.67
Piaseczno Lake	1994.02.13	−1.0	11.57	8.71	9.83
Piaseczno Lake	1994.02.20	0.0	11.51	7.57	10.54
Piaseczno Lake	1994.02.20	−3.0	12.19	7.71	10.81
Piaseczno Lake	1994.02.20	−10.0	13.51	6.87	10.04
Piaseczno Lake	1994.02.20	−20.0	10.83	2.48	10.70
Piaseczno Lake	1994.02.20	−26.0	15.23	n. a.	10.02
Piaseczno Lake	1994.02.20	−29.0	13.49	n. a.	n. a.
Piaseczno Lake diurnal	1993.08.29	0.0	11.55	8.56	10.70
Piaseczno Lake diurnal	1993.08.29	0.0	10.56	7.72	10.89
Piaseczno Lake diurnal	1993.08.30	0.0	9.89	9.51	10.22
Piaseczno Lake diurnal	1993.08.30	0.0	11.29	9.98	10.91
Piaseczno Lake diurnal	1993.08.31	0.0	10.24	10.09	9.23
Piaseczno Lake diurnal	1993.08.31	0.0	13.15	7.34	8.54
Piaseczno Lake diurnal	1994.02.12	−1.0	12.61	9.50	10.13
Piaseczno Lake diurnal	1994.02.12	−1.0	14.52	11.18	10.27
Piaseczno Lake diurnal	1994.02.12	0.0	14.46	9.09	10.21
Piaseczno Lake diurnal	1994.02.13	−1.0	13.58	7.39	9.82
Piaseczno Lake diurnal	1994.02.13	−1.0	14.91	8.76	n. a.
Piaseczno Lake diurnal	1994.02.13	−1.0	11.57	8.71	9.83
Rożnowskie Lake	1993.08.26	0.0	n. a.	4.98	6.19

1	2	3	4	5	6
Rożnowskie Lake	1993.08.26	0.0	27.78	4.98	4.97
Skrzynka Lake	1993.09.08	0.0	0.50	n. a.	13.77
Skrzynka Lake	1993.09.08	0.0	1.25	n. a.	11.51
Solina Lake	1993.08.27	0.0	4.66	−0.80	1.98
Solina Lake	1993.08.27	0.0	4.73	0.00	1.38
Solina Lake	1993.08.27	−6.0	4.94	−0.94	n. a.
Solina Lake	1993.08.27	−10.0	4.37	n. a.	2.62
Sulistrowiczki Lake	1994.07.03	0.0	70.30	5.64	5.51
Sulistrowiczki Lake	1994.07.03	0.0	67.70	6.44	6.03
Sulistrowiczki Lake	1994.07.04	0.0	63.65	8.31	4.19
Sulistrowiczki Lake	1994.07.04	0.0	64.10	4.76	6.23
Sulistrowiczki Lake	1994.07.04	0.0	67.00	6.14	5.53
Sulistrowiczki Lake	1994.07.04	0.0	65.40	8.97	7.29
Sulistrowiczki Lake	1994.07.04	0.0	66.24	6.99	5.19
Sulistrowiczki Lake	1994.07.05	0.0	62.24	7.76	6.88
Sulistrowiczki Lake	1995.08.01	0.0	34.26	5.28	14.50
Sulistrowiczki Lake	1995.08.01	0.0	28.23	5.73	11.68
Sulistrowiczki Lake	1995.08.02	0.0	n. a.	6.07	12.81
Sulistrowiczki Lake	1995.08.03	0.0	11.12	7.91	n. a.
Sulistrowiczki Lake	1995.08.03	0.0	5.00	7.15	14.40
Sulistrowiczki Lake	1995.08.03	0.0	6.94	5.48	13.69
Sulistrowiczki Lake	1995.08.03	0.0	6.05	6.90	13.49
Szurpiły Lake	1993.09.05	0.0	7.66	5.66	3.11
Szurpiły Lake	1993.09.05	−2.8	9.36	2.49	3.23
Szurpiły Lake	1993.09.05	−10.0	4.82	n. a.	4.12
Warchały Lake	1993.09.06	0.0	79.39	−0.14	5.58
Wądołek Lake	1993.09.02	−5.5	2.12	n. a.	16.15
Wądołek Lake	1993.09.02	−6.5	1.95	n. a.	12.63
Wielki Staw Lake	1993.08.22	0.0	5.11	6.11	7.70
Wielki Staw Lake	1993.08.22	−4.0	4.26	8.55	6.49
Wielki Staw Lake	1993.08.22	−6.0	1.53	7.02	10.65
Wielki Staw Lake	1993.08.22	−21.5	3.69	7.22	7.00
Wigry Lake	1993.09.03	0.0	22.74	n. a.	2.64
Wigry Lake	1993.09.03	−2.8	23.34	2.15	n. a.
Wigry Lake	1993.09.03	−10.0	16.25	5.98	n. a.
Wigry Lake	1993.09.03	0.0	17.34	2.39	n. a.
Wigry Lake	1993.09.03	0.0	20.66	4.21	2.88
Wigry Lake	1993.09.03	−3.2	21.35	n. a.	2.83
Wigry Lake	1993.09.03	−10.0	23.46	2.48	n. a.
Wigry Lake	1993.09.03	−16.0	21.94	2.99	n. a.
Wigry Lake	1993.09.03	−27.0	17.71	3.84	2.20
Wigry Lake	1993.09.03	0.0	26.76	3.71	3.95
Wigry Lake	1993.09.03	0.0	20.18	n. a.	3.08
Wigry Lake	1993.09.03	0.0	22.13	3.07	3.02
Wigry Lake	1993.09.03	−3.0	26.06	2.73	1.70
Wigry Lake	1993.09.03	−7.5	21.26	2.17	4.16
Wisła River	1993.05.03	0.0	65.59	7.84	5.54
Wisła River	1993.08.31	0.0	71.18	9.09	n. a.
Wisła River	1993.09.07	0.0	78.24	7.40	6.75
Wisła River	1993?	0.0	58.82	9.72	6.45

n. a. – not analyzed