

Rare earth element geochemistry of Lake Baikal sediment: its implication for geochemical response to climate change during the Last Glacial/Interglacial transition

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Abstract

Sediments deposited on the bottom of Lake Baikal have contributed to the understanding of a long-term environmental history of continents. Rare earth elements (REEs) along with major elements and loss on ignition (LOI) of Baikal sediments were determined with the aim of evaluating their suitability for a new paleoenvironmental proxy. Our interest is concentrated on paleoenvironmental change during the Last Glacial/Interglacial transition (LGIT). Chondrite-normalized REE patterns for Baikal sediments show a similar variation to those for typical upper continental crustal materials. Three parameters of $(La/Yb)_n$ (n : chondrite-normalized value) ratio, $\Sigma REE/TiO_2$ and Eu anomaly were used to express detailed characteristics of Baikal sediments. Depth profile of $(La/Yb)_n$ ratio shows abrupt change, whose timing corresponds to the beginning of climatic warming inferred from the profiles of SiO_2/TiO_2 and LOI. In addition, $(La/Yb)_n$ ratio, $\Sigma REE/TiO_2$ and the degree of Eu anomaly correlate with each other. This suggests that inflow process of particulate materials into the lake may have changed during the LGIT. The analytical results of this study lead to the conclusion that REE is a useful paleoenvironmental proxy in the Baikal region.

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1. Introduction

Lake Baikal is located in the south of eastern Siberia, close to the Mongolian border. It is 640 km long and 40–50 km wide (widest point 80 km), and the deepest lake on the earth. The average depth of the lake is about 730 m and the maximum 1640 m. Its watershed occupies about 557,000 km². The lake itself contains about 23,000 km³ of water, which is about 20% of the world's reserve of surface fresh water (Van Malderen et al., 1996). This freshwater lake is underlain by a thick sediment sequence (~7500 m), which records a continuous history of continental environments (Hutchinson et al., 1992).

Major constituents of Baikal sediment are roughly divided into biogenic and non-biogenic materials. Biogenic components of Baikal sediment are primarily biogenic silica and organic materials. Biological activity is closely related to climatic conditions, and biogenic silica and organic carbon contents of sediments in interglacial periods are higher than those in glacial periods. Diatomaceous ooze and mud are deposited during interglacial periods, whereas diatom-barren silty clay during cold glacial intervals (Prokopenko et al., 1999, 2001a, b). In particular, biogenic silica produced by diatoms has been utilized as a sensitive warm/cold indicator (e.g. Colman et al., 1995; Williams et al., 1997; Prokopenko et al., 2001a, b). On the other hand, non-biogenic materials are mainly detrital silicate minerals, which were transported into the lake via rivers and the air, although authigenic Fe–Mn oxides are observed in some sediment layers (Granina et al., 2004).

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Since such detrital materials have distinct chemical compositions reflecting their provenance, it is expected that geochemical response to paleoenvironmental change is also recorded in detrital component of sediment. Therefore, studies on chemical composition of Baikal sediment have been advanced (Phedorin et al., 1998, 2000a, b; Goldberg et al., 2000, 2001; Chebykin et al., 2002).

Rare earth elements (REEs) have received considerable attention and contributed to geochemical studies in various fields. This is due to their chemical properties characterized by 4f electronic configurations (Henderson, 1984). In particular, REEs in trivalent state behave as a coherent group of elements in geochemical processes. Cerium and Eu exceptionally change their oxidation states into tetra- and di-valence, respectively, according to redox conditions, which cause their unique and anomalous behaviour compared with other REEs. REE abundances in geochemical samples are often discussed using traditional chondrite-normalized patterns plotted against the atomic number, “Masuda–Coryell plot” (Henderson, 1984). The REE abundance patterns provide fingerprints of geochemical processes to form the respective samples. In case of marine environments, REE abundances in Pacific sediments provide the information on the relative contribution of detrital materials (Chinese loess) and authigenic components (Fe–Mn oxides and phosphates: Takebe, 2005). This indicates that REE abundances in sediments have potential of a proxy for earth surface environments. The purpose of this study is to examine whether REE can be a new paleoenvironmental proxy in the Baikal region. For this aim, we focus our interest on the Last Glacial/Interglacial transition (LGIT).

2. Sample

In this study, we used a 4.66 m core, Ver99-G-12, recovered from Buguldeika Saddle in the Selenga Delta area of Lake Baikal (Fig. 1). The sampling point (52°31′36″N, 106°9′8″E) of the core is located near the BDP93 coring site (BDP Baikal Drilling Project Members, 1997). The drill site is characterized by undisturbed hemipelagic sedimentation controlled mainly by the supply of fine suspended particles from the Selenga River, which supplies half of water flowing into Lake Baikal. Radiocarbon (^{14}C) ages of total organic carbon (TOC) in selected Ver99-G-12 core samples were determined by Soma et al. (2006). From the results of their radiocarbon analysis, the average sedimentation rate at the sampling point of Ver99-G-12 was estimated to be about 17.3 cm/1000 yr, which is very close to 17.6 cm/1000 yr at the BDP93 drill site (Colman et al., 1996; Prokopenko et al., 1999). Moreover, the depositional age of the sediment at the bottom of the core was estimated at 27,800 ^{14}C yr BP, which means that the Ver99-G-12 core covers LGIT.

Forty-seven samples were subsampled for REE and major element analyses at 10 cm intervals from bottom to top of the core except the two samples of the uppermost

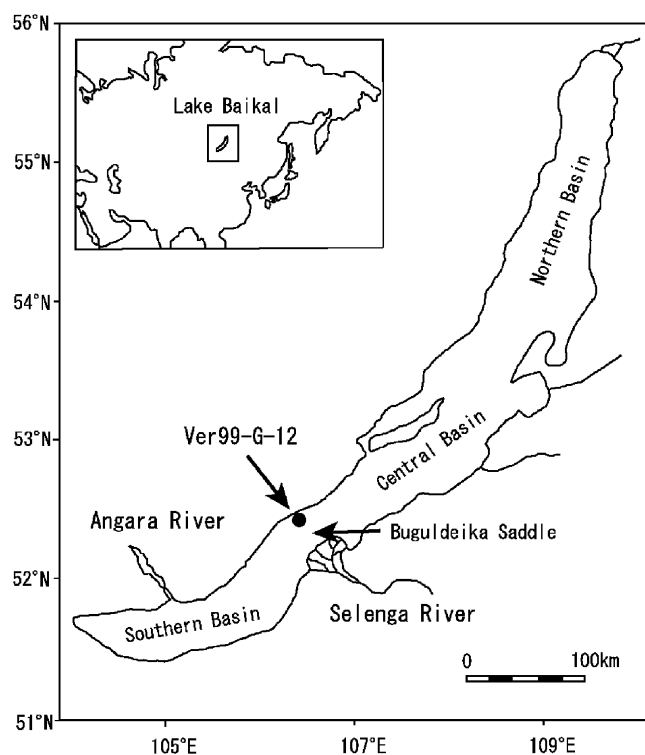


Fig. 1. Location map showing core sampling site of Ver99-G-12.

part subsampled at a 7 cm interval because of lack of a 3-cm-thick sediment layer. Additional 12 samples were also subsampled at core depths of 160–190 and 250–280 cm. According to the ^{14}C ages, these two intervals correspond to the Younger Dryas event and LGIT. Each sediment sample was ground with an agate mortar after drying overnight at moderate temperature of about 40 °C.

3. Methods

3.1. REE

REE concentrations in sediment samples were determined by ICP-MS according to the procedures of Yamamoto et al. (2005). About 40 mg of each sample was first digested with 1 ml 38% HF and 0.5 ml 70% HClO_4 in an open-top Teflon beaker on a hotplate at about 160 °C. After evaporation to dryness, a 0.5 ml mixture of 38% HF and 70% HClO_4 (2:1 by volume) was added to the residue and again heated at about 160 °C. After complete evaporation of the acids, the residue was dissolved in 2 ml 1.7 M HCl and centrifuged at 12,000 rpm. The separated residue was fused with about 50 mg of $\text{Na}_2\text{CO}_3\text{--H}_3\text{BO}_3$ (3:1 by weight) in a Pt crucible at 880 °C. The fusion product was dissolved in 1.7 M HCl and subsequently combined with the 1.7 M HCl soluble fraction after HF– HClO_4 decomposition. Then, REEs in the sample solution were separated from major elements and Ba using cation column exchange chemistry. Finally, each sample solution was adjusted to about 20 ml of 2% HNO_3 and

measured by ICP–MS (HP-4500) at Nagoya University. Details on the analytical procedures and measurement condition in ICP–MS determination are described in Yamamoto et al. (2005).

In order to check analytical accuracy and precision of REE data, we made replicate analyses of a reference rock (JB-1a) issued by the Geological Survey of Japan (GSJ). Results of the replicate analyses are tabulated in Table 1 (See supplementary data) together with those of Baikal sediment samples. Analytical precision for REE was estimated to be 5% or less. The averages of the replicate analyses are in good agreement with the reference values within errors.

3.2. Major element

Major element concentrations in sediment samples were determined by X-ray fluorescence (XRF) techniques on fused glass beads (Takebe and Yamamoto, 2003). Dry sediment samples were calcined at 1000 °C for 2 h before preparing glass beads, and then loss on ignition (LOI) was obtained gravimetrically. Glass bead samples were prepared by fusing 0.7 g of the calcined samples with 6.0 g lithium tetraborate in a Pt crucible at 1050 °C. Calibration curves were obtained according to the method of Sugisaki et al. (1977), with GSJ standard rock samples. XRF measurement was performed with a Shimadzu SXF-1200 equipped with a Rh X-ray tube (40 kV, 70 mA) at Nagoya University. Analytical precision for major elements was estimated to be <1%. The analytical results of major elements and LOI are listed in Table 2 (See supplementary data).

4. Results

4.1. Profiles of $\text{SiO}_2/\text{TiO}_2$ and LOI

The main sources of Si in Baikal sediment are biogenic silica and detrital silicate minerals, while Ti is mainly of detrital origin. Consequently, $\text{SiO}_2/\text{TiO}_2$ can be an indicator of the relative contribution of biogenic debris to detrital silicate minerals (e.g. Takebe and Yamamoto, 2003). On the other hand, LOI is practically the sum of organic materials, hydroxyl group of clay minerals and water in biogenic opal (diatom frustules). LOI is also controlled by the relative abundances of biogenic debris (diatom and organic materials) and detrital materials (clay minerals). Oxidation of Fe(II)O to Fe(III) $_2$ O $_3$ during calcination affects LOI values, but it is negligible in the following discussion.

Depth profiles of $\text{SiO}_2/\text{TiO}_2$ and LOI for the Ver99-G-12 core samples are shown in Fig. 2a and b, respectively. Biogenic silica and TOC reported by Soma et al. (2006) are also plotted for comparison. The contribution of biogenic silica and TOC to $\text{SiO}_2/\text{TiO}_2$ and LOI is clearly observed. Both $\text{SiO}_2/\text{TiO}_2$ and LOI show an increase at around 280 cm core depth toward the surface of the core, except a

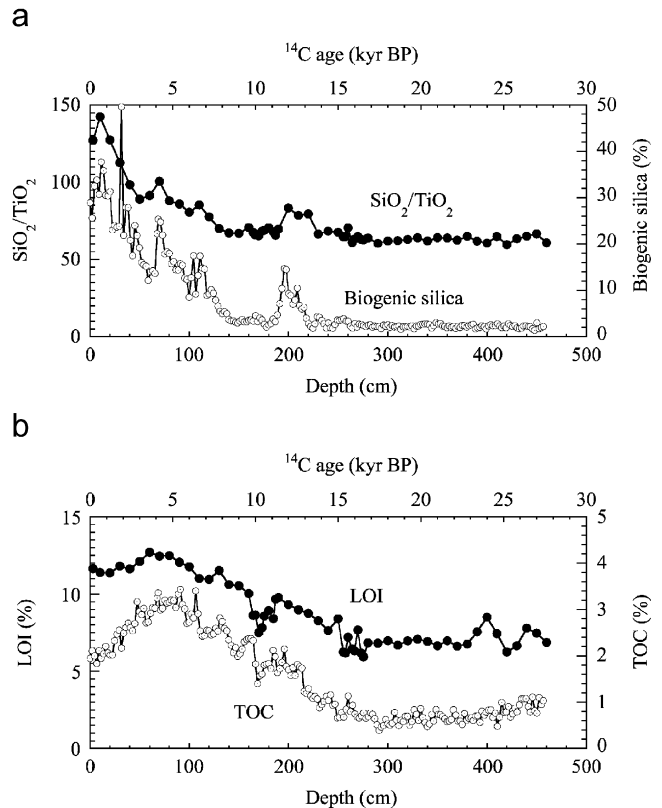


Fig. 2. Depth profiles of (a) $\text{SiO}_2/\text{TiO}_2$ and (b) LOI. Biogenic silica and TOC data by Soma et al. (2006) are also plotted for comparison. The age–depth model is based on Soma et al. (2006).

drop at around 170 cm core depth. Drops in $\text{SiO}_2/\text{TiO}_2$ (biogenic silica) and LOI (TOC) at around 170 cm core depth correspond to the Younger Dryas event. In this way, the Ver99-G-12 core preserves paleoclimatic records during the LGIT.

4.2. REE characteristics of Baikal sediment

Chondrite-normalized REE patterns for Baikal sediments are shown in Fig. 3a. The REE patterns exhibit variation typical of the average compositions of upper continental crust such as North American shale composite (NASC), Post-Archean Australian average shale (PAAS) and Chinese loess (Gromet et al., 1984; Taylor and McLennan, 1988; Gallet et al., 1996). REE patterns for the average shales and Chinese loess are characterized by light REE enrichment and negative Eu anomaly (Fig. 3b). The REE characteristics of the Baikal sediments have no pronounced difference throughout the core samples in the chondrite-normalized patterns (Fig. 3a). Their REE characteristics, however, include small but significant variation as discussed below.

Ratio of La to Yb is often used to express a slope of REE pattern. The $(\text{La}/\text{Yb})_n$ ratio (n : chondrite-normalized value) of the Baikal sediments drops sharply at 280 cm core depth (Fig. 4). Except for several samples, the $(\text{La}/\text{Yb})_n$

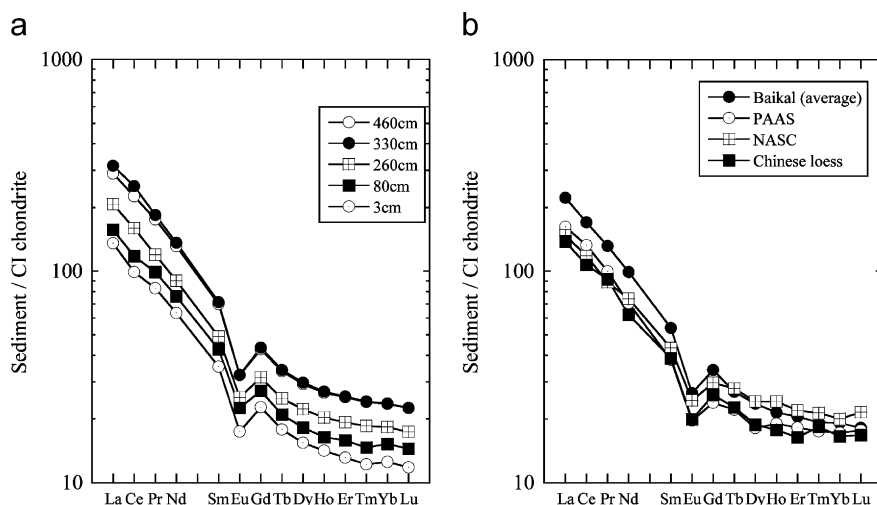


Fig. 3. (a) Chondrite-normalized REE patterns for Baikal sediments and (b) Comparison of REE patterns between the average of Baikal sediment and typical upper continental materials. Chondritic values by Anders and Grevesse (1989) are used for normalization with a modification of Tb (0.0348 ppm), Ho (0.0525 ppm) and Tm (0.0234 ppm) (Ebihara, M., 2002, pers. comm.). REE data of PAAS and Chinese loess are quoted from Taylor and McLennan (1988) and Gallet et al. (1996), respectively. NASC values of Gromet et al. (1984) modified by Kawabe et al. (1998) are also plotted.

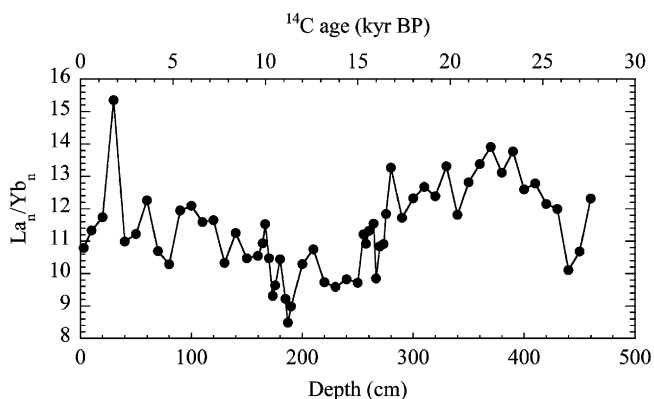


Fig. 4. Depth profile of $(La/Yb)_n$ ratio, where the suffix “n” denotes a chondrite-normalized value. The age–depth model is based on Soma et al. (2006).

ratios are 9–12 above 280 cm core depth, while 11.5–14 below 280 cm core depth. The depth of the $(La/Yb)_n$ boundary (i.e. 260–280 cm) is consistent with the beginning of climatic warming observed in the depth profiles of SiO_2/TiO_2 and LOI (Fig. 2a and b), although clear response to the Younger Dryas event is not recognized.

5. Discussion

5.1. What controls REE characteristics?

We use here two parameters of total REE (ΣREE)/ TiO_2 and Eu anomaly as well as $(La/Yb)_n$ in order to discuss the REE characteristics of Baikal sediments in more detail. ΣREE is normalized to TiO_2 because REE concentrations of bulk sediment samples are diluted by biogenic silica with low REE contents. These three parameters show good correlations with each other (Fig. 5a–c).

In order to assess the potential of REE as a paleoenvironmental proxy, we should consider what controls REE abundances of sediment. As mentioned above, Baikal sediments consist of biogenic materials (diatom frustules and organic materials) and non-biogenic materials (detrital materials and authigenic Fe–Mn oxide). Biogenic silica does not contribute to bulk REE amounts of sediments and solely dilutes bulk REE concentrations. It is well-known that Fe–Mn oxide, such as deep sea ferromanganese nodules, is highly enriched in REE (e.g. Elderfield et al., 1981; Ohta et al., 1999). However, the contribution of Fe–Mn oxides is possibly minor because Fe and Mn concentrations do not correlate with $\Sigma REE/TiO_2$, Eu anomaly and $(La/Yb)_n$ (Fig. 6a and b). It is also unlikely that organic materials control these REE characteristics because of low TOC of 0.5–3.6% (Soma et al., 2006). Probably, inorganic detrital materials predominantly control REE characteristics of Baikal sediment in the Selenga area.

5.2. Response of detrital component to climatic change

From Fig. 4 and the correlation observed in Fig. 5a–c, two hypotheses on the change of paleoenvironment surrounding Lake Baikal can be conducted: one is the possibility that inflow process of particulate materials into the lake via the Selenga River may have changed during the LGIT. Change of the Selenga River system, which covers a huge catchment area, could result in transportation of different particle composition. For example, abundance of heavy minerals in sediment, even if it is minor, can affect bulk REE concentrations because they are highly enriched in REE (Gromet and Silver, 1983; Suzuki et al., 1990). The other is the possibility that the relative contribution of aeolian dust to riverine particulate materials may have

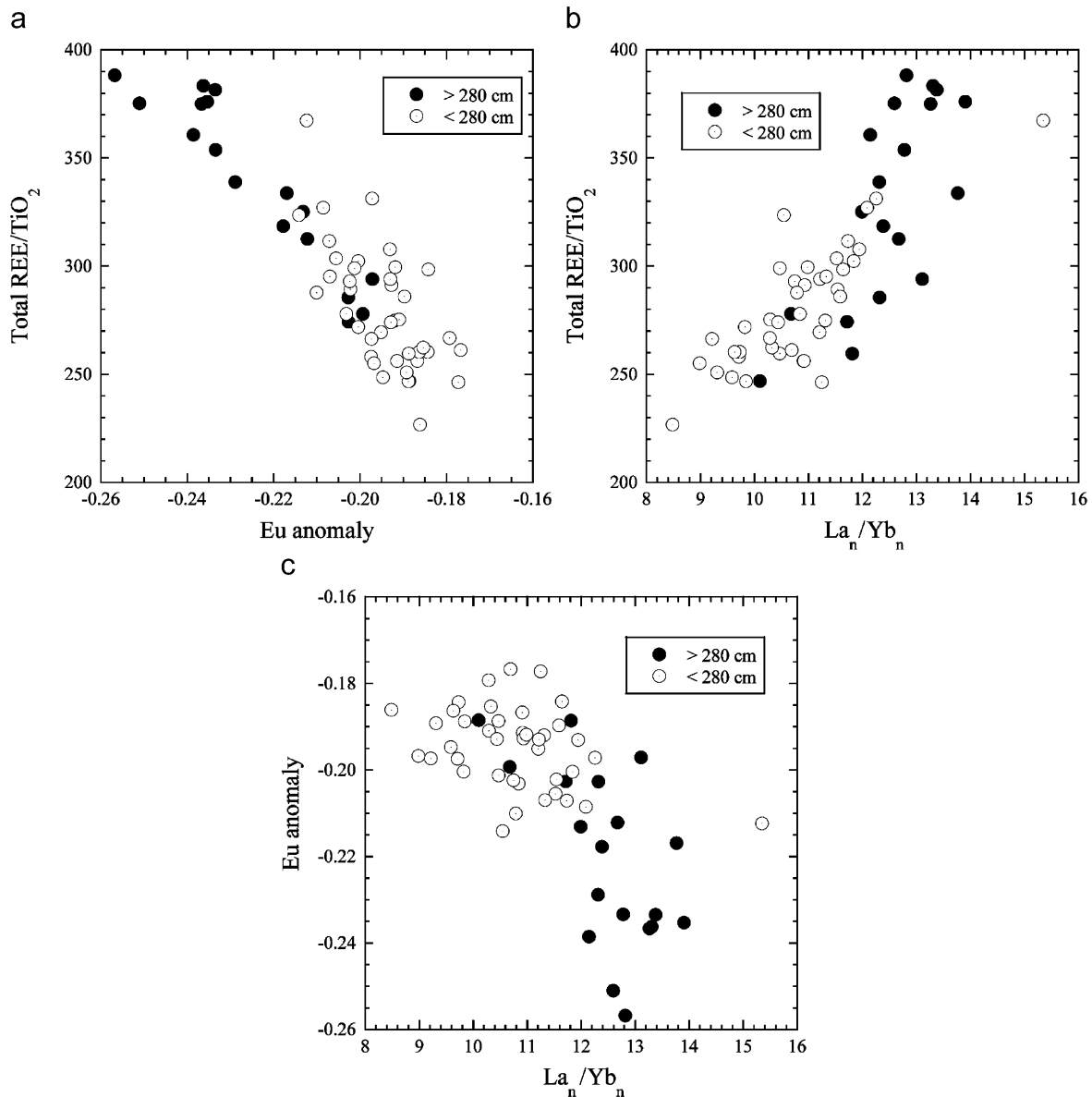


Fig. 5. Correlation plots between $\Sigma\text{REE}/\text{TiO}_2$, Eu anomaly and $(\text{La}/\text{Yb})_n$. ΣREE is recalculated on LOI free basis. Europium anomaly is defined as $\log\{\text{Eu}_n/(\text{Sm}_n \times \text{Gd}_n)\}$. The data above 280 cm are plotted as a dotted circle, while those below 280 cm as a filled circle.

changed. This is linked to flux of aeolian dust and riverine particles into Lake Baikal. Bobrov et al. (2001) analyzed REE concentrations in aeolian and riverine suspended particles in the Selenga area. Their data show that $(\text{La}/\text{Yb})_n$ ratio of aeolian dust is 7.6, whereas those of riverine particles are 12.5–13.8. This suggests that REE abundances in Baikal sediment may be explained by mixing of aeolian and riverine particles. If the second possibility is accepted, the relative flux of aeolian dust in the post-glacial period is higher than that in the Last Glacial period. However, the second possibility is inconsistent with previous works, which suggested the importance of the contribution of aeolian dust during arid glacial periods (Peck et al., 1994; Edgington et al., 1996). Therefore, the first possibility is more acceptable than the second one.

It has been demonstrated that REE characteristics in Baikal sediments preserve paleoenvironmental records during the LGIT (Figs. 4 and 5a–c). It is expected that the use of REE is extended to long core samples in order to discuss long-term glacial/interglacial cycles.

6. Conclusions

We analyzed major elements, LOI and REEs in Baikal sediments of a short core in the Selenga Delta area. The potential of REE as a new paleoenvironmental proxy were examined in this study. Depth profiles of $\text{SiO}_2/\text{TiO}_2$ and LOI exhibit variation reflecting climatic change during the LGIT. This means that the core used in this study preserves good climatic records and is suitable for the examination of REE. Chondrite-normalized REE patterns for Baikal

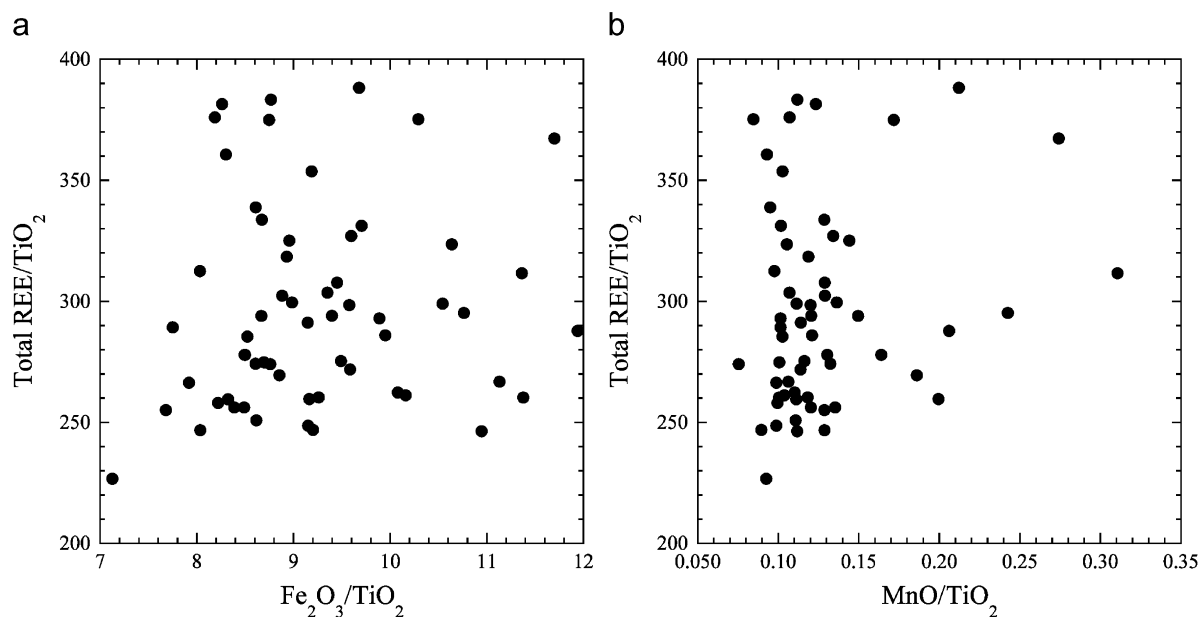


Fig. 6. $\Sigma\text{REE}/\text{TiO}_2$ plotted against (a) $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and (b) MnO/TiO_2 .

sediments are very similar to those for typical upper continental crustal materials. Depth profile of $(\text{La}/\text{Yb})_n$ ratio shows abrupt change at the middle of the core. The timing of the change corresponds to the beginning of climatic warming inferred from the profiles of $\text{SiO}_2/\text{TiO}_2$ and LOI. Furthermore, three parameters of $(\text{La}/\text{Yb})_n$ ratio, $\Sigma\text{REE}/\text{TiO}_2$ and Eu anomaly correlate with each other. This suggests that the Selenga River system may have changed during the LGIT. From our analytical results, it can be concluded that REEs are a useful indicator to trace the circulation of detrital materials in the Baikal region.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.quascirev.2007.02.004](https://doi.org/10.1016/j.quascirev.2007.02.004).

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