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Glacial-interglacial changes in organic carbon, nitrogen and sulfur accumulation in Lake Baikal sediment over the past 250 kyr

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The waters of modern Lake Baikal circulate well and maintain oxic conditions for the entire lake in spite of its great depth. Past oxic/anoxic conditions in the water column are not known. Because reconstruction of paleo-redox conditions involved with climate changes provides information on dynamics of lake water circulation and biological activity, high-resolution analyses of total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) concentrations, and gamma ray density (GRD) were carried out using 492 sediment samples over the past 250 kyr (every other 1 cm from the 10 m core Ver98-1 St.5 taken from the Academician Ridge at 325 m water depth). Fifteen events of high TS/TOC ratio (>0.2 atomic) are observed; these are much larger than TS/TOC ratio of typical freshwater sediment (0.001–0.070) and also normal oxic marine sediments (0.13 in average). The sulfur occurs as pyrite by X-ray diffraction (XRD) analysis, probably being produced by sulfate-reducing bacteria (SRB). Such high TS/TOC ratios indicate high SRB activity in the lake and a high input of sulfate to the lake. A high TS/TOC layer often accompanies a decrease of TOC/TN ratio to *ca*. 5 (atomic). In particular, during a rapid cooling such as the Younger Dryas event, the TOC/TN ratio decreases steeply from 10.4 to 7.8 just prior to the increase of TS/TOC ratio from 0.02 to 0.55. Because the low TOC/TN ratio suggests low terrestrial organic matter contribution to the lake, saline water inflow from rivers could diminish to result in decreased water circulation in the lake. The rapid cooling event may restrict deep-water ventilation and create less oxic conditions in Lake Baikal.

INTRODUCTION

A number of studies on sediment core samples from Lake Baikal have been reported since 1992. Paleoclimatic changes in the Eurasian continental interior have been well documented in the Baikal core sediments, which have a linkage with global paleoclimatic changes (e.g., Lake Baikal Paleoclimate Project Members, 1992; Carter and Colman, 1994; Kashiwaya *et al*., 2001). Lake Baikal sediment is a significant and unique subject for paleoenvironmental investigations in the continent. The Lake Baikal sediment also provides important clues that reveal variations in biological activity in the continental interior with respect to the climatic changes. For example, pollen analysis shows 57 alternations between forest taiga and subarctic desert around Lake Baikal during the past 5 million years (Kawamuro *et al*., 2000).

In modern Lake Baikal, more than 2000 biological species exist partly because the whole water body is completely oxygenated in spite of

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****Present address: Graduate School of Environmental Studies, Nagoya University, 1 Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan* its great depth (1634 m, Fryer, 1991). In the deepest part of lake, dissolved oxygen occurs at *ca*. 9 mg/l (Weiss *et al*., 1991), suggesting large-scale vertical convection in the lake. The mean residence time of major ions in the lake is estimated to be 330 years (Falkner *et al*., 1991). Nevertheless deep water exchanges rapidly. Weiss *et al*. (1991) showed that the renewal time of the bottom water is *ca*. 8 years. The mechanism of modern large-scale of water ventilation remains unclear. Spring thermal bars, which are large, long-lived thermal and density fronts separating regions of water bodies having temperatures above and below that of maximum density, may play a significant role for sinking of water (Shimaraev *et al*., 1993). However, the thermal bar process has been reported to be effective only to 200–300 m water depth (Peeters *et al*., 1996; Granin *et al*., 2000). Circulation by river inflow involved with ice melting has also been proposed by Hohmann *et al*. (1997), in which bottom water in southern slope of Selenga delta (Kukui Canyon) had "high salinity (increasing from 95 to 107 mg/kg), increase of turbidity flow (low light transmission) and dissolved oxygen concentration" immediately after ice melting. Furthermore, Peeters *et al*. (1996) suggested that the Academician Ridge, the boundary between the northern and central basins, played an important role in formation of northern basin deep-water, because northern basin water has relatively low salinity compared to the central and southern basins, which are gradually more saline with increasing depth. While the water body of the central basin has relatively higher salinity due to Selenga River discharge, that of the northern basin has a relatively lower salinity by dilution from the upper Angara River. Consequently, a high saline water body with low temperature from the central basin encounters the northern basin water mass below 50 m water depth at the Academician Ridge and is found in deeper parts of the northern basin (Hohmann *et al*., 1997). However, a discrepancy still remains in salt mass balance (Peeters *et al*., 1997).

In contrast to the modern oxygenated water body of Lake Baikal, past redox changes of water column have not yet been clarified. Although a large number of marine paleo-redox changes have been studied, lacustrine paleo-redox changes, especially for large-continent interior, have not been often reported. For marine sediments, sulfur concentration has often been used to infer anoxia (Raiswell and Berner, 1985; Leventhal, 1982). This is because sulfide (mostly as pyrite) formation by sulfate-reducing bacteria (SRB) is promoted under anoxic conditions (Berner, 1984; Wilkin and Barnes, 1997). Also as for lake sediments, total sulfur concentration and its ratio to total organic carbon (TS/TOC) may be a paleo-redox proxy because of accumulation of excess sulfur relative to organic carbon under euxinic condition (Davison *et al*., 1985). Sulfur concentrations have been reported from seventeen short core samples in Lake Baikal (47–8790 ppm, Takamatsu *et al*., 2000). However, mechanism of sulfur distributions in sediments and relation to lake environments have not been elucidated. In this study, we carried out high-resolution elemental analyses of organic carbon, nitrogen and sulfur to infer past oxic/anoxic conditions and to reconstruct the dynamics of lake water circulation and biological activity in Lake Baikal over the past 250 kyr.

SEDIMENT SAMPLE AND METHODS

A 9.96 m piston core (Ver98-1 St.5 PC) and 1.9 m pilot core (Ver98-1 St.5 TW) were taken from the Academician Ridge, Lake Baikal (53°44′33″ N, 108°24′35″ W; water depth, 325 m) in August 1998. The sediment core was stored at 4°C until analysis. The lowest 1.7 m of the Ver98-1 St.5 piston core was disturbed, based on flow-in structure, and was not used for this study. Academician Ridge is isolated from direct fluvial or downslope sedimentation, and therefore little or no turbidity complicates recovery of a continuous sediment core (Peck *et al*., 1994; Colman *et al*., 1995). In previous studies, two long cores (*ca*. 200 m and 600 m) were drilled at BDP-96 and BDP-98, respectively, from the Academician Ridge. Some important climate and environment

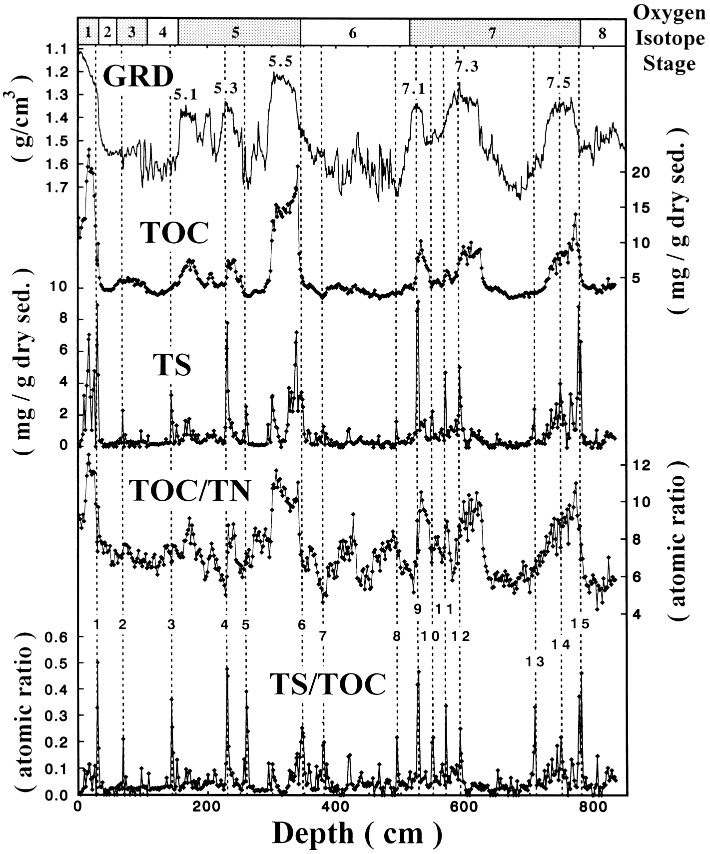

Fig. 1. Down core variations for gamma ray density (GRD), total organic carbon (TOC), total sulfur (TS), atomic TOC/TN ratio and atomic TS/TOC ratio in the Ver98-1 St.5 piston core from the Academician Ridge. The dashed lines indicate the obvious increasing layers of atomic TS/TOC ratio (>0.2; peak 1–15). Oxygen isotopic stages (OIS) are shown on the top, and substages are shown on the GRD profile (after Imbrie et al., 1984).

changes have been reported using these long sediment cores (Kawamuro *et al.*, 2000; Kashiwaya *et al.*, 2001).

Attenuation of gamma rays through the sediment core (Gamma Ray Density) was determined using a Multi Sensor Core Logger (GEOTEC, UK). Gamma ray exposure was performed for 5 seconds at 5 mm intervals. The analytical error is less than 1% in duplicate analyses. Gamma ray density (GRD) was calculated using the following equation (Weber *et al.*, 1997).

$$\text{GRD} \times \text{thickness} = a - b \times \ln \text{(gamma count rates)}.$$

Calibration coefficients a and b were determined by measuring actual densities every 20 cm and calculated at each depth. The pilot core sample was not available for this measurement because of insufficient hardness of sediment facies.

The sediment samples were taken at every other 1 cm, and their outer rims were removed to avoid contamination. The discrete samples were freeze-dried and powdered. Total sulfur (TS), total nitrogen (TN), total carbon concentrations were determined using an elemental analyzer (NA-1500, FISONS). After acid treatment with 6 M HCl, total organic carbon (TOC) was determined on the carbonate free samples. The acid treatment was performed as following. Several drops 6 M HCl were added to about 100 mg dried sample,

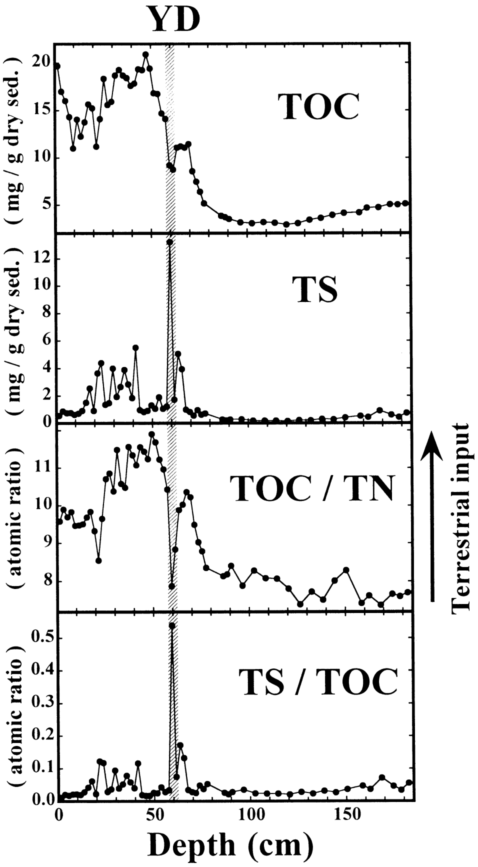

Fig. 2. Down core variations for TOC, TS, atomic TOC/TN ratio and atomic TS/TOC ratio in the Ver98-1 St.5 pilot core from the Academician Ridge. The shaded area denotes the layer of Younger Dryas event (YD).

which were left in HCl vapor for 2 days. Subsequently the samples were transferred to a desiccator containing NaOH pellets for 5 days to remove HCl. Finally the acid-treated sample was freeze-dried for complete removal of water. The concentrations were calibrated using an organic compound standard (2,5-Bis-(5-tert-butyl-benzoxazol-2-yl)-thiophene). The analytical standard deviations of TS, TN and TOC were less than 5%, 2% and 2%, respectively. The samples with high TS concentrations were treated with excess 6 M HCl followed by 12 M HCl/10 M HF (1/1 by volume) to dissolve silica and clay minerals. The resulting residue was analyzed by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

Vertical profiles of the physical and chemical properties for the piston and pilot cores are shown in Figs. 1 and 2, respectively. GRD varies between 1.09 and 1.75 g/cm^3. The physical properties such as density, porosity and P-wave velocity have been used as a facies indicator (Schulz *et al.*, 1998; Weber *et al.*, 2001). These physical properties for Lake Baikal sediment mainly reflect the ratio of terrigenous clastic materials and authigenic biogenic opal, corresponding to glacial-interglacial cycles (Oda *et al.*, 2002). A high abundance of diatom frustules causes low sediment density during interglacial periods (1.34 g/cm^3 in average from this study). In contrast, a low abundance of diatom frustules causes high sediment density during glacial periods (1.56 g/cm^3 in average from this study). Oda *et al.* (2002) revealed that the oxygen isotope stages (OIS) correlated well with the biogenic opal record from Lake Baikal. Based on the correlation including one anchor point (Brunhes/Matsuyama boundary), this age model suggests a time difference within a few thousand years between age dating by density profile and actual age. GRD distributions in this study are consistent with the previous reports of biogenic opal contents for Lake Baikal (Carter and Colman, 1994; Peck *et al.*, 1994; Baikal Drilling Project BDP96 (LegII) Members, 1997). Density changes in the piston core revealed that the Ver98-1 St. 5 core contains OIS 1–7, corresponding to approximately the past 250 kyr (after Imbrie *et al.*, 1984).

TOC concentration ranges from 1.9 to 22.0 mg/g dry sediment. The TOC variation is consistent with previous studies on core sediments from the Academician Ridge, northern and southern basins (Ishiwatari *et al.*, 1992; Horiuchi *et al.*, 2000), which clearly show glacial-interglacial cycles. During warm periods, high TOC values indicate enhancement of primary production by greater delivery of soil-derived nutrients into lake and large supply of land-derived organic matter into lake by climate humidification. Because atomic TOC/TN ratios are relatively high (up to 12.5), major source of organic carbon is terrestrial higher plants in warm periods. Ishiwatari *et al.* (1992)

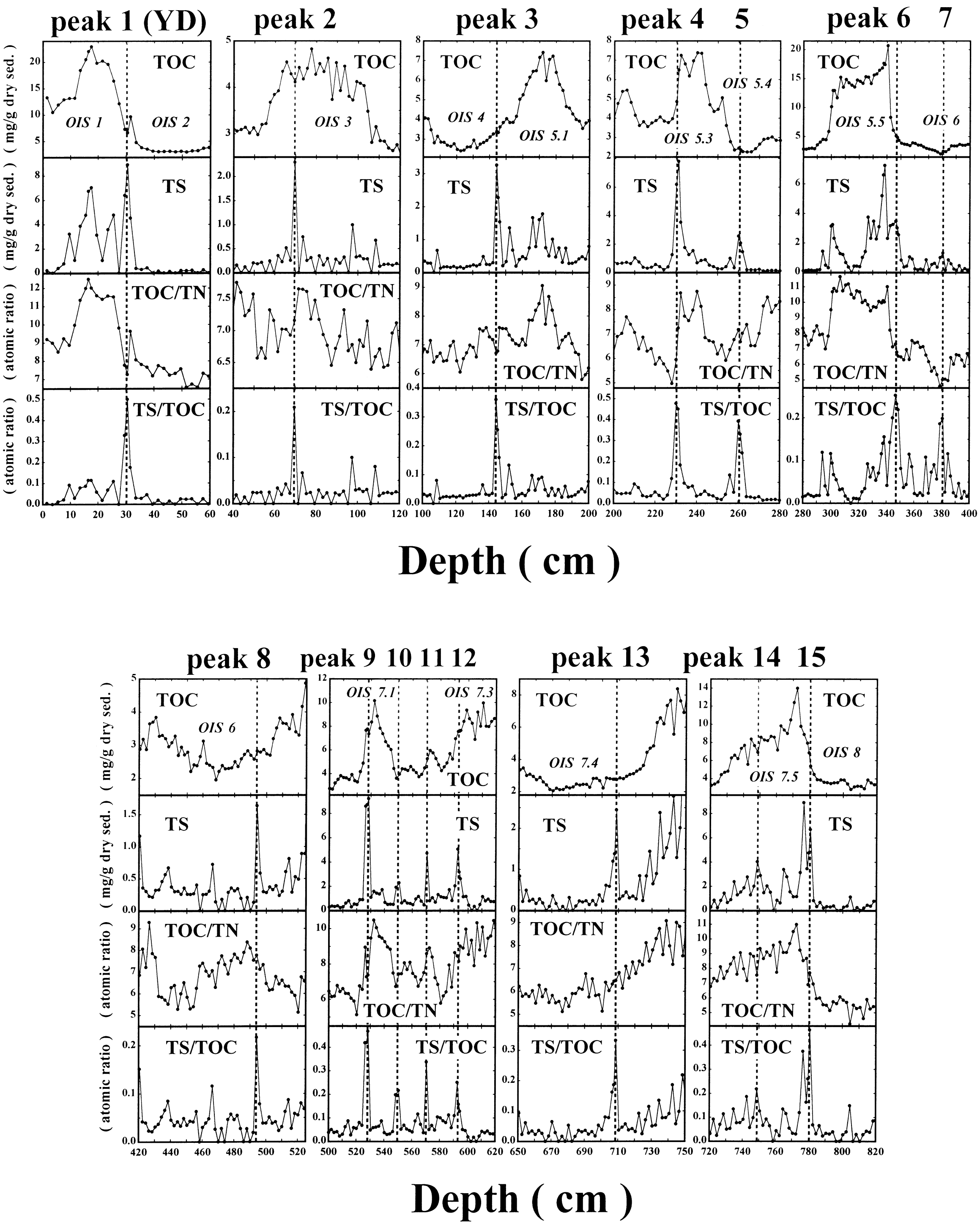

Fig. 3. Down core variations for TOC, TS, atomic TOC/TN ratio and atomic TS/TOC ratio from the VER98-1 St.5 piston core plotted on an expanded scale from Fig. 1. The dashed lines indicate the obvious increasing layers of atomic TS/TOC ratio (peaks 1–15). Peak 1 corresponds to Younger Dryas event (YD). OIS are shown on the TOC profiles.

and Yamamoto and Ishiwatari (1995) also suggested increasing flux of allochthonous organic materials relative to autochthonous organic materials in warm periods by stable carbon isotope analyses and biomaker analyses, respectively. As also reported by Yamamoto and Ishiwatari (1995) and Horiuchi *et al.* (2000), an abrupt decrease of TOC concentration (11.5 to 7.8 mg/g dry sed.) at 60 cm depth in the pilot core (Fig. 2) is observed; this feature corresponds to the Younger Dryas event (11–12 kyr by AMS ^{14}C dating, Tani *et al.*, 2002). An abrupt increase of TS (from 0.2 to 13.2 mg/g dry sed.) and atomic TS/TOC (from 0.02 to 0.55) is observed during the Younger Dryas, which is accompanied by a rapid decrease of atomic TOC/TN (from 10.4 to 7.8, Fig. 2). Similarly, at least fifteen TS/TOC increases (including Younger Dryas event, peak 1 in Fig. 3) are recognized in the piston core sediment mostly during TOC/TN decrease periods (peaks 1, 2, 3, 4, 6, 7, 9, 10 and 14 in Figs. 1 and 3) or starting points of TOC/TN decrease (peaks 5, 11 and 12 in Figs. 1 and 3).

As shown in Fig. 4, TOC-TS plot in modern environments represent a positive correlation with an average TS/TOC slope of 0.13 for oxic normal marine sediments and with an average TS/TOC slope of 0.051 for freshwater sediments under low sulfate concentrations (Berner, 1982). The TS/TOC slope becomes much larger (*ca.* 0.3) in sediments under euxinic condition (Raiswell and Berner, 1985). In addition, the TOC-TS correlation sometimes crosses at a positive value of TS axis. This is because sulfate reduction occurs in the anoxic water column by SRB (Raiswell and Berner, 1985). The fifteen high S events are plotted in a TS/TOC > 0.13 region shown as filled triangles in Fig. 4. Evidently, the TS/TOC ratios of high S concentration layers are high compared to the TS/TOC ratios of freshwater and normal marine sediments (Fig. 4). XRD analysis of acid-treated samples indicates that the sulfur in the sediments occurs mostly as pyrite. Considering the high S concentration (up to 13.4 mgTS/g dry sed.) and the TS/TOC ratios up to 0.55, the fifteen high TS/TOC events may be due to the formation of pyrite by high SRB activity and high supply of sulfate at the near surface sediment (possibly in the water column) under anoxic depositional conditions. In contrast, other high sulfur concentration layers are observed in OIS 5.5 (325–340 cm, 2.3–7.2 mgTS/g dry sed.) and in the subsurface layer (10–25 cm, 1.1–7.1 mgTS/g dry sed.). These two high sulfur concentration layers have low TS/TOC ratios (0.02–0.16), probably because of sulfate reduction in the sediment during early diagenesis.

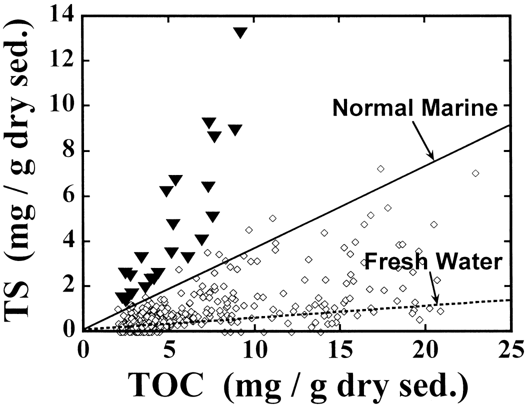

Fig. 4. Plot of TS vs. TOC for the Ver98-1 St.5 sediment core. The records from obvious increasing layers of atomic TS/TOC ratio and other layers are shown as filled triangle and open diamond shape, respectively. Solid and dashed line indicate the regression line from normal marine (oxygenated bottom water) and freshwater, respectively (after Berner, 1984).

Autochthonous organisms such as algae and bacteria provide organic matter with low atomic TOC/TN ratio (*ca.* 4–9), because N-containing compounds such as amino acids and proteins are relatively abundant in algae and bacteria. In Lake Baikal, the TOC/TN ratios of autotrophic picoplankton and heterotrophic bacteria are 4.6 and 4.7, respectively (Nagata *et al.*, 1994). In contrast, terrigenous higher plants provide allochthonous organic matter with high TOC/TN ratios (>*ca.* 20) because of abundant N-free organic matter such as lignin and cellulose. In this study, the C-N slope of cool periods (4.4) is lower than that of warm periods (10.9), as shown in Fig. 5. The C-N slope of Ver98-1 St.5 sediment core

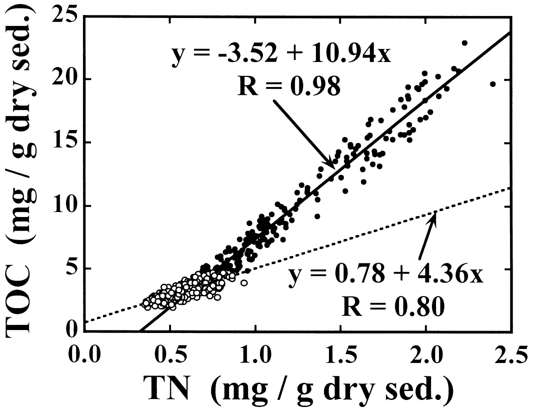

Fig. 5. Relationship between TOC and TN for the Ver98-1 St.5 sediment core. The records from layers of cool periods and warm periods are shown as open circles and filled circles, respectively.

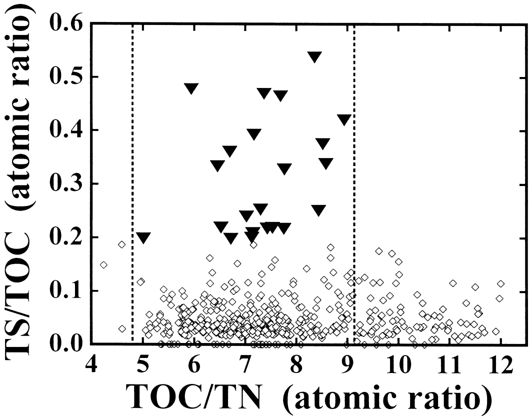

Fig. 6. Plot of atomic TS/TOC ratio vs. atomic TOC/TN ratio for the Ver98-1 St.5 sediment core. The records from obvious increase layers of atomic TS/TOC ratio and other layers are shown as filled triangle and open diamond shape, respectively. Dashed lines indicate the TOC/TN data range for less oxic condition periods in this study (see text).

reveals different modes of organic contribution (autochthonous or allochthonous) in response to climate changes. This TOC/TN ratio difference suggests that the abrupt TOC/TN decrease is a result of the decrease of river influx to the lake caused by freezing of surface water and/or decrease of precipitation. In addition, as shown in an TS/TOC - TOC/TN plot (Fig. 6), the high TS/TOC layers are observed in the area of relatively low TOC/TN ratios (between 4.8 and 9.2). This result suggests that the decrease of inflow from rivers is one of the factors for decrease of large-scale lake water circulation that provides adequate dissolved oxygen into the deeper parts of Lake Baikal. TOC concentration is not so low (about 8 mg/g dry sed.) in the Younger Dryas, so organic production in surface waters continued even during cooling periods. The supply of organic matter consumes dissolved oxygen in the water column, as well as limiting the rate of bacterial sulfate reduction (Wijsman *et al.*, 2001).

Academician Ridge may be a key location to infer the mechanism of redox changes in Lake Baikal. This is because the central basin deep-water body flows to northern basin over the Academician Ridge to form the northern basin deep-water body (Peeters *et al.*, 1996; Hohmann *et al.*, 1997). Our study reveals occurrence of less oxic conditions in cooling periods at the Academician Ridge over the last 250 kyr, which also suggests that deep-water ventilation in Lake Baikal had stopped or extremely weakened during cooling. Rapid and dynamic fluctuations in depositional conditions as well as water circulation systems must be caused by river inflows with different saline concentrations, probably supplied by Selenga River.

Changes to less oxic conditions associated with the minimal supply of land-derived organic matter are mainly observed in transition periods from cool to warm periods (peaks 1, 5, 6, 10 and 15 in Fig. 3) and from warm to cool periods (peaks 4, 9, 11 and 12 in Fig. 3). However, this phenomenon is not observed at all transition periods. For example, TS/TOC peaks in the transition period of OIS from 7.4 to 7.3 (642–645 cm) are not observed. Instead of a high TS/TOC peak in this case, vivianite was found in the low TOC/TN layer of transition period of OIS from 7.4 to 7.3. This may be attributable to sulfate limitation available to bacterial reduction in lake water. Thus the supply of sulfate to the lake should be another factor in controlling SRB activity in the lake. The increase of TS/TOC ratio is sometimes recognized without TOC/TN decrease (i.e., cooling events), which may involve sulfate inputs through river inflow (peaks 8 and 13 in Fig. 3).

An abrupt cooling event such as the Younger Dryas event in the transition period from glacial to interglacial is now considered as effect of global oceanic thermohaline circulation changes (Bond and Lotti, 1995; van Kreveld *et al.*, 2000). Therefore, by analogy in lacustrine settings, river delivery of higher saline water to Lake Baikal could decrease, and lake water ventilation was inactivated during the glacial to interglacial period. However, in the transition periods from interglacial to glacial (for example, peaks 4 and 9), the origin of the TOC/TN decrease associated with TS/TOC enhancement remains unclear. One possibility is that climate transition from interglacial to glacial period around Lake Baikal occurred in extremely short term, which is compatible to the rapid event of Younger Dryas event. In addition, TOC, TN and TOC/TN decreases are recognized prior to GRD increases (i.e., decreases of biogenic opal) in the transition periods from interglacial to glacial (Fig. 1). This is very likely because a change to drier climate that was responsible for deterioration of land vegetation had occurred in advance of the cooling event. The expeditious deterioration of land vegetation should be due to northward expansion of the southern desert. Moreover, clearly different slopes in C-N plot between interglacial and glacial periods (Fig. 5) suggest apparent deterioration of land vegetation around Lake Baikal in cooling periods.

CONCLUSIONS

High-resolution TOC, TN and TS analyses of Lake Baikal core sediments reveal that at least fifteen cycles of intermittent creation of less oxic environments occurred over the past 250 kyr, which is inferred from the high TS/TOC ratio (>0.2). TOC and TOC/TN ratio variations are largely controlled by influx of terrestrial organic matter into Lake Baikal, rather than changes in primary productivity in lake during the late Quaternary. The high TS/TOC ratio is often observed just after the lower TOC/TN ratio of the sediment, which indicates that terrestrial input becomes lower during the less oxic events. This observation may support the theory that relatively saline water inflow from rivers causes large-scale circulation that ventilates deep waters of Lake Baikal. Thus, the decrease of allochthonous matter influx into the lake will be connected with less oxic condition. In addition, rapid cooling events could lead to decrease of riverine inflow associated with ice melting in every spring. Consequently deep water ventilation could stopped or extremely weakened. Since lake water circulation exerts a great influence especially on the geochemical cycle and biological activity in Lake Baikal, reconstruction of paleo-redox conditions and water circulation changes in the lake are indispensable to identify detailed changes in biological activity and lake ecosystems with respect to climate changes.

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