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Biological and environmental changes in Lake Baikal during the late Quaternary inferred from carbon, nitrogen and sulfur isotopes

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Abstract

An 8-m continuous sediment core, approximately 250-ky-old at the bottom, from Academician Ridge in Lake Baikal, has been analyzed for the stable isotopes of carbon, nitrogen and sulfur, in order to study the paleoclimatic and paleobiological changes that occurred in the Eurasian continental interior. These isotopic changes are closely related to changes in vertical lake-water circulation between glacial and interglacial periods. Sedimentary organic carbon in cool periods is more enriched in ^{13}C (-23.8% on average) than that in warm periods (-27.0% on average). The ^{13}C -enrichment of organic carbon suggests a decrease of land-derived organic matter influx to the lake, less precipitation, and loss of terrestrial vegetation around Lake Baikal in cool periods. Pyrite in high total sulfur/total organic carbon (TS/TOC) layers shows strong depletion in ^{34}S (-20.8% to -32.4%) during climate transitions from glacial to interglacial periods at the beginning of oxygen isotope stages (OIS) 1, 5 and 7. The ^{34}S -depleted pyrite indicates augmentation of dissimilatory sulfate reduction by sulfate reducing bacteria (SRB) at the sediment–water interface. Enhancement of aqueous sulfate concentrations and limitation of oxygen circulation to the surface sediments might also occur in the climate transition periods. The $\delta^{15}\text{N}$ values of total nitrogen increase abruptly by $\sim 2\%$ just after the $\delta^{34}\text{S}$ negative peaks, which may result from low nutrient concentrations in the euphotic zone associated with water circulation changes in Lake Baikal.

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1. Introduction

Lake Baikal is one of the oldest and largest lakes in the world. Over the age span of the lake, more

than 2000 species of organisms have evolved and currently live in the lake with two-thirds of them endemic. The limnological conditions of Lake Baikal must have been affected by both its tectonic history and the changes in the east Eurasian continental climate [1]. Paleoclimatic changes in the Eurasian continental interior have been well documented in the previous studies of sediment cores from Lake Baikal, which have been closely linked to changes in global paleoclimate [2,3]. These

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results have indicated that Milankovitch forcing equally affected climate in the east Siberia region over the past 12 My [4]. However, details of environmental changes in the lake, including past water circulation, geochemical cycles and ecosystem structure, are still largely unknown. For example, in the deepest part of modern Lake Baikal, the concentration of dissolved oxygen is approximately 9 mg/l, which suggests a large-scale vertical convection in the lake in spite of its great depth (1634 m in maximum) [5]. While the high dissolved oxygen concentration of the bottom waters in Lake Baikal must have contributed to the evolution of a diverse biota, the exact mechanism of this large-scale water ventilation remains unclear [6].

Most paleoclimate and paleoenvironmental investigations have centered on several proxies including stable isotopic compositions (e.g. carbon, oxygen, nitrogen and sulfur) in marine sediments [7,8]. In particular, the sulfur isotope record of marine sedimentary pyrite has proven to be a useful means for deducing the role of bacterial sulfate reduction in anoxic environments with the evaluation of the global sulfur cycle, type and availability of organic matter, and availability of sulfate [9]. In general, however, the marine isotope records do not necessarily reflect environmental variations related to the climates of continental interiors. Very few studies have been carried out on paleoredox conditions and sulfur cycles using the sulfur isotope signatures of both sulfate and sulfide in sediments from lakes, largely because of their low sulfate concentrations ($[\text{SO}_4^{2-}]$) in most freshwater systems. The normal range of $[\text{SO}_4^{2-}]$ in freshwater lakes is about 50–300 μM , with an average of about 110 μM [10]. The $[\text{SO}_4^{2-}]$ in modern Lake Baikal ($57.4 \pm 1.3 \mu\text{M}$, [11]) is relatively low compared to the reported values from other freshwater lakes around the world.

Earlier, Watanabe et al. [12] analyzed total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) concentrations as well as gamma ray density (GRD) in a sediment core, VER98-1 St.5, from Lake Baikal. The distributions of GRD (distinguishing between highly compacted glacial sediment and biogenic opal content), TOC and TN show similar variations, indicating that the core contains a continuous record from oxygen isotope stages (OIS) 1 to 7, over the past 250 ky [13]. In contrast, the TS distri-

bution does not correlate with the changes in GRD, TOC and TN. Most of the layers containing high concentrations of sulfur (up to 9 mg/g dry sed.) were observed in transition periods from cool to warm, or warm to cool. Fifteen thin layers with high TS/TOC ratios (0.2 to 0.5 atomic ratio) were observed, these ratios being much larger than the average TS/TOC ratios found in other freshwater (0.051) or normal oceanic marine sediment (0.13) [14].

Rabinovich and Grinenko [15] reported concentrations of sulfate and sulfur isotopic compositions in lake water from several Eurasian lakes. The $\delta^{34}\text{S}$ for sulfate in Lake Baikal were +7.1‰ to 7.8‰. The mean $\delta^{34}\text{S}$ value for sulfates in 22 large Eurasian rivers is +8.2‰, which is a commonly observed value for sulfates in the upper part of the earth's crust. The water in the Selenga River, the largest river flowing into Lake Baikal (50% of total river flow into the lake), has $[\text{SO}_4^{2-}]$ of 60 μM with $\delta^{34}\text{S}$ value of +5.7‰ to +6.9‰ [15]. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of phytoplankton have been studied in the present food webs in Lake Baikal [16]. Seasonal variations in the $\delta^{13}\text{C}$ for phytoplankton are small ($-28.0 \pm 1.1\%$, *Aulacoseira baicalensis*) presumably because of the large concentration of HCO_3^- in the system (66.5 mg/l). Similarly, no significant variation was found in $\delta^{15}\text{N}$ values for phytoplankton between April and August ($+4.2 \pm 0.6\%$).

In this paper, we describe 250-ky stable isotope records of TOC, TN, TS and reduced sulfur for a sediment core from Lake Baikal. The purpose of this study is to attempt to unravel the history of this lacustrine environment through its stable isotopic changes, particularly with respect to the biological activity related to paleoclimatic changes in the late Quaternary. Sulfur and nitrogen isotopic compositions of Lake Baikal sediments have not been reported before. These measurements will provide the means to further elucidate the influence of climate fluctuations upon important biogeochemical processes in the lake, past redox changes and large-scale vertical deep water circulation mechanisms.

2. Samples and analytical methods

A ~10-m piston core (VER98-1 St.5 PC) was taken in August 1998 from the Academician Ridge

(53°44'33"N; 108°24'35"W, water depth: 325 m), a relatively shallow area between the north and central basins of Lake Baikal. The sediment core was sliced every 1 cm. About 400 samples taken at every other 1 cm were freeze-dried and powdered. Subsequently, these samples were treated with 6 M HCl to remove carbonate [12]. Stable carbon isotopic compositions of total organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$) for the carbonate-free samples and bulk nitrogen isotopic compositions ($\delta^{15}\text{N}_{\text{TN}}$) were measured using an elemental analyzer (EA; FISON NA-1500) interfaced to an isotope ratio mass spectrometer (IRMS; Finnigan MAT delta-S) via a Finnigan MAT ConFlo II split interface. Carbon and nitrogen isotopic compositions were calibrated using an acetanilide ($\delta^{13}\text{C} = -25.9\text{‰}$ and $\delta^{15}\text{N} = +0.8\text{‰}$) and expressed in per mil (‰) relative to Vienna–Pee Dee belemnite (VPDB) and atmospheric nitrogen (AIR). Standard deviations of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements for sediment samples were generally less than $\pm 0.1\text{‰}$ and $\pm 0.3\text{‰}$, respectively.

For sulfur-rich layers, sediment samples were further treated with 12 M HCl/10 M HF (1:1 by volume) followed by organic solvent (methanol, dichloromethane and hexane) to provide a pyrite- and kerogen (solvent-insoluble and high-molecular organic matter)-enriched fraction to determine sulfur isotopic compositions of reduced sulfur (pyrite) [17]. The resulting residue was analyzed by X-ray diffraction (XRD). The 89 bulk sediments and 30 pyrite-enriched samples were combusted using an EA. The resultant SO_2 was collected from the effluent of the EA under liquid-nitrogen temperature, and purified in a vacuum line. Sulfur isotopic analysis was carried out using a Finnigan MAT delta-S mass spectrometer by a conventional dual inlet. Sulfur isotopic compositions of bulk sediment ($\delta^{34}\text{S}_{\text{TS}}$) and pyrite in the HCl/HF-treated samples ($\delta^{34}\text{S}_{\text{py}}$) were calibrated using an IAEA standard (silver sulfide, $\delta^{34}\text{S} = +0.3\text{‰}$) and expressed relative to Vienna–Cañon Diablo troilite (VCDT). Standard deviations of the $\delta^{34}\text{S}$ measurements were generally less than $\pm 0.5\text{‰}$. Samples of pyrite were analyzed for semi-quantitative elemental composition with SEM–EDS (Scanning electron microscope–energy dispersive spectrometer, JEOL, 8900R/RL). The bulk sediment samples were coated with Au. The microprobe measurements were made at 15 kV and 2×10^{-8} A probe current.

3. Results

Vertical distributions of concentrations of total organic carbon (TOC) and total nitrogen (TN), $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ are shown in Fig. 1 along with the time scale from the oxygen isotope stages (OIS) described by Imbrie et al. [13]. The concentrations of TOC and TN, and the OIS estimation were reported in the previous study [12].

3.1. $\delta^{13}\text{C}$ of total organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$)

The $\delta^{13}\text{C}_{\text{TOC}}$ values vary widely from -29.3‰ to -21.1‰ . During the past 250 ky, TOC was relatively higher in concentration and more depleted in ^{13}C during warm periods than in cool periods when the reverse was true. (Fig. 1). The mean $\delta^{13}\text{C}_{\text{TOC}}$ values for warm and cool periods are -27.0‰ and -23.6‰ , respectively. The depth profile of $\delta^{13}\text{C}_{\text{TOC}}$ is very similar to that of TOC (Fig. 1). However, the fluctuation of $\delta^{13}\text{C}_{\text{TOC}}$ between -27.4‰ and -21.8‰ during OIS 6.3 is larger relative to the fluctuation of TOC concentration (Fig. 1) than those observed in the last glacial. The $\delta^{13}\text{C}_{\text{TOC}}$ fluctuations from 0 to 50 cm in depth are similar to those found in another 1.2-m sediment core from Academician Ridge as measured by Horiuchi et al. [18], whose radiocarbon ages are used to date the present core. The abrupt $\delta^{13}\text{C}_{\text{TOC}}$ shift from -28.4‰ to -26.1‰ at 30 cm in depth corresponds to the Younger Dryas (YD) event, which is a millennial scale rapid cooling at the early stage of the Holocene (ca. 12 ky BP). The record of the YD event in sediment cores from Lake Baikal has been reported earlier in terms of photo-synthetic pigments [19].

3.2. $\delta^{15}\text{N}$ of total nitrogen ($\delta^{15}\text{N}_{\text{TN}}$)

$\delta^{15}\text{N}_{\text{TN}}$ values fluctuate between $+3.9\text{‰}$ and $+7.9\text{‰}$. Generally, TN is higher in concentration and more ^{15}N -depleted during warm periods, and lower in concentration and more ^{15}N -enriched during cool periods (Fig. 1). In particular, sediment layers in OIS 5.5 and early stage of OIS 1 are the most ^{15}N -depleted (minimum of $+3.9\text{‰}$). The depth profile of $\delta^{15}\text{N}_{\text{TN}}$ is similar to that of TN and TOC concentrations and $\delta^{13}\text{C}_{\text{TOC}}$ except the early stages of OIS 1, OIS 5.5 and 7.5. The mean $\delta^{15}\text{N}_{\text{TN}}$ values of warm

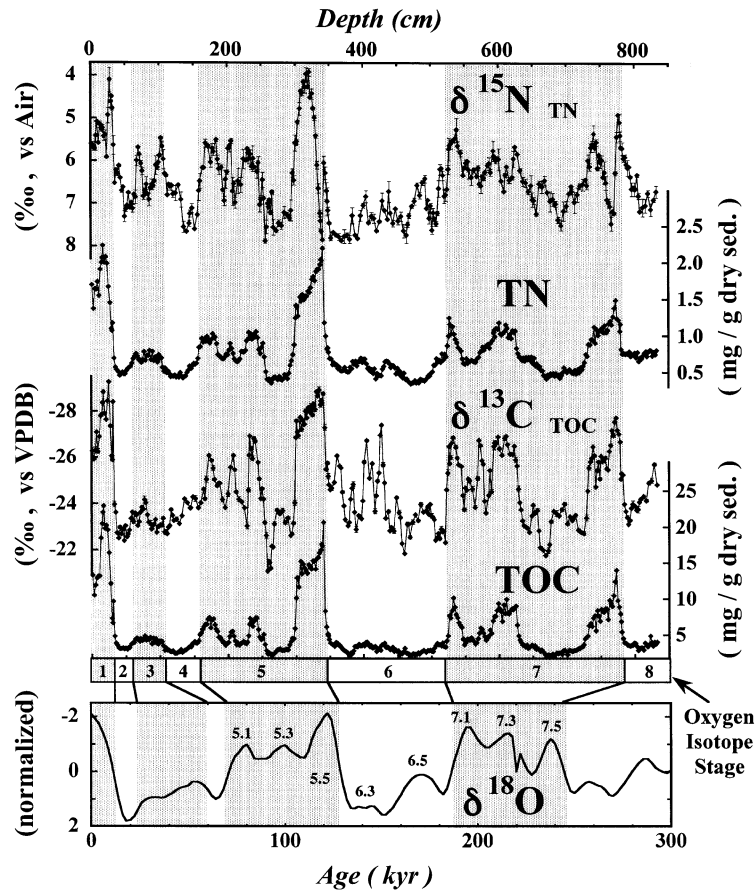


Fig. 1. Vertical distributions for $\delta^{15}\text{N}_{\text{TN}}$ and $\delta^{13}\text{C}_{\text{TOC}}$ in the VER98-1 St.5 piston core from Academician Ridge, Lake Baikal. Profiles of total organic carbon (TOC) and total nitrogen (TN) are from the same core [13], and the stacked, smoothed foraminiferal $\delta^{18}\text{O}$ record from open ocean sites as a function of age in the SPECMAP time scale are also shown for comparison [14]. Oxygen isotopic stages and substages are represented on the $\delta^{18}\text{O}$ profile. The shaded areas indicate layers of interglacial period.

and cool periods except during these three layers are $+5.5\text{‰}$ and $+6.7\text{‰}$, respectively. The $\delta^{15}\text{N}_{\text{TN}}$ shifts in these three anomalous layers at warm periods are distinctive from the shifts in the other parameters. These three layers have a similar $\delta^{15}\text{N}_{\text{TN}}$ -fluctuation pattern, where $\delta^{15}\text{N}_{\text{TN}}$ value decreases at the beginning of warming and then abruptly increases by $\sim 2\text{‰}$.

3.3. $\delta^{34}\text{S}$ of total sulfur ($\delta^{34}\text{S}_{\text{TS}}$) and pyrite sulfur ($\delta^{34}\text{S}_{\text{Py}}$)

The distribution of sulfur (TS) in the core, the $\delta^{34}\text{S}_{\text{TS}}$ values and TS/TOC atomic ratios are shown in

Fig. 2. This distribution of TS relative to TOC and TN appears to be more complicated. When these data are compared with the TS/TOC ratio, it is clear that there are many depths at which there appears to be a considerable excess of TS by a factor of 2 to 4 (labelled 1–15 in Fig. 2). The $\delta^{34}\text{S}_{\text{TS}}$ values vary markedly between -24.5‰ and $+32.4\text{‰}$, with major excursions below 0‰ occurring coincident with a few of the TS/TOC excursions in peaks 1, 6, 7 and 15. Most of the values of $\delta^{34}\text{S}_{\text{TS}}$ were closely constrained between $+15\text{‰}$ and -5‰ . Values of $\delta^{34}\text{S}_{\text{TS}} > +15\text{‰}$ occur when the value of TOC increases to a maximum during interglacials (300–340 and 520–600 cm in depth) The largest enrich-

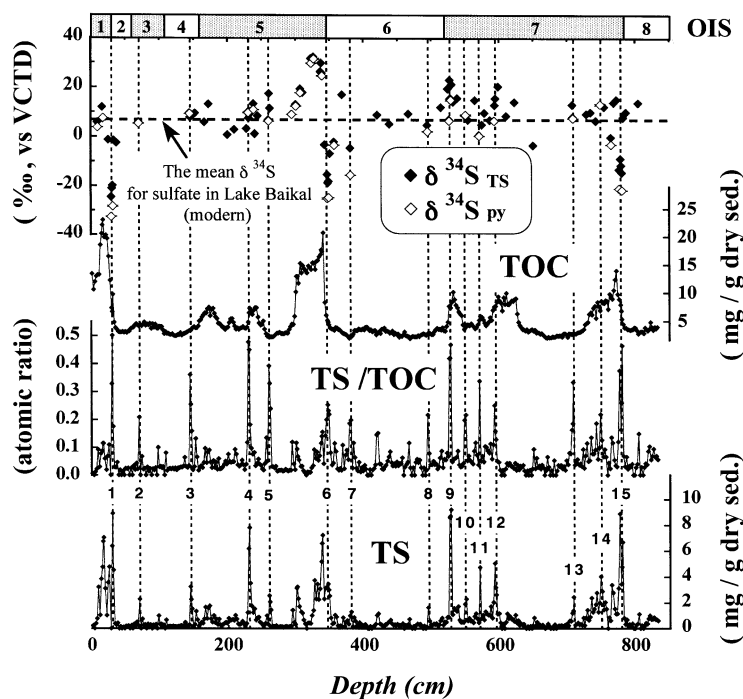


Fig. 2. Vertical distributions for $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$ in the VER98-1 St.5 piston core from Academician Ridge, Lake Baikal. The records from $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$ are shown as filled and open symbols, respectively. The horizontal dashed line in the $\delta^{34}\text{S}$ profile indicates the mean sulfur isotopic composition of aqueous sulfate in modern Lake Baikal [18]. The profiles of TOC, TS/TOC atomic ratio and total sulfur (TS) from the same core reported by Watanabe et al. [13] are also shown for comparison. The vertical dashed lines indicate layers with high TS/TOC atomic ratio (>0.2 ; peaks 1–15 [13]). Oxygen isotopic stages (OIS) are represented on the top of $\delta^{34}\text{S}$ profile.

ment ($\delta^{34}\text{S}_{\text{TS}} = +32.4\text{‰}$) is observed in the late stage of OIS 5.5 around 327 cm in depth. Sulfur isotopic compositions at the sediment water interface (10 to 18 cm in depth) are similar to those of modern sulfate in Lake Baikal water ($+7.8\text{‰}$, [15]). On the other hand, $\delta^{34}\text{S}_{\text{TS}}$ values in the YD event (~ 30 cm in depth) are

dramatically lower (-19‰ to -24‰). The ^{34}S -depleted total sulfur are found not only in the YD event but also in the layers at 348 and 780 cm in depth (-18.2‰ and -13.3‰ , respectively).

X-ray diffraction analysis indicates that pyrite is common in the HCl/HF-treated residues throughout

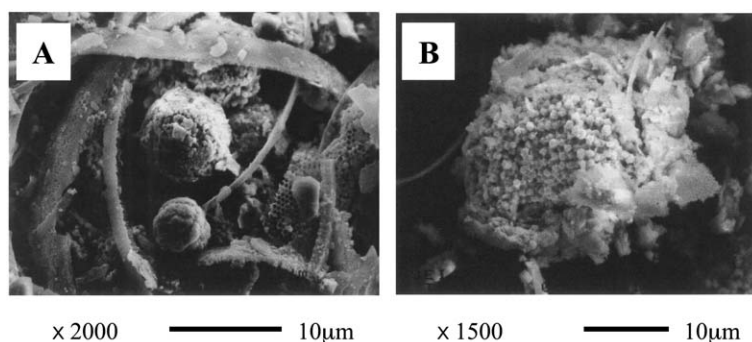


Fig. 3. Scanning electron micrographs of pyrite framboids from (A) 348-cm depth (peak 6 in Fig. 2) and (B) 547-cm depth (peak 9 in Fig. 2).

the sediment core. Sulfur-bearing minerals other than pyrite are seldom observed. Mass balance calculation of sulfur determined by EA indicates that sulfur in the HCl/HF-treated fractions is present as pyrite in the proportion of 39–90% of total sulfur. In addition, according to SEM–EDS analysis, the pyrite in 348 (peak 6) and 527 cm (peak 9) core depths is present as a framboid form (Fig. 3). The pyrite sulfur is generally similar or more isotopically depleted relative to total sulfur throughout the core. The difference between $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$ ($\Delta_{\text{TS-py}}$) is very small (-0.4‰ to $+2.6\text{‰}$, average $+0.7\text{‰}$) except in those layers having high S/C peaks 1, 6, 7 and 15. The $\Delta_{\text{TS-py}}$ values in these four layers range between $+6.3\text{‰}$ and $+9.6\text{‰}$, indicating that pyrite sulfur is extremely ^{34}S -depleted compared to bulk samples. The largest ^{34}S -depletion is observed in the layer corresponding to the Younger Dryas event ($\delta^{34}\text{S}_{\text{py}} = -32.4\text{‰}$).

4. Discussion

4.1. Paleoclimate and biological changes inferred from $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$

Differences in $\delta^{13}\text{C}_{\text{TOC}}$ values have been used to provide clues to the nature of the sources of sedimentary organic matter in lakes, because the two end-member values (autochthonous vs. allochthonous) differ significantly in their isotopic compositions [20,21]. The major sources of organic matter in sediments include planktonic algae (autochthonous) and terrestrially derived remnants of vegetation (allochthonous). The $\delta^{13}\text{C}_{\text{TOC}}$ value for modern dominant phytoplankton (diatoms) in Lake Baikal varies from -25‰ to -30‰ [16,22]. This range of $\delta^{13}\text{C}_{\text{TOC}}$ values is similar to that of typical $\delta^{13}\text{C}_{\text{TOC}}$ from C_3 plants. Terrestrial organic matter exhibits a wide $\delta^{13}\text{C}$ variation, depending on the photosynthetic pathways used by plants around watershed. C_3 plants generally have $\delta^{13}\text{C}$ values ranging from -32‰ to -20‰ ($\sim -27\text{‰}$ on average), whereas C_4 plants have values ranging between -17‰ and -9‰ ($\sim -14\text{‰}$ on average) [23]. Most C_4 plants are uncommon at temperature below 10 °C , because of their adaptation to dry climate and high temperature [24]. Although some C_4 plants such as *Muhlenbergia* sp. or *Spartina* sp. are found between 60 °N and 65

°N latitude in modern environments [23], compound specific isotope analysis suggests that the presence of C_4 -type vegetation has been negligible around Lake Baikal during the past 25 ky [25]. In contrast, the difference in $\delta^{13}\text{C}_{\text{TOC}}$ between cool and warm periods is up to $\sim 6\text{‰}$ ($\sim 3\text{‰}$ on average) in this study (Fig. 1) confirming either the dominance of C_3 plants in the region or autochthonous phytoplankton in the lake.

The relationship between $\delta^{13}\text{C}_{\text{TOC}}$ value and TOC concentration gives a logarithmic regression line ($r=0.88$; Fig. 4a). The $\delta^{13}\text{C}_{\text{TOC}}$ value of this study is negatively correlated with TOC/TN ratio ($r=0.80$; Fig. 4b). TOC/TN atomic ratios in cool periods are relatively low, ranging from 4.2 to 9.2 (6.7 on average; [12]). The low TOC/TN ratio suggests little supply of land-derived organic materials into lake, probably due to a decline in precipitation resulting in much less inputs of carbon from terrestrial vegetation. Therefore, variations in $\delta^{13}\text{C}_{\text{TOC}}$ are mainly controlled by input of terrestrial organic materials to Lake Baikal. The linear negative correlation between $\delta^{13}\text{C}_{\text{TOC}}$ and TOC/TN ratio confirms that ^{13}C -depleted organic matter in warm periods (-27.0‰ on average) is contributed by large amounts of terrestrial C_3 plants, and that dominant source of ^{13}C -enriched organic matter in cool periods (-23.6‰ on average) is planktonic algae.

The ^{13}C -enriched organic matter in cool periods could be caused by small isotopic fractionation characteristic of cyanobacteria during carbon fixation. The rubisco purified from cyanobacteria has been found to discriminate against ^{13}C by as little as 17.8‰ , and that from higher plants can range up to 29‰ [26,27]. A putative $\delta^{13}\text{C}_{\text{TOC}}$ of cyanobacteria ($\sim -24\text{‰}$) is similar to $\delta^{13}\text{C}_{\text{TOC}}$ values of sedimentary organic carbon during cool periods for Lake Baikal (-23.6‰ on average). Cyanobacteria blooms of up to 2×10^6 cells/ml are observed at the stratified water column in modern summer Lake Baikal [28]. The availability of CO_2 (aq) should be one of the major factors controlling carbon isotopic compositions of phytoplankton [29]. Diatom frustule (biogenic opal) abundance is negligible during glacial periods in Lake Baikal in the Quaternary [30]. The inorganic carbon-rich condition in Lake Baikal is due to chemical weathering of soils and rocks by runoff [11]. Low river inflow in cool period would result in decrease of

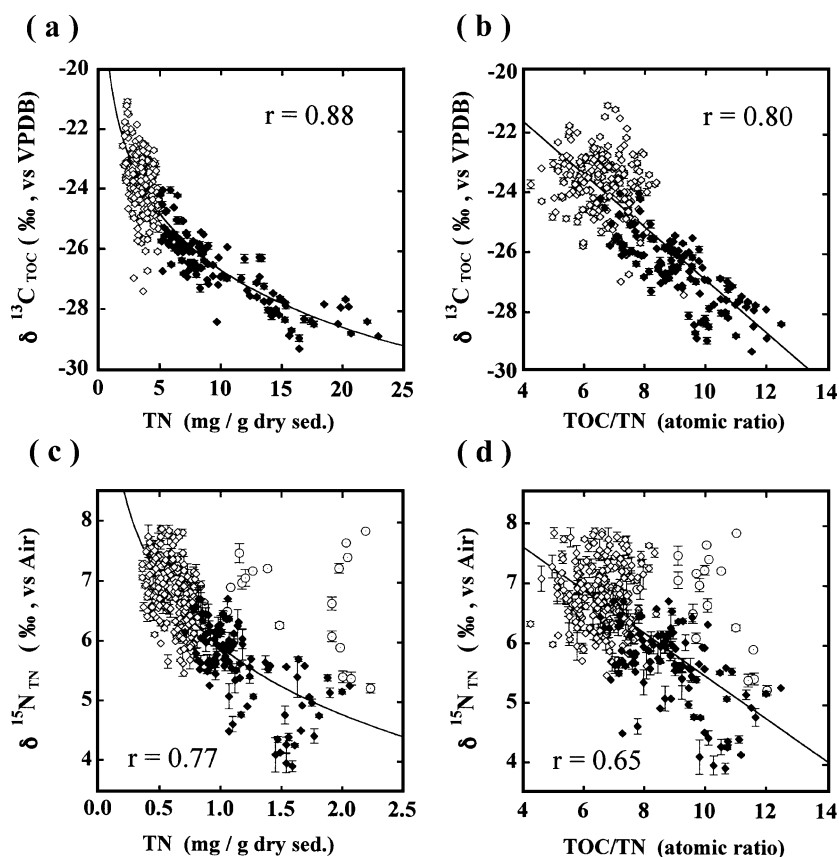


Fig. 4. Correlation plots of (a) TOC and $\delta^{13}\text{C}_{\text{TOC}}$, (b) TOC/TN and $\delta^{13}\text{C}_{\text{TOC}}$, (c) TN and $\delta^{15}\text{N}_{\text{TN}}$, (d) TOC/TN and $\delta^{15}\text{N}_{\text{TN}}$ for the VER98-1 St.5 piston core. The records from warm and cool periods are shown as filled and open diamonds, respectively. The open circles indicate anomalous $\delta^{15}\text{N}_{\text{TN}}$ layers in warm periods (see text).

bicarbonate supply from rivers. Therefore, growth of the ^{13}C -enriched phytoplankton might be associated with low CO_2 diffusion rates in comparison with photosynthetic CO_2 fixation in aquatic environments, which suppress carbon isotopic discrimination. Because of increase in CO_2 solubility by low temperature in surface water (approximately 2°C in summer, [31]) and low primary productivity (TOC < 5 mg/g dry sed.) in the cool periods, CO_2 limitation is not likely in Lake Baikal. Hence, the $\delta^{13}\text{C}_{\text{TOC}}$ value of $\sim -24\text{‰}$ is likely derived from cyanobacteria.

In OIS 6.3, the $\delta^{13}\text{C}_{\text{TOC}}$ change from -27.4‰ to -21.8‰ is coincident with a change of TOC/TN atomic ratio from 5.5 to 9.3 [12]. TOC and TN concentrations in the OIS 6.3 (up to 4 and 0.7 mg/g dry sed., respectively) are similar to those in the OIS 3 warm period (Fig. 1). Additionally, pollen and bio-

genic silica concentration (diatom abundance) in OIS 6.3 slightly increased in the Academician Ridge sediment core [3,32]. Therefore, ^{13}C -depleted organic matter in OIS 6.3 could be derived from terrestrial organic matter attributable to the increase of humidity and slight amelioration of climate conditions around Lake Baikal.

Generally, $\delta^{15}\text{N}_{\text{TN}}$ has negative correlations with TN (Fig. 4c) and TOC/TN (Fig. 4d). However, the variation in the $\delta^{15}\text{N}_{\text{TN}}$ values tend to have a larger fine-structure than seen in the TN values. Excluding the data from three unusual layers in warm periods (early stages of OIS1, 5.5 and 7.5, see above, Figs. 1 and 4c), correlation coefficients between TN and $\delta^{15}\text{N}_{\text{TN}}$, TOC/TN and $\delta^{15}\text{N}_{\text{TN}}$ are 0.77 and 0.65, respectively. The more random nature of the $\delta^{15}\text{N}_{\text{TN}}$ values, particularly during the warm periods, suggests

that environmental factors controlling $\delta^{15}\text{N}_{\text{TN}}$ are more complex than those controlling $\delta^{13}\text{C}_{\text{TOC}}$. Many processes can influence the isotopic composition of bulk sedimentary nitrogen [21,33]. The dominant factors controlling $\delta^{15}\text{N}$ are: (1) the source of organic matter (allochthonous or autochthonous); (2) the $\delta^{15}\text{N}$ of nitrate assimilated by phytoplankton from lake water; (3) the extent of the kinetic isotope effect in nutrient uptake by phytoplankton; (4) denitrification; (5) nitrogen fixation; and (6) diagenesis. Nevertheless, as shown in Fig. 5, a weak positive correlation is observed between $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ ($r=0.64$). This relationship has been usually interpreted as mixing between terrestrial and lacustrine sources of organic matter, providing that terrestrial and lacustrine organic matter are depleted and enriched in both ^{13}C and ^{15}N , respectively [21].

Typically, the source of nitrogen for terrestrial plants is by nitrogen fixation in root nodules of legumes, and from direct deposition in rain. Hence, land-derived organic matter is less depleted in ^{15}N (-7‰ to $+2\text{‰}$, [34,35]) than organic matter of phytoplankton in Lake Baikal ($+4.2 \pm 0.6\text{‰}$), a value very close to the $\delta^{15}\text{N}$ value of nitrate in Selenga River [16]. Post-depositional degradation of sedimentary organic matter is characterized by an enrichment in ^{15}N due to preferential release of isotopically lighter N_2 [36]. However, this diagenetic effect is likely to be similar through the core, because most of $\delta^{15}\text{N}_{\text{TN}}$ variations in general parallel the other

chemical and isotopic parameters (Fig. 1). The conclusion from the variations in $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}_{\text{TN}}$ is that the dominant source of relatively ^{15}N -depleted organic matter in warm periods ($+3.9\text{‰}$ to $+6.2\text{‰}$) is terrestrial plants, while that of more ^{15}N -enriched organic matter in cool periods ($+5.5\text{‰}$ to $+7.9\text{‰}$) is due to phytoplankton growth in the lake. The importance of the three unusual layers of $\delta^{15}\text{N}_{\text{TN}}$ in warm periods will be discussed later in Section 4.3.

4.2. Redox depositional changes inferred from $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$

Near the sediment surface of Lake Baikal, the $\delta^{34}\text{S}_{\text{TS}}$ value ($+5.7\text{‰}$ to $+11.9\text{‰}$ from 10 to 16 cm) is close to modern sulfate $\delta^{34}\text{S}$ values in the lake water ($+7.1\text{‰}$ to $+7.8\text{‰}$, [15]). For most samples, no significant difference between $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$ is observed (Table 1). This observation is explained by diagenetic pyrite formation in a ‘closed’ or ‘semi-closed’ system under low sulfate concentrations. The sulfate concentration in modern Lake Baikal water is low (ca. $50\ \mu\text{M}$, see above), so the depth of effective sulfate diffusion into sediments is much lower compared to marine sediments. Consequently, sulfate reduction by sulfate reducing bacteria (SRB) in freshwater sediments is sulfate-limited. Although anaerobic decomposition of organic matter may be promoted by methanogenesis, high rates of bacterial sulfate reduction have been observed in surface sediments of freshwater lakes [37]. As a result, the $\delta^{34}\text{S}$ value of resultant sulfide is close to that of initial sulfate due to rapid dissimilatory sulfate reduction under sulfate-limiting conditions. In this case, the sedimentary $\delta^{34}\text{S}_{\text{TS}}$ record indicates not only temporal changes in $\delta^{34}\text{S}$ of sulfate, but also variations in sulfate concentration in the lake over time.

Extreme ^{34}S -depletion (down to -32.4‰) is observed at high TS/TOC peaks in OIS layers 1, 5, 6 and 15 (Fig. 2). A large difference between $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$ is also observed in these four layers (Table 1). As shown in Fig. 6a, two sulfur isotopic behaviors are distinguished using a plot of $\delta^{34}\text{S}_{\text{TS}}$ vs. $\delta^{34}\text{S}_{\text{py}}$. In the ^{34}S -enriched group (open circles in Fig. 6), $\delta^{34}\text{S}_{\text{TS}}$ is equal to $\delta^{34}\text{S}_{\text{py}}$. In contrast, $\delta^{34}\text{S}_{\text{py}}$ is lower by 7.7‰ relative to $\delta^{34}\text{S}_{\text{TS}}$ in the ^{34}S -depleted group (filled circles in Fig. 6). This result indicates that ^{34}S -enriched components coexist in these four layers.

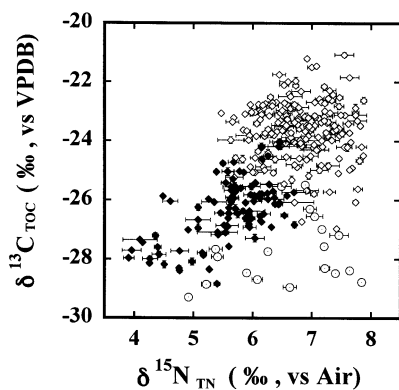


Fig. 5. A correlation plot of $\delta^{15}\text{N}_{\text{TN}}$ and $\delta^{13}\text{C}_{\text{TOC}}$ for the VER98-1 St.5 piston core. The records from warm and cool periods are shown as filled and open diamonds, respectively. The open circles indicate anomalous $\delta^{15}\text{N}_{\text{TN}}$ layers in warm periods (see text).

Table 1

Chemical characteristics and isotopic compositions in sulfur-rich layers in the Lake Baikal sediment core

Depth (cm)	TOC (mg/g dry sed.)	TS (mg/g dry sed.)	$\delta^{34}\text{S}_{\text{TS}}$ (‰, vs VCDT)	$\delta^{34}\text{S}_{\text{py}}$ (‰, vs VCDT)	$\delta^{34}\text{S}_{\text{sol}}$ (‰, vs VCDT)	$\Delta_{\text{sol-py}}$ (‰, vs VCDT)
10	13.18	3.23	5.7	4.1	10.5	6.4
18	22.96	7.06	8.3	7.8	9.6	1.8
30	7.31	6.40	-24.5	-32.4	-3.8	28.6
32	9.68	4.54	-19.9	-28.1	25.2	53.3
70	4.12	2.03	5.8	5.6	7.4	1.8
144	3.39	3.26	9.6	9.6	9.6	0.0
230	4.86	6.20	9.9	10.1	9.7	-0.4
238	6.97	1.53	13.4	11.3	20.1	8.8
260	2.45	2.57	6.8	6.6	7.2	0.6
294	4.51	1.44	9.1	9.1	9.5	0.4
300	10.16	3.15	13.1	12.7	14.2	1.5
307	15.25	1.28	19.4	18.1	20.6	2.5
323	14.18	1.02	31.7	30.1	36.5	6.4
327	15.27	3.75	32.4	31.9	33.8	1.9
339	17.42	7.24	25.7	25.1	27.0	1.9
347	5.14	5.48	-15.3	-24.9	17.9	42.8
349	4.36	2.55	-18.2	-24.5	26.6	51.1
357	3.44	1.05	-2.1	-3.1	2.0	5.1
381	2.47	1.31	-7.6	-15.3	9.3	24.6
494	2.82	1.64	-4.8	2.5	9.3	6.8
526	7.67	8.60	6.9	6.8	7.4	0.6
528	7.35	9.21	15.7	15.2	16.7	1.5
550	3.94	2.29	8.5	8.2	10.5	2.3
570	5.25	4.74	0.7	0.7	1.0	0.3
593	7.55	5.06	6.6	6.8	6.3	-0.5
709	2.75	2.45	8.0	7.9	8.1	0.2
749	6.91	4.04	13.1	13.5	12.9	-0.6
765	9.37	3.39	-0.2	-2.8	5.2	8.0
777	8.88	8.09	-13.3	-20.8	4.2	25.0
781	5.40	6.69	-14.6	-21.5	38.3	59.8

The shaded areas indicate layers with extremely ^{34}S -depleted sulfur compound.

The $\delta^{34}\text{S}$ value of sulfur components soluble in HCl/HF-organic solvent ($\delta^{34}\text{S}_{\text{sol}}$) is calculated using the simple mass balance equations as follows:

$$\delta^{34}\text{S}_{\text{TS}} = \delta^{34}\text{S}_{\text{py}}f_{\text{py}} + \delta^{34}\text{S}_{\text{sol}}f_{\text{sol}} \quad (1)$$

$$f_{\text{py}} + f_{\text{sol}} = 1 \quad (2)$$

$$\Delta_{\text{sol-py}} = \delta^{34}\text{S}_{\text{sol}} - \delta^{34}\text{S}_{\text{py}} \quad (3)$$

where f_{py} and f_{sol} are the fraction of pyrite sulfur (including kerogen-bound sulfur) and sulfur soluble in HCl/HF-organic solvent, respectively. Sulfur components soluble in HCl/HF-organic solvent include sulfates, iron monosulfide, elemental sulfur and organic sulfur except kerogen-bound sulfur.

The $\Delta_{\text{sol-py}}$ value in the four layers ranges from 24.6‰ to 59.8‰, being larger than that of other layers (Table 1). The four layers probably contain sulfate and organic sulfur compounds produced by assimilatory sulfate reduction. It is reported that the isotopic fractionation associated with sulfate assimilation is small ($\delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{organic-S}} = 0.9 - 2.8$ ‰) [38]. However, original organic sulfur compounds would decompose during early diagenesis. The extremely low $\delta^{34}\text{S}$ layers in Lake Baikal have relatively low TOC concentrations (<10 mg/g dry sed. in Fig. 6b), indicating that incorporation of organic sulfur compounds is not important. On the other hand, it is likely that abundant sulfates have been supplied to the four layers. The $\Delta_{\text{sol-py}}$ values decrease abruptly in the ^{34}S -depleted layers, even though $\delta^{34}\text{S}_{\text{py}}$ still holds

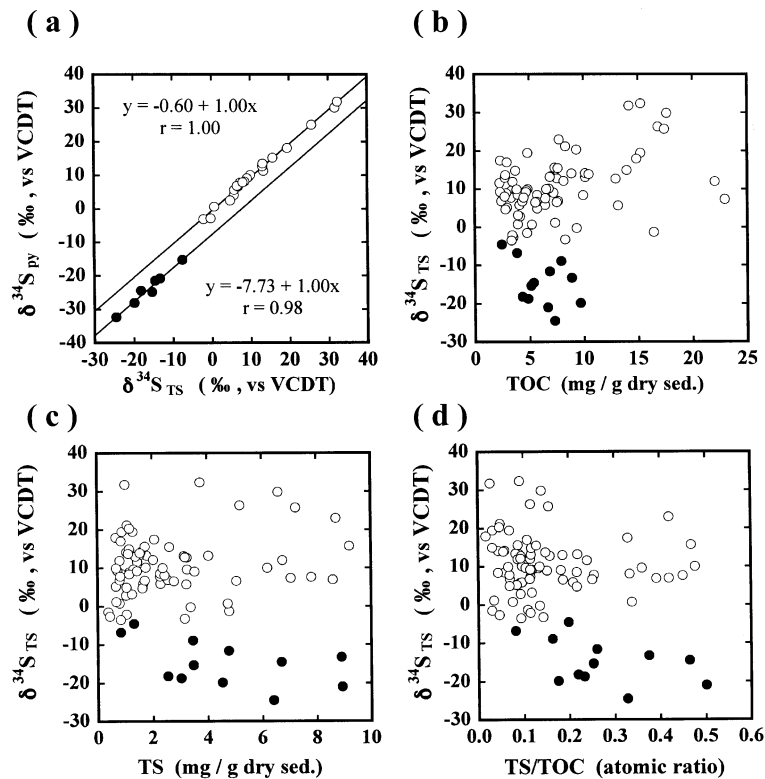


Fig. 6. Correlation plots of (a) $\delta^{34}\text{S}_{\text{TS}}$ and $\delta^{34}\text{S}_{\text{py}}$, (b) TOC and $\delta^{34}\text{S}_{\text{TS}}$, (c) TS and $\delta^{34}\text{S}_{\text{TS}}$, (d) TS/TOC and $\delta^{34}\text{S}_{\text{TS}}$ for the VER98-1 St.5 piston core. The isotopically heavy and light groups are shown as filled and open circles, respectively (see text).

smaller values (Table 1). For example, pyrite at 30-cm depth shows large ^{34}S -depletion (-32.4‰). The $\Delta_{\text{sol-py}}$ value decreases by 25 ‰ at 32–30-cm depth, indicating that loss of ^{34}S -enriched sulfate occurred and $\delta^{34}\text{S}$ of iron monosulfide and elemental sulfur have an effect on $\delta^{34}\text{S}_{\text{sol}}$ values. Probably the sulfate enhancement occurred very rapidly. In contrast, $\delta^{34}\text{S}_{\text{sol}}$ values of other layers are very close to $\delta^{34}\text{S}_{\text{py}}$ ($\Delta_{\text{sol-py}} = -0.6\text{‰}$ to $+8.0\text{‰}$, $+2.5\text{‰}$ on average), indicating that no sulfate remained.

In the modern watershed of Lake Baikal, a lithogenic sulfur contribution by surface runoff and groundwater input is the main source of sulfate in the lake water. An increase in sulfate concentrations in the lake is possibly due to enhancements of tectonic activity. For example, the sulfate concentrations of Lake Tanganyika have risen because of tectonic activity [39]. However, large-scale tectonic activity in the transition periods from glacial to interglacial around the Lake Baikal is not likely. Rather, an abrupt

increase in precipitation followed by weathering of soils could occur within less than 300 years at the beginning of the Bølling–Allerød warm phase [40]. Therefore, sulfate concentrations in the transition periods from glacial to interglacial could increase rapidly by wetter climate with warming. As shown in Fig. 2, enhancements of TS concentration and $\Delta_{\text{sol-py}}$ values occurred within a few centimeters in sediment depth (ca. 1000 years).

The extreme ^{34}S -enrichment in OIS 5.5 ($+19.4\text{‰}$ to $+31.9\text{‰}$ at 307 to 339 cm) is of particular interest. One interpretation is that $\delta^{34}\text{S}$ of lakewater sulfate in OIS 5.5 was isotopically heavier. Half of modern Lake Baikal water comes from surface runoff of the Selenga River [41]. Sulfate of the modern Selenga River ($+5.7\text{‰}$ to $+6.9\text{‰}$) is a little depleted in ^{34}S relative to sulfate in Lake Baikal ($+7.1\text{‰}$ to $+7.8\text{‰}$). However, $\delta^{34}\text{S}$ values of sulfate in the Lena River vary widely from $+2.8\text{‰}$ to $+32.0\text{‰}$. [15]. High $\delta^{34}\text{S}$ (up to $+32.0\text{‰}$) values are typical for Cambrian

evaporites in the Siberian platform [15]. This suggests a substantial contribution of sulfate to the Lena River from groundwater. The sulfur isotopic composition of lake water sulfate is unlikely to remain constant over lake history, because of drastic changes of paleoenvironment and tectonic changes of lake watersheds [42]. In particular, the lake water level rose 120 to 150 m above the present level in ca. 200 ky ago, because the lake became a closed reservoir as a result of uplifting in the Pre-Baikalye area [42]. The age of modern Angara River is approximately 50 to 60 ky based on geomorphological data and molecular biology studies of gammarid population around its mouth [43]. Therefore, ^{34}S -enriched sulfate could gradually accumulate with increasing erosion of the Cambrian evaporates, and with increasing of underground water input during expansion of lake surface area.

Another possible interpretation involves sulfate or sulfide diffusion, advection and reaction in a semi-closed system after burial, as seen in sapropel at Mediterranean [44]. The ^{34}S -enrichment of sulfide in 307–339 cm involves a high TOC concentration (up to 17.4 mg/g dry sed.). Assuming that diagenetic formation of pyrite in the organic-rich layers is Fe-limited, excess HS^- is able to migrate downwards as sulfides. This results in the formation of pyrite below organic-rich layers by reaction of this HS^- with solid-phase Fe^{3+} , and Fe^{2+} diffusing upwards. Consequently, pyrite with ^{34}S -depleted and high TS/TOC ratio can occur in and below the organic-rich layers under sulfate-rich conditions [44]. In this study, the ^{34}S -enrichment (up to +31.9‰) with organic-rich layers occurs just above the high TS/TOC layer (peak 6 in Fig. 2). Therefore, downward migration of sulfidization is not likely, indicating that sulfates in the Lake Baikal became ^{34}S -enrichment in the early OIS 5.5.

Only four layers (peaks 1, 5, 6 and 15 in Fig. 2) show obvious ^{34}S -depletion among 15 S-rich layers with high TS/TOC ratios. There is no correlation between $\delta^{34}\text{S}_{\text{TS}}$ and TS, and $\delta^{34}\text{S}_{\text{TS}}$ and TS/TOC ratio through the core (Fig. 6c and d). This observation suggests that factors controlling pyrite formation are different in each high TS/TOC layer. Pyrite formation is ultimately limited by: (1) sulfate concentration; (2) concentration and availability of organic matter to SRB; (3) concentration and reactivity of iron; (4) the oxygen concentration in bottom

water; and (5) availability and type of oxidants [9,45]. In the ^{34}S -enriched group shown as open circles in Fig. 6, sulfate is likely limited. In contrast, TOC concentration of the ^{34}S -depleted group (filled circles in Fig. 6) is relatively low (less than 10 mg/g dry sed.). The amount of organic matter could limit dissimilatory sulfate reduction in the ^{34}S -depleted group.

The ^{34}S -depletion during the climate transition suggests early pyrite formation in an ‘open’ system. Therefore, most of the pyrites in these sediments were formed at the sediment–water interface. The occurrence of anoxic SRB activity near the sediment surface indicates restriction of oxygen supply to the deeper parts of the lake. Large-scale water circulation in the lake could weaken in the climate transition periods. Sulfate concentrations in the lake water may also increase by seasonal redox changes near the sediment surface. SRB activity and pyrite formation could be promoted by arrest of deep water circulation, and increase of primary productivity in summer. Although oxygen and sulfate transport into deep water and pyrite oxidation are promoted by weak water circulation with ice melting in spring, repetition of these events may limit oxygen invasion into the deeper part of Lake Baikal. As a result, gradual accumulation of sulfate followed by high TS with the large ^{34}S -depletion of sulfide by SRB could occur in the climate transitions.

4.3. Environmental changes in the transitions from glacial to interglacial periods

Expanded plots of $\delta^{15}\text{N}_{\text{TN}}$, TOC/TN ratio, $\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{34}\text{S}_{\text{py}}$ and $\delta^{34}\text{S}_{\text{TS}}$ for 0–50, 280–400 and 730–820 cm, corresponding to the three climate transition periods from glacial to interglacial, are shown in Fig. 7. As the TOC/TN values start to increase and $\delta^{13}\text{C}_{\text{TOC}}$ decrease, the $\delta^{15}\text{N}_{\text{TN}}$ changes occur. First, ^{15}N becomes more depleted followed immediately by an abrupt shift to ^{15}N -enrichment, almost coincident with strong ^{34}S -depleted sulfide. The $\delta^{15}\text{N}_{\text{TN}}$ decrease could be result from N_2 fixation by cyanobacteria or a larger kinetic isotope effect during nitrate uptake of phytoplankton under high nutrient supply conditions in the lake.

In contrast, low nutrient conditions in euphotic zone lead to the $\delta^{15}\text{N}_{\text{TN}}$ increase. As discussed

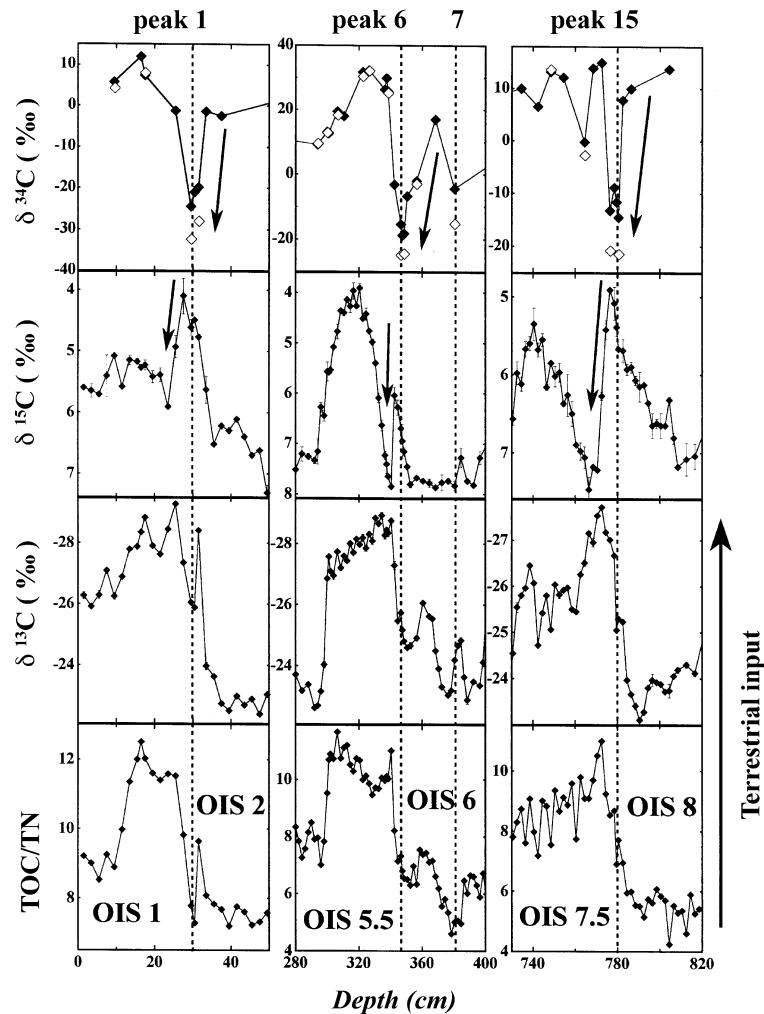


Fig. 7. Vertical distributions for $\delta^{34}\text{S}$, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ and TOC/TN atomic ratio from the VER98-1 St.5 piston core plotted on an expanded scale from Figs. 1 and 2. The dashed lines indicate the layers with high TS/TOC atomic ratio (peaks 1, 6, 7, and 15). Peak 1 corresponds to the Younger Dryas event (YD). Oxygen isotopic stages (OIS) are shown on the TOC/TN atomic ratio profiles. The arrows on the $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$ profiles indicate anomalous changes during climate transition periods (see text).

before, the extremely ^{34}S -depleted pyrite could be formed under less oxic conditions at sediment–water interface in the climate transition, while the oxic/anoxic changes depend on large scale deep-water circulation characteristics of Lake Baikal [46]. Hence, these three unusual $\delta^{15}\text{N}_{\text{TN}}$ shifts in the climate transitions could be caused by the following mechanisms: (1) weakness of deep-water circulation followed by the decrease of oxygen transport into deeper water resulting in less oxic conditions near the surface sediment; (2) enhancement of sulfate reduc-

tion by SRB in an open system at the water–sediment interface (^{34}S -depleted pyrite); (3) suppression of nitrate transport from deep water to the euphotic zone; and (4) shift to ^{15}N -enrichment of particulate organic nitrogen. Gradual changes in ^{15}N -depletion by 0.8–3.5‰ are observed just after an abrupt increase of $\delta^{15}\text{N}_{\text{TN}}$. Because TS still maintains its high concentration in these layers (up to 7.3 mg/g dry sed., Fig. 2), the $\delta^{15}\text{N}_{\text{TN}}$ values most likely reflect relatively low ventilation in Lake Baikal deep-water after $\delta^{34}\text{S}$ negative peaks.

Deep-water circulation and redox changes in the lake could occur at least three times in the climate transition periods (high TS/TOC of peaks 1, 6 and 15 in Figs. 2 and 7). The large scale deep-water circulation may have been initiated by higher salinity water inflow from the Selenga River [46]. The layers of peak 1 (Younger Dryas) and 6 show large TOC/TN decreases though peak 15 has a small TOC/TN decrease. The TOC/TN decrease indicates low influx with high salinity from the Selenga River resulting in probable deep water circulation. The TOC/TN decrease in the peak 15 is small and short-lived, but a larger change might be observed by much higher resolution analysis. The approximate ages of peaks 1, 6 and 15 are 12, 128 and 245 ky, respectively [12,47]. Change of the drainage system in Lake Baikal by impacts of tectonic activity and consequent effect on deep-water circulation is unlikely, because approximate ages for the formation of the Angara River mouth and formation of the closed system associated with tectonic activity are estimated to be 60 and 200 ky, respectively [42]. Instead, the systematic variations of $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$ indicate climate-related formation of less oxic conditions in Lake Baikal.

5. Conclusions

Variations in stable isotopic compositions of TOC, TN, TS and pyrite sulfur in the Lake Baikal sediment core are interpreted as proxies for climatic and environmental changes that can be of local, regional, and even global significance. $\delta^{13}\text{C}_{\text{TOC}}$ fluctuations suggest that the predominant source of organic matter into the sediment changed from allochthonous to autochthonous in response to global climate changes over the past 250 ky. Terrestrial C3 higher plants and phytoplankton such as cyanobacteria were the dominant organic source in warm and cool periods, respectively. Rapid $\delta^{34}\text{S}_{\text{py}}$ decreases at climate transition periods suggest that active sulfate reduction by SRB occurred at the water–sediment interface in the transition from cool to warm periods. This result implies that the $[\text{SO}_4^{2-}]$ increase and less oxic conditions took place in the climate transition periods. The rapid increase of precipitation with warming could give rise to the $[\text{SO}_4^{2-}]$ increase in the lake. The decrease of dissolved oxygen concentrations at sediment surface

could be caused by the weakening of deep water ventilation. Also, $\delta^{15}\text{N}_{\text{TN}}$ excursions suggest low vertical mixing and low nutrient condition in these periods. Fluctuations of lake water circulation and depositional conditions correspond to global climatic and environmental changes.

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References

- [1] M.G. Grosswald, Late Weichselian ice sheet of northern Eurasia, *Quat. Res.* 13 (1980) 1–32.
- [2] Lake Baikal Paleoclimate Project Members, Initial results of U.S.–Soviet paleoclimate study of Lake Baikal, *Eos Trans. AGU* 73 (1992) 457–462.
- [3] S.J. Carter, S.M. Colman, Biogenic silica in Lake Baikal sediments: results from 1990–1992 American cores, *J. Great Lakes Res.* 20 (1994) 751–760.
- [4] K. Kashiwaya, S. Ochiai, H. Sakai, T. Kawai, Orbit-related long-term climate cycles revealed in a 12-Myr continental record from Lake Baikal, *Nature* 410 (2001) 71–73.
- [5] R.F. Weiss, E.C. Carmack, V.M. Koropalov, Deep-water renewal and biological production in Lake Baikal, *Nature* 349 (1991) 665–669.
- [6] F. Peeters, R. Kipfer, R. Hohmann, M. Hofer, D.M. Imboden, G.G. Kodenev, T. Khozder, Modeling transport rates in Lake Baikal: gas exchange and deep water renewal, *Environ. Sci. Technol.* 31 (1997) 2973–2982.
- [7] S.E. Calvert, B. Nielsen, M.R. Fontugne, Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels, *Nature* 359 (1992) 223–255.
- [8] T.W. Lyons, Sulfur isotopic trends and pathways of iron sul-

- fide formation in upper holocene sediments of the anoxic black sea, *Geochim. Cosmochim. Acta* 61 (1997) 3367–3382.
- [9] J.W.M. Wijisman, J.J. Middelburg, P.M.J. Herman, M.E. Böttcher, C.H.R. Heip, Sulfur and iron speciation in surface sediments along the northwestern margin of the black sea, *Mar. Chem.* 74 (2001) 261–278.
- [10] R.G. Wetzel, *Limnology: Lake and River Ecosystems*, third edition, Academic Press, New York, 2000, pp. 289–330.
- [11] K.K. Falkner, C.I. Measures, S.E. Herbelin, J.M. Edmond, R.F. Weiss, The major and minor element geochemistry of Lake Baikal, *Limnol. Oceanogr.* 36 (1991) 413–423.
- [12] T. Watanabe, H. Naraoka, M. Nishimura, M. Kinoshita, T. Kawai, High-resolution organic carbon, nitrogen and sulfur distributions of the Lake Baikal sediment over the past 250 kyr, *Geochem. J.* 37 (2003) 439–502.
- [13] J. Imbrie, J.D. Hays, D.G. Martinson, A. McIntyre, A.C. Mix, J.J. Morley, N.G. Pisias, W.L. Prell, N.J. Shackleton, The orbital theory of Pleistocene climate: support from a revised chronology of the marine 18O record, in: A. Berger, J. Imbrie, J. Hays, G. Kulka, B. Saltzman (Eds.), *Milankovitch and Climate, Part I*, Reidel, Boston, 1984, pp. 269–305.
- [14] R.A. Berner, Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance, *Am. J. Sci.* 282 (1982) 451–473.
- [15] L. Rabinovich, V.A. Grinenko, Sulfate sulfur isotope ratios for USSR river water, *Geochem. Int.* 16 (1979) 68–79.
- [16] K. Yoshii, N.G. Melnik, O.A. Timoshkin, N.A. Bondarenko, P.N. Anoshko, T. Yoshioka, E. Wada, Stable isotope analyses of the pelagic food web in Lake Baikal, *Limnol. Oceanogr.* 44 (1999) 502–511.
- [17] Y. Watanabe, H. Naraoka, D.J. Wronkiewicz, K.C. Condie, H. Ohmoto, Carbon, nitrogen and sulfur geochemistry of Archean and Proterozoic shales from the Kaapvaal Craton, South Africa, *Geochim. Cosmochim. Acta* 61 (1997) 3441–3459.
- [18] K. Horiuchi, K. Minoura, K. Hoshino, T. Oda, T. Nakamura, T. Kawai, Paleoenvironmental history of Lake Baikal during the last 23000 years, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 157 (2000) 95–108.
- [19] Y. Tani, K. Kurihara, F. Nara, N. Itoh, M. Soma, Y. Soma, A. Tanaka, M. Yoneda, M. Hirota, Y. Shibata, Temporal changes in the phytoplankton community of the southern basin of Lake Baikal over the last 24,000 years recorded by photosynthetic pigments in a sediment core, *Org. Geochem.* 33 (2002) 1621–1634.
- [20] P.A. Meyers, Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes, *Org. Geochem.* 27 (1997) 213–250.
- [21] S. Huon, F.E. Grousset, D. Burdloff, G. Bardoux, A. Mariotti, Sources of fine-sized organic matter in North Atlantic Heinrich Layers: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ tracers, *Geochim. Cosmochim. Acta* 66 (2002) 223–239.
- [22] N.O. Ogawa, K. Yoshii, N.G. Melnik, N.A. Bondarenko, O.A. Timoshkin, N.S. Smirnova-Zalumi, V.V. Smirnov, E. Wada, Carbon and nitrogen isotope studies of the pelagic ecosystem and environmental fluctuations of Lake Baikal, in: K. Minoura (Ed.), *Lake Baikal: A Mirror in Time and Space for Understanding Global Change Processes*, Elsevier, 2000, pp. 262–272.
- [23] A.G. Schwarz, R.E. Redman, C_4 grasses from the boreal forest region of northwestern Canada, *Can. J. Bot.* 66 (1987) 2424–2430.
- [24] W. Larcher, H. Bauer, Ecological significance of resistance to low temperature, in: O.L. Lange, P.S. Nobel, C.B. Osmond, H. Ziegler (Eds.), *Physiological Plant Ecology I: Responses to the Physical Environment*, Springer-Verlag, Berlin, Heidelberg, 1981, pp. 403–437.
- [25] D. Brinca, K. Yamada, R. Ishiwatari, H. Uemura, H. Naraoka, Molecular-isotopic stratigraphy of long-chain *n*-alkanes in Lake Baikal Holocene and glacial age sediments, *Org. Geochem.* 31 (2000) 287–294.
- [26] R.D. Guy, M.L. Fogel, J.A. Berry, Photosynthetic fractionation of the stable isotopes of oxygen and carbon, *Plant Physiol.* 101 (1993) 37–47.
- [27] S. Sakata, J.M. Hayes, A.R. McTaggart, R.A. Evans, K.J. Leckrone, R.K. Togasaki, Carbon isotope fractionation associated with lipid biosynthesis by a cyanobacterium: relevance for interpretation of biomarker records, *Geochim. Cosmochim. Acta* 61 (1997) 5379–5389.
- [28] T. Nagata, K. Takai, K. Kawanobe, D. Kim, R. Nakazato, N. Guselnikova, N. Bondarenko, O. Monogawara, T. Kostrova, V. Drucker, Y. Satoh, Y. Watanabe, Autotrophic picoplankton in southern Lake Baikal: abundance, growth and grazing mortality during summer, *J. Plankton Res.* 16 (1994) 945–959.
- [29] E.A. Laws, B.N. Popp, R.R. Bidigare, M.C. Kennicutt, S.A. Macko, Dependence of phytoplankton carbon isotopic composition on growth rate and $[\text{CO}_2]_{\text{aq}}$: theoretical considerations and experimental results, *Geochim. Cosmochim. Acta* 59 (1995) 1131–1138.
- [30] S.M. Colman, J.A. Peck, E.B. Karavanov, S.J. Carter, J.P. Bradbury, J.W. King, D.F. Williams, Continental climate response to orbital forcing from biogenic silica records in Lake Baikal, *Nature* 378 (1995) 769–771.
- [31] M.N. Shimaraev, N.G. Granin, A.A. Zhadanov, Deep ventilation of Lake Baikal waters due to spring thermal bars, *Limnol. Oceanogr.* 38 (1993) 1068–1072.
- [32] T. Oda, K. Minoura, C. Fujimura, T. Nakamura, T. Kawai, Vegetation history of the Baikal drainage basin during the last 250,000 years, *Jpn. J. Palynol.* 46 (2000) 81–92.
- [33] G.H. Haug, T.F. Pedersen, D.M. Sigman, S.E. Calvert, B. Nielsen, L.C. Peterson, Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr, *Paleoceanography* 13 (1998) 427–432.
- [34] E. Wada, Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments, in: Y. Horibe, E.D. Goldberg, K. Samuhashi (Eds.), *Isotope Marine Chemistry*, Uchida Rokakuho, Tokyo, 1980, pp. 375–398.
- [35] E.-D. Schulze, F.S. Chapin III, G. Gebauer, Nitrogen nutrition and isotope differences among life forms at the northern tree-line of Alaska, *Oecologia* 100 (1994) 406–412.
- [36] M.F. Lehmann, S.M. Bernasconi, A. Barbieri, J.A. McKenzie, Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis, *Geochim. Cosmochim. Acta* 66 (2002) 3573–3584.

- [37] N.R. Urban, P.L. Brezonik, L.A. Baker, L.A. Sherman, Sulfate reduction and diffusion in sediments of Little Rock Lake, Wisconsin, *Limnol. Oceanogr.* 39 (1994) 797–815.
- [38] I.R. Kaplan, S.C. Rittenberg, Microbiological fractionation of sulphur isotopes, *J. Gen. Microbiol.* 34 (1964) 195–212.
- [39] B.F. Jones, C.J. Bowser, The mineralogy and related chemistry of lake sediments, in: A. Lerman (Ed.), *Lakes—Chemistry, Geology, Physics*, Springer-Verlag, New York, 1978, pp. 179–235.
- [40] E.P. Chebykin, D.N. Edgington, M.A. Grachev, T.O. Zheleznyakova, S.S. Vorobyova, N.S. Kulikova, I.N. Azarova, O.M. Khlystov, E.L. Goldberg, Abrupt increase in precipitation and weathering of soils in East Siberia coincident with the end of the last glaciation (15 cal kyr BP), *Earth Planet. Sci. Lett.* 200 (2002) 167–175.
- [41] L.M. Sorokovikova, T.V. Khodzher, V.N. Sinyukovich, L.P. Golobokova, N.D. Bashenkhaeva, O.G. Netavetaeva, Atmospheric and riverine input of nutrients and organic matter into Lake Baikal, in: K. Minoura (Ed.), *Lake Baikal: A Mirror in Time and Space for Understanding Global Change Processes*, Elsevier, 2000, pp. 236–246.
- [42] V.D. Mats, S. Fujii, K. Mashiko, E.Y. Osipov, I.M. Yefimova, A.V. Klimansky, Changes in the Lake Baikal levels and runoff direction in the Quaternary period, in: K. Minoura (Ed.), *Lake Baikal: A Mirror in Time and Space for Understanding Global Change Processes*, Elsevier, 2000, pp. 15–34.
- [43] K. Mashiko, R. Kamaltynov, H. Morino, D.Y. Sherbakov, Genetic differentiation of gammarid (*Eulimnogammarus cyaneus*) populations in relation to past environmental changes in Lake Baikal, in: K. Minoura (Ed.), *Lake Baikal: A Mirror in Time and Space for Understanding Global Change Processes*, Elsevier, 2000, pp. 262–272.
- [44] H.F. Passier, J.J. Middelburg, B.J.H. van Os, G.J. De Lange, Diagenetic pyritisation under eastern Mediterranean sapropels caused by downward sulphide diffusion, *Geochim. Cosmochim. Acta* 60 (1996) 751–763.
- [45] R.T. Wilkin, H.L. Barnes, Pyrite formation in an anoxic estuarine basin, *Am. J. Sci.* 297 (1997) 620–650.
- [46] R. Hohmann, R. Kipfer, F. Peeters, G. Piepke, D.M. Imboden, M.N. Simaraev, Processes of deep-water renewal in Lake Baikal, *Limnol. Oceanogr.* 42 (1997) 841–855.
- [47] H. Oda, K. Nakamura, K. Ikehara, T. Nakano, M. Nishimura, O. Khlystov, Paleomagnetic record from Academician Ridge, Lake Baikal: a reversal excursion at the base of marine oxygen isotope stage 6, *Earth Planet. Sci. Lett.* 202 (2002) 117–132.