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Origin and dynamics of Fe and Mn sedimentary layers in Lake Baikal

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Abstract

Remobilization and accumulation of iron and manganese were measured by porewater and sediment–core analyses at six contrasting sedimentary environments of Lake Baikal, with bulk sedimentation rates varying between 0.8 and 0.02 mm year^{-1}. The results allow for the distinction between two types of Fe and Mn diagenesis in areas of relatively high sedimentation and in regions of low sedimentation rates. In the first case, only small Fe/Mn enrichments near the sediment–water interface were observed in the central and southern basins, at the high sediment flux area near the Selenga Delta, and in Maloe More strait. Massive sedimentary layers enriched in Fe and Mn were found within the upper 15–25 cm of the sediments exclusively in Northern Baikal and in the underwater Academician Ridge, which are characterized by low sedimentation rates and deep sulfate penetration depths in the porewaters. The Mn content in the enriched layers ranged from 10^{-5} mol cm^{-2} at the sites near the Selenga Delta up to 10^{-2} mol cm^{-2} at Academician Ridge. The accumulation times for the enriched Fe/Mn layers, calculated from the size of the Fe and Mn oxide pools and the diffusive fluxes into the enriched zones, also varied by a factor of 1000. They ranged from a few years near the Selenga Delta to several thousand years for the sites at Academician Ridge and Northern Baikal. These values were generally congruent with the sediment age of the accumulation zones calculated from sedimentation rates.

These findings have significant implications for paleolimnological studies. Iron and manganese dynamics at sites with high sedimentation rates is dominated by allochthonous input, which is only partially dissolved close to the sediment surface. In contrast, the massive Fe/Mn sedimentary layers at sites of slow sedimentation are of autochthonous origin. Slow dissolution and reprecipitation maintain their constant position with respect to the sediment surface and prevent burial as long as the sedimentation regime remains constant. Buried Fe/Mn sedimentary layers widespread in Lake Baikal may therefore serve as general indicators for low sedimentation rates and as specific proxies for sudden changes in the sediment regime.

Keywords: Lake Baikal; Sediment; Early diagenesis; Iron; Manganese

1. Introduction

Lake Baikal in southeastern Siberia is the world's deepest lake and the largest freshwater resource. It formed in a tectonic depression and harbors a great

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diversity of endemic species. Ice sheets never covered the lake during the Pleistocene epoch. Therefore, the sediments extending over 7 km in thickness represent a unique paleoclimatic archive, which allows for the interpretation of climate cycles ranging over several million years by means of diatom, geomagnetic, geochemical, and other proxies (Kuzmin et al., 1997; Grachev et al., 1998). Callender and Granina (1997) presented a limnological review of material balances in Lake Baikal mainly based on the Russian literature. Kashiwaya et al. (2001) recently interpreted geomagnetic proxies of a 12-million-year record and found evidence of orbit-related climate cycles. Because of its remote location, the lake also serves as a reference site for quantifying recent anthropogenic disturbances in trace metal cycles (Boyle et al., 1998) and for studying the diagenetic behavior of trace elements (Müller et al., 2002). For both long-term geomagnetic studies and more recent pollution histories, the sedimentary dynamics of iron and manganese minerals in Lake Baikal should be understood in detail.

Fe and Mn are both known to play an important role at the oxic–anoxic interface of sediments due to their distinct redox chemistry since the reduced forms are well soluble while the oxidized species from oxyhydroxides are of very low solubility (Stumm and Morgan, 1996). After the depletion of oxygen and nitrate, oxyhydroxides of manganese and iron, and sulfate are reduced in freshwater sediment. Precipitates of reduced iron and manganese can be found in the form of pyrite, iron sulfides, and rhodochrosite (Friedl et al., 1997). The ratio of Fe:Mn in freshwater sediments may be used as an indicator of former redox conditions (Wersin et al., 1991). These solid phases are important redox buffers in freshwater sediment. In marine sediments, the redistribution of Fe and Mn during early diagenesis has been recognized and modeled for many years (Lynn and Bonatti, 1965; Bender, 1971; Bonatti, 1971; Robbins and Callender, 1975; Froelich et al., 1979; Aller, 1980).

Within the sediments of Lake Baikal, distinct zones of iron and manganese accumulation are well known. They spread over all three lakes' basins and are also found in the underwater Academician Ridge that separates the northern and central basins. In spite of the spectacular patterns of Fe/Mn crusts and concretions in Baikal sediments, only a few studies address this subject. Amirzhanov et al. (1993) distinguished between shallow water disc-shaped nodules with high Fe content and deep-water elliptic or dome-shaped nodules with high Mn content. Granina (1991) and Granina et al. (1992, 1993) investigated the porewater concentrations of Fe and Mn and described the formation of Fe/Mn-enriched layers and crusts at the oxic–anoxic interface within the sediment. These authors hypothesized that a low sedimentation rate and a low content of organic carbon were prerequisites for the formation and preservation of crusts.

Measurements of O_2 concentration profiles with microelectrodes confirmed that Fe/Mn accumulations were related to O_2 penetration depth in the sediment and thus to the sedimentation rates in the different regions of the lake (Granina et al., 2000). The distinct layers of Fe/Mn precipitates are positioned precisely at the redox interface of the sediment. At some locations, the Fe/Mn sedimentary layers amount to solid crusts of up to 1 cm thickness. According to the geochemical features of these metals, Fe and Mn precipitates were sometimes spatially separated in the vertical redox gradient. Selective enrichments of elements like P and As were observed in the Fe crusts, while Mo and Cd accumulated preferentially in the Mn oxides (Müller et al., 2002).

There are layers enriched in Fe and Mn hydroxides and Fe/Mn crusts buried also in the reducing part of the sediment. They are relics that were once positioned at the water–sediment oxic interface but are slowly dissolving now in the anaerobic sediment (Mizandrontsev, 1984; Granina et al., 1993). Relics of such layers and crusts are also found deep (meters) below the sediment–water interface (Deike et al., 1997; Mats et al., 2000; Zhmodik et al., 2001; Granina et al., 2003), and their fate is assumed to be related to changes in sedimentation rate, trophic state of the lake, tectonic events, and a specific diagenetic redistribution of sedimentary Fe and Mn.

Accumulations of Mn and Fe oxides are well known from marine and some lacustrine environments. They occur in the shape of nodules growing on the sediment surfaces of deep ocean basins (>4500 m) as Mn crusts in locations with high bottom currents and as ferromanganese concretions in shallow marine environments and freshwater lakes (Glasby, 2000; Burdige, 1993; Schimmield and Pedersen, 1990; Davison, 1985, 1993). The characteristic patterns are caused by the specific geochemical properties of these metals, sea-bottom topography, sedimentation rates, and the diagenetic processes in the sediment. Mn and Fe oxides are used as electron acceptors when O_2 and NO_3^-, which are energetically more favorable oxidants, are depleted. However, they contribute less than 10% in general to the mineralization of organic carbon (Bender and Heggie, 1984). The mineral phases of Fe/Mn crusts in marine and freshwater environments are difficult to characterize since they are mostly amorphous to X-ray analysis (Deike et al., 1997; Burns and Burns, 1981; Boughriet et al., 1996; Friedl et al., 1997; Perret et al., 2000).

Until now, no systematic attempt has been made to explain the biogeochemistry of the diagenetic pathways that lead to the formation, dissolution, and reformation of the Fe/Mn precipitates in Lake Baikal. The setting of this deep lake with its three different basins, underwater sills, and river deltas provides a unique opportunity to analyze the time scales and processes as a function of different sedimentation regimes. Therefore, our study aims to understand the formation of Fe/Mn layers and the diagenetic redox processes involved in their continuous reformation that depend on the redox environments typical of the areas caused by the different sedimentation regimes. We document the results concerning the formation of Fe/Mn sedimentary layers in six contrasting regions of Lake Baikal (i.e., near the Selenga River Delta, in the southern, central, and northern basins, Academician Ridge, and the strait of Maloe More). By comparing porewater fluxes of Fe^{2+} and Mn^{2+} with the accumulated amounts of Fe and Mn oxides within the enriched layer, we calculate the accumulation time of the layers for steady-state conditions and relate it to the age of the respective sediment. These dynamic parameters are then used to derive a quantitative relation between sedimentation rates, sulfate reduction, and accumulated Fe/Mn pool.

2. Study sites and methods

2.1. Characterization of sampling sites

Fe/Mn sedimentary layers were studied at six regions of Lake Baikal (Fig. 1), which exhibit different sedimentation rates and a range of sources of the sediment material. A short characterization of the lake regions selected from the literature (Agafonov, 1990; Granina et al., 1993; Mackay et al., 1998; Nelson et al., 1994; Vologina et al., 2000) is given below; sedimentation rates are represented in Table 1. The sediments and porewaters were collected at the following regions:

1. The region near *the delta of the Selenga River* which is the largest tributary to Lake Baikal supplying 50% of the water input, about 75% of total suspended particles, and 50% of particulate organic carbon (C_{org}) of terrestrial origin. A transect of sediment cores was sampled along the Selenga River delta towards the profundal of the lake.
2. *Southern Baikal* is up to 1425 m deep, and sediments are comprised of relatively coarse materials with a small fraction of diatomaceous ooze due to a substantial dilution of biogenic sedimentary material by terrigenous particles. Input of fluvial suspended particles into the southern basin is almost twice as high as that into the northern basin. Turbidites of terrigenous material in the form of slumps are common in Southern Baikal.
3. *Central Baikal* is the deepest basin with water depth up to 1642 m. The narrow shape and the steep slopes of the basin cause sediment slides. Three large tributaries—the Selenga, Barguzin, and Turka Rivers— influence the currents and sedimentation. Together, these three tributaries contribute 80% of the suspended particles and about 57% of the particulate C_{org} input into Lake Baikal. The sedimentation rate in Central Baikal is heterogeneous and affected by turbidites.
4. *Northern Baikal* is up to 920 m deep and both sedimentation rate and concentration of sedimentary C_{org} are lower than in the other two basins, which may be due to the lowest biological productivity in the northern basin. There is one large tributary, the Upper Angara River, which supplies 15% of the total suspended sediments entering the lake annually. Numerous small tributaries enter the lake along the eastern shore. Turbidites of different origin are widespread within the sediments of Northern Baikal.

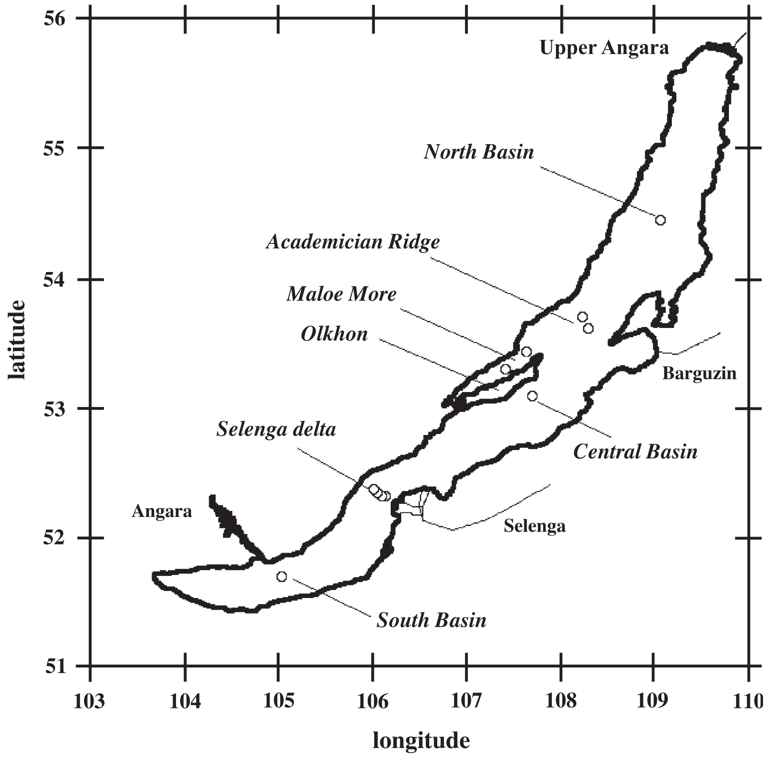

Fig. 1. Map of Lake Baikal and locations of the sampling sites.

5. *Academician Ridge* is a large underwater sill at 250–400 m below the water surface that separates the central and northern basins. The ridge is isolated from sources of terrigenous material. Water currents above the ridge caused by the specific local hydrological conditions (Shimaraev et al., 1996; Hohmann et al., 1997) prevent high rates of sedimentation and are the reason for the large heterogeneity of sediments.
6. *Maloe More* is a strait separated from the Central Basin by Olkhon Island. Water depths reach from a few tens of meters at the southern end to 300–350 m in the northern part of the strait. Thus far, no sedimentation rates have been measured in Maloe More due to sandy sediments. The geomorphic features of this area described in detail by Patrikeeva (1959) indicate high rates of resuspension of previously deposited sediments. Three major tributaries, as well as temporal streams fed by rain and melting water, supply substantial amounts of suspended particles. The local wind, 'sarma,' famous for its enormous strength, causes high waves that erode the shores of Olkhon Island and resuspension of sediments.

2.2. Sampling and analytical methods

During the summers of 1994 and 1996, two expeditions were undertaken to Lake Baikal to sample sediments and porewaters. In 1994, the sediments were retrieved with a box corer and subcores of around 30 cm length were sampled with 7-cm PVC tubes. In 1996, sediment cores of 7 cm in diameter and 70 cm in length were sampled using a gravity corer (Kelts et al., 1986). Turbidites were not observed in the sediment depths investigated except when explicitly mentioned. The cores were extruded in sections of 0.5–2 cm, packed and

Table 1
Characterization of the main regions of Lake Baikal and mean sedimentation rates selected from the literature

Lake region	Volume [km^3]	Water outflow [km^3 $year^{-1}$]	Sedimentation rates [mm $year^{-1}$]
Southern Baikal	6230	60	0.65[a]
Central Baikal	8940	40	0.24[a]
Northern Baikal	7840	14	0.14[b]
Near Selenga River Delta			0.80[c]
Academician Ridge			0.02[d]

No sedimentation rate data are available for Maloe More.
[a] From Edgington et al. (1991).
[b] The lowest sedimentation rates averaged from the data published by Ogura et al. (1992), Pampoura and Sandimirov (1993), and Granina et al. (1993).
[c] The average from the data published in Edgington et al. (1991), Kuptsov and Bogdanov (1991), and Mackay et al. (1998).
[d] The lowest sedimentation rates averaged from the data published by Colman et al. (1993) and Vologina et al. (2000).

sealed in polycarbonate boxes. In 1994, the porewaters were sampled with a whole-core squeezer system (Bender et al., 1987; Jahnke, 1988): sediment cores were transferred in a Plexiglas tube and pressure was applied with two pistons. Water samples were acidified with 100 μl of HNO_3 (concentrated, suprapure). In 1996, submersible in situ dialysis plates (Hesslein, 1976; Brandl and Hansel-mann, 1991; Urban et al., 1997) were deployed at two sites. The 'peeper' plate, with a vertical resolution of 1 cm, was mounted on a tripod and equilibrated in the sediment for 5 days. Before retrieval, a protecting cover was released mechanically to seal the dialysis plates and thus minimize diffusive losses during retrieval. Samples were withdrawn without air contact with a syringe and hypodermic needle through a septum at the side of the dialysis plate. Approximately 8 ml of porewater obtained from each depth was transferred to evacuated vials holding 100 μl of concentrated HNO_3 (suprapure). After transport of about 2 week, the sediment samples were freeze-dried, ground in an agate mortar, and acid-digested with 4 ml of HNO_3 (concentrated, suprapure) and 1 ml of H_2O_2 in a microwave oven. Fe and Mn were determined with inductively coupled plasma and optical emission spectroscopy (ICP-OES; Spectro Analytical Instruments). Accuracy was 10% for Fe and 12% for Mn (based on rock standard samples). Sulfate concentrations were determined by ion chromatography (Metrohm IC 690, Switzerland).

2.3. Calculations

The accumulation time of Fe and Mn layers has been calculated for steady-state conditions (Table 2). The vertical concentration profiles of particulate Fe and Mn were normalized to a moles-per-sediment volume of the section that contained enrichments. Average background concentrations were obtained from the undisturbed sections below accumulation zones. The total amount of Fe and Mn in the enriched layer was calculated by integration over the peak profiles in the enriched layers, and background concentrations were subtracted from these integrated peak profiles. In a second step, the steady-state fluxes of Fe^{2+} and Mn^{2+} in the accumulation horizon were determined from porewater profiles with Fick's first law and diffusion coefficients for Fe^{2+} and Mn^{2+} of 4.1×10^{-6} and 3.7×10^{-6} cm^2 s^{-1}, respectively (Li and Gergory, 1974). Mass accumulation rates or sedimentation rates of Mn and Fe were calculated from the concentrations of these metals in the top sediment layer and multiplied with the sedimentation rate of total particulate matter estimated for this location (Table 1). The time required for the accumulation of enriched layers was estimated by dividing the content of Fe and Mn within these layers (mol m^{-2}) by the diffusive flux directed towards the enriched layers (mol m^{-2} $year^{-1}$). The accumulation time could then be compared with the approximate age of the center of layers (cm) calculated using average sedimentation rates of the respective region (cm $year^{-1}$) (Table 2). The factor of Mn and Fe enrichment in the accumulation zone was calculated by dividing the peak concentration by the background concentration and is presented in Table 3. The turnover rates were calculated in terms of electron fluxes of Mn, Fe, and SO_4^{2-}: porewater fluxes of Fe, Mn, and SO_4^{2-} were multiplied by factors one, two, and eight, as these are the required number of electrons to be transferred in

Table 2
Accumulation time of Fe/Mn layers in recent Baikal sediments in comparison with their age calculated from sedimentation rates

Lake region	Station	Water depth	Depth interval in section	Metal amount in section		Diffusive fluxes		Accumulation rate		Accumulation time		Sediment age
				Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	
		m	cm	mol cm^{-2}		mol cm^{-2} day^{-1}		mol cm^{-2} day^{-1}		years		years
(1) Near Selenga Delta	94-13	30	0–1.5	9.7×10^{-6}		2.1×10^{-8}		3.9×10^{-9}	1.1×10^{-7}	1		15
	94-05	80	0–1.5	2.0×10^{-5}		1.8×10^{-9}		4.2×10^{-9}	9.2×10^{-8}	30		15
	94-06	140	0–2.5	2.4×10^{-5}	3.0×10^{-4}	2.0×10^{-9}		5.4×10^{-9}	1.0×10^{-7}	30		30
	94-07	275	0–2.5	3.1×10^{-5}		6.5×10^{-9}		7.0×10^{-9}	9.3×10^{-8}	15		30
	94-08	580	0–1.5	3.3×10^{-5}	3.4×10^{-4}	2.5×10^{-9}	2.9×10^{-9}	1.2×10^{-8}	1.4×10^{-7}	35	320	15
(2) Southern Baikal	94-02	1475	0–3.5	1.8×10^{-4}	5.6×10^{-4}	5.6×10^{-9}	3.4×10^{-9}	1.7×10^{-8}	4.5×10^{-8}	90	450	50
(3) Central Baikal	94-09	1630	0–4.2	1.3×10^{-3}	2.0×10^{-3}	7.7×10^{-9}	6.4×10^{-9}	2.2×10^{-8}	2.3×10^{-8}	460	860	170
(4) Northern Baikal	94-10	895	7.5–18	5.6×10^{-3}		8.2×10^{-9}		9.3×10^{-10}		1870		680
			8.5–16		2.3×10^{-3}		5.7×10^{-9}		8.9×10^{-9}		1100	930
(5) Academician Ridge	94-11	380	6–28	1.1×10^{-2}		3.3×10^{-9}		7.4×10^{-11}		9130		5000
			10–30		1.0×10^{-2}		4.0×10^{-9}		1.2×10^{-9}		6850	8460
	96-60	280	0–2.5	2.6×10^{-4}	2.5×10^{-4}							960
			5.5–12	8.5×10^{-4}		4.1×10^{-9}		1.4×10^{-10}		570		3460
			7.0–12		1.8×10^{-3}		3.5×10^{-10}		2.4×10^{-9}		14,100	3460
	96-110	280	0–4	3.7×10^{-4}	5.5×10^{-4}							865
			11–13	1.0×10^{-3}	6.2×10^{-4}	2.3×10^{-9}	2.2×10^{-10}	5.8×10^{-11}	1.5×10^{-9}	1260	7730	4620
			19–22	1.3×10^{-5}	2.1×10^{-4}							7690
(6) Maloe More	94-12	280	0–0.5	2.3×10^{-6}	9.0×10^{-6}	2.1×10^{-9}	2.1×10^{-9}			3	10	
	96-52	120	0–3.5	7.6×10^{-6}	2.1×10^{-4}	2.6×10^{-9}	6.8×10^{-9}			8	85	

Table 3
Enrichment factors for Fe and Mn, and sulfate concentration gradient in the porewater, dSO_4/dz, in the cores from 10 stations

Region	Station	Enrichment factor Fe	Enrichment factor Mn	dSO_4/dz [μmol l^{-1} cm^{-1}]
(1) Near Selenga Delta	94-13	–	2	− 53
	94-05	–	2	− 40
	94-06	1.2	3	− 23
	94-07	–	3	− 23
	94-08	2	6	− 20
(2) Southern Baikal	94-02	3	16	− 15
(3) Central Baikal	94-09	2.6	7	− 13
(4) Northern Baikal	94-10	12	25	− 6.4
(5) Academician Ridge	94-11	11	105	− 3.5
(6) Maloe More	94-12	1.1	4	− 1.8

order to reduce Fe and Mn and oxidize S(II), respectively.

3. Results

3.1. The region near the Selenga Delta

There were remarkable changes in the sediment features when moving from the shallowest station (30 m, 94-13) towards the deepest station (580 m, 94-08) along the Selenga transect (Fig. 1). The increase in water depth at a greater distance from the Selenga Delta was accompanied by a decrease in sedimentary C_{org} (data not shown), visible increase in the thickness of the oxidized layer, and a decrease in the SO_4^{2-} flux in the sediment (Table 3). The Mn was enriched in the surface layers by factors of two to six compared to contents in the older sediment, whereas the top-core Fe enrichment was significant only in the cores sampled at depths below 500 m. Porewater concentrations of Mn and Fe increased sharply about 2 cm below the surface (data not shown).

In the region near the Selenga Delta, the rate of sedimentation ranges widely, up to 0.8 mm $year^{-1}$ on average (Table 1). With this sedimentation rate, one obtains values of 15–30 years for the age of the sediments bearing Mn enrichments (Table 2). These values corresponded well with the accumulation time calculated from porewater fluxes and Mn contents, which are of 1 year for the Mn layer at the shallowest site (30 m water depth) and of 15–35 years for all other stations in this transect (Table 2). This indicates that sediment accumulation and reductive dissolution of Mn were in a steady state.

Changes in porewater chemistry between the Selenga Delta front and the pelagic part were clearly visible in the sulfate porewater profiles (Fig. 2a). Sulfate penetration depth was only 3 cm at the shallowest station near the delta (94-13) and increased to 8 cm towards the deepest site offshore (94-08). Correspondingly, sulfate concentration gradients calculated from these profiles ranged from −53 to −20 μmol l^{-1} cm^{-1}, decreasing with depth (Table 3). Iron sulfide was identified visually as black spots and stripes in the reduced mud. These observations are supported by a number of studies, which reported the formation of authigenic iron sulfides in sediments of Lake Baikal (Goldyrev, 1972; Mizandrontsev, 1975; Granina, 1991; Callender and Granina, 1992).

3.2. Southern Baikal

The enrichment of Fe and Mn in the upper part of core 94-02 (1425 m; Fig. 3a) from the southern basin was significantly larger, which is in line with the lower sedimentation rate compared to the region near the Selenga Delta. Due to diagenetic redistribution of Mn and Fe in the oxidized layer of station 94-02, the peaks of particulate accumulations were 0.75 and 3 cm below the sediment surface, respectively. The precipitation zones were enriched by a factor of three in Fe and by a factor of 16 in Mn (Table 3). Porewater concentrations of Fe and Mn in the oxidized zone decreased close to detection limits in most samples (Fig. 3b). Sediment age of 50 years agreed with Mn accumulation time of 90 years (Table 2). A relic of former Fe/Mn accumulation was buried in the reduced sediment at a depth of 7 cm, and is visible just below the oxidized zone as yellow-red ocher stripes. Particulate Mn had dissolved and almost completely disappeared from this relic, whereas a substantial amount of Fe still remained.

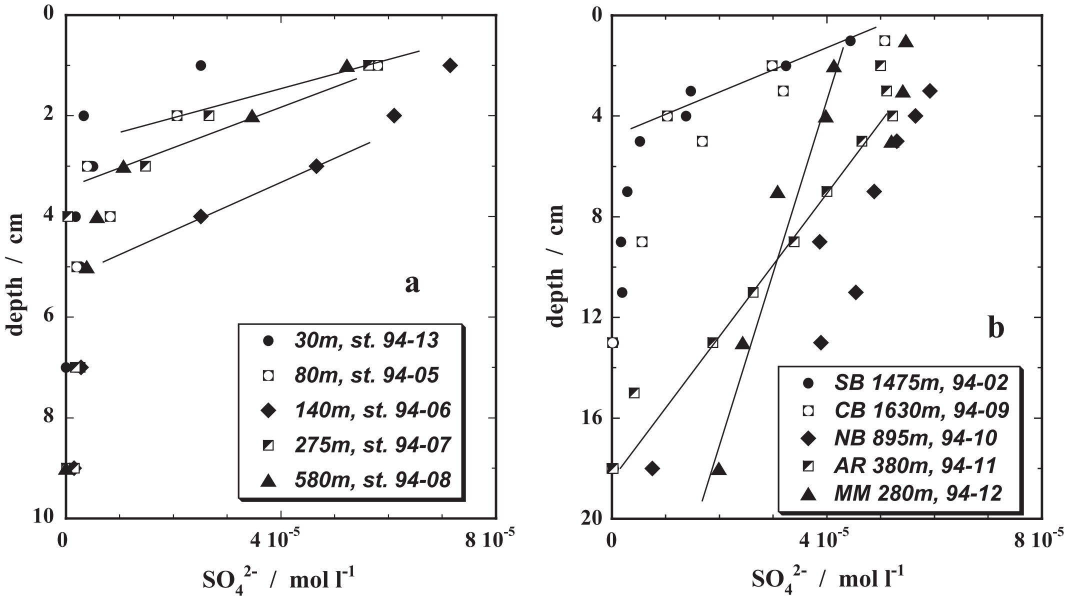

Fig. 2. Sulfate porewater concentrations in the sediments from (a) the Selenga transect, (b) the southern basin 'SB', central basin 'CB', northern basin 'NB', Academician Ridge 'AR', and Maloe More 'MM'.

3.3. Central Baikal

Analysis of particulate Fe and Mn in core 94-09 revealed several layers in the oxidized zone (Fig. 3c), which were enriched in both elements. Mackay et al. (1998) also observed a similar pattern in this region. Below the oxidized zone, several relic oxidized layers represented by brown plates, hard chunks, and crusts were conspicuous not only due to their consistency and color, but also because of their low water content (24–67%) compared to the surrounding soft sediment (76–85%). We suggest that the hemipelagic sedimentation in this part of the lake was interrupted several times by turbidites: there was sudden input of terrigenous material of fluvial origin by sediment slumping. The small increase in particulate Mn at 12–20 cm and the increase in Fe at 8.5–18 cm (Fig. 3c) were caused by dense relics of older Fe/Mn layers. The sharp Fe peak, as well as the high ratio of particulate Fe/Mn typical of the relic zone depleted in Mn, further corroborate the diagenetic origin of this relic enrichment. Porewater concentrations of Fe and Mn increased from the surface downwards to the zone of enriched layers and crusts (Fig. 3d), indicating dissolution in the anoxic zone. The accumulation time calculated according to the porewater fluxes directed towards the crusts was 460 years for the Mn layer. Using the sedimentation rate of 0.24 mm year^{-1} for the central basin (Edgington et al., 1991), we obtained 170 years for the age of sedimentary layer bearing the Mn layer.

The large tributaries in the central basin carry substantial amounts of reactive C_{org}. Its decomposition enhances sulfate reduction, which again results in the formation of sulfide. The porewater sulfate gradient was -13 μmol l^{-1} cm^{-1} (Table 3), suggesting moderate concentration of sedimentary C_{org}. Sulfate disappeared from the porewaters at a depth of 13 cm (Fig. 2b), and authigenic Fe sulfides appeared as gray and black "wormholes" below a depth of 12 cm.

3.4. Northern Baikal

Moving northwards to station 94-10, the oxidized layer extended over the upper 17 cm of the sediment core (Fig. 5a,b). Apart from a small and sharp Mn layer at 2 cm depth, most Fe and Mn accumulated in the lowest part of the oxidized layer as a thick enriched zone. In accordance with the specific redox features of iron and manganese, there was a distinct vertical separation of both elements: Mn had a max-

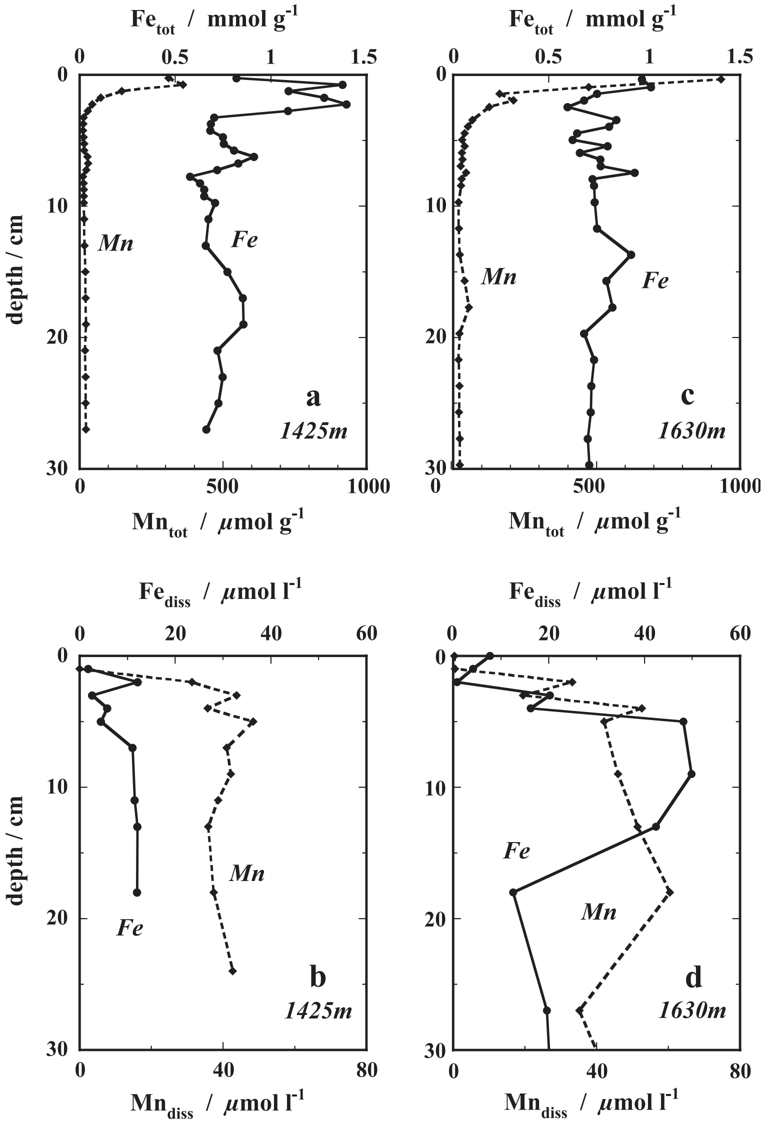

Fig. 3. Sediment profiles of particulate and porewater concentrations of Fe and Mn in the cores from the southern (a, b: 1425 m, core 94-02) and central basins (c, d: 1630 m, core 94-09).

imum at a depth of 9.5 cm and Fe at 13 cm. Such dynamic diagenetic separation due to the chemical Fe and Mn differentiation within the oxidized zone is well pronounced in the deep-water sediments in Lake Baikal (Knyazeva, 1954; Leibovich, 1983; Mizandrontsev, 1984; Granina, 1991; Granina et al., 1993, 2000; Müller et al., 2002). The Mn layer was enriched by a factor of 25 and Fe by a factor of 12 (Table 3). According to the porewater Mn gradient, the formation time for the Mn layer was 1870 years. At a sedimentation rate of 0.14 mm year^{-1} (Table 1), the age of this sediment zone was estimated as 680 years (Table 2). The accumulation time for Fe of 1100 years and the age of the Fe crust of 930 years correspond well. The small gradient of sulfate (-6.4 µmol l^{-1} cm^{-1}; Table 3) and the extremely deep penetration depth (>27 cm depth; Fig. 2b) both suggest a rather small content of organic carbon.

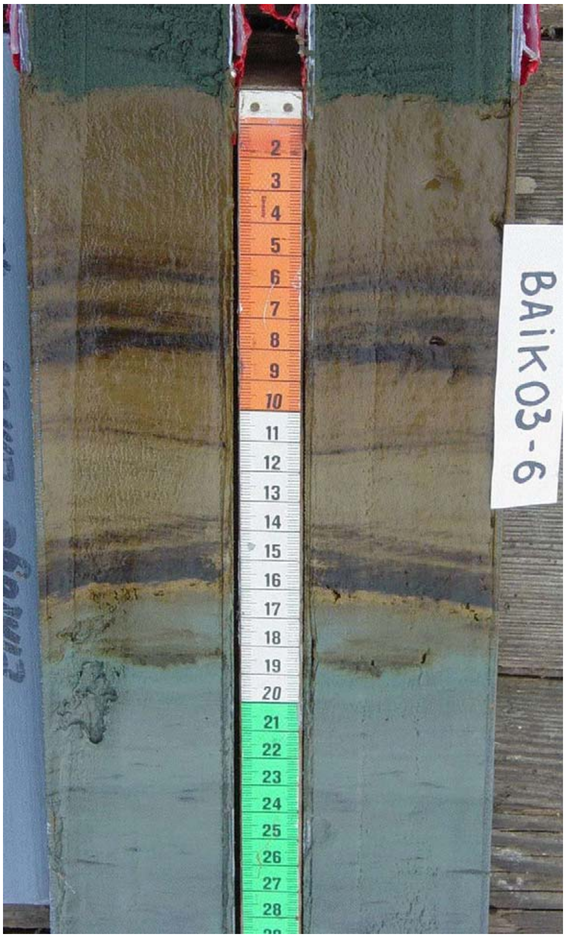

Fig. 4. Sediment core (BAIK03-6, 53 56.131 N, 108 53.940 E) from 367 m water depth at Academician Ridge containing bands of Fe (lower) and Mn (upper) accumulations at 15–16 cm sediment depth. (photo: Mike Sturm)

3.5. Academician Ridge

Three sites (94-11, 96-60, and 96-110) were studied at Academician Ridge, and porewater peeper 2 was deployed there. The topography of the Academician Ridge is very heterogeneous, and sedimentation rates are low because the ridge is far away from any sources of terrigenous material. Moreover, the ridge is a natural boundary for the permanent cyclic currents in the central and northern basins (Shimaraev et al., 1996), and massive water movements constantly directed over the sill from the south to the north (Hohmann et al., 1997) prevent sedimentation in this region. All cores enclosed spectacular thick brown-black enriched layers near the redox interface within the sediment (Figs. 4 and 5c, e, and f). Similar to core 94-10 (Fig. 5a), the Fe and Mn layers in core 94-11 were well separated (Fig. 5c) due to diagenetic redistribution of the elements according to their geochemical features. At Academician Ridge (core 94-11), this separation was more pronounced than in Northern Baikal. Cores 96-60 and 96-110 both held enrichments in the first few centimeters of the sediment, at around 10 cm, and relics of enriched layers or crusts deeper in the sediment (Fig. 5e and f). There were several solid-phase Fe and Mn peaks. Nonsteady-state redox processes must have caused multiple layers since only one peak is expected according to the thermodynamic equilibrium model (e.g., Burdige and Gieskes, 1983). This is a special case, which has been omitted from the present study because we consider only steady-state conditions in our approaches and calculations in this work. Porewater Mn was below detection limit above 7 cm (Fig. 5g), which coincided closely with the depth of Mn precipitates. In accordance with the vertical separation of Mn and Fe layers, dissolved Mn in the porewater was found closer to the sediment surface than dissolved Fe.

The accumulation times calculated from the upward porewater flux of Mn were 9130, 570, and 1260 years for the three cores from Academician Ridge. The ages of the Mn layers were 5000, 3460, and 4620 years (Table 2). High-time ranges were also calculated from the porewater Fe fluxes for the formation of Fe crusts with 6850, 14100, and 7730 years. The ages of the Fe layers were calculated to be 8460, 3460, and 4620 years. The extremely long accumulation times and ages of the sediments bearing enriched layers agreed with the small sedimentation rate on the ridge. Calculation of the sediment age was afflicted with errors due to the uncertain value for the sedimentation rate. The differences between calculated values may have been caused by the pronounced heterogeneity of topographic locations and corresponding alterations in the sediment. The enrichment factors were extremely high with values of 105 and 11 for Mn and Fe, respectively (Table 3). Academician Ridge sediments are known for their high O_2 penetration depth (Martin et al., 1998). In accordance, we observed the disappearance of sulfate only at 18 cm after exhibiting a small gradient of -3.5 μmol l^{-1} cm^{-1} (Fig. 2b, Table 3).

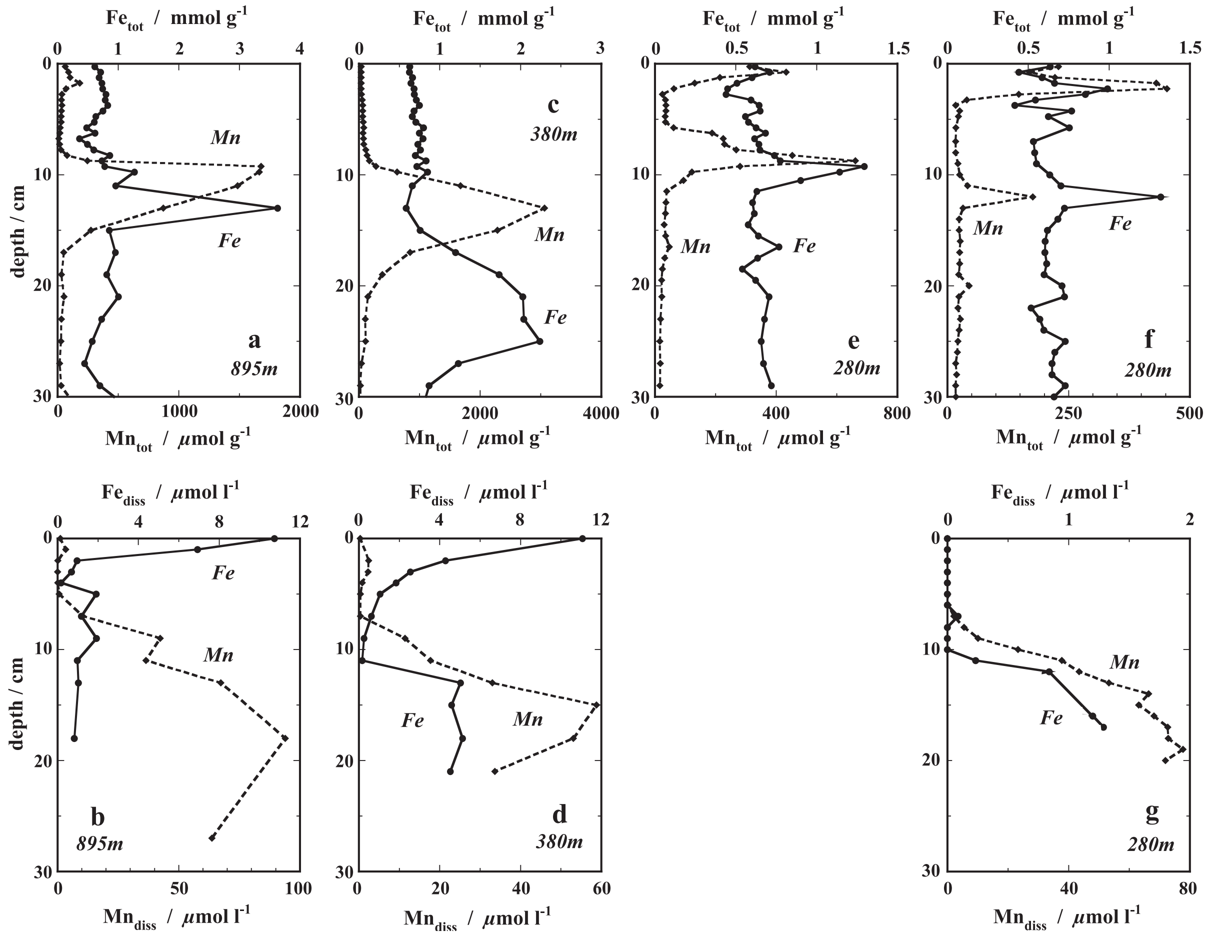

Fig. 5. Sediment profiles of particulate and porewater concentrations of Fe and Mn in the cores from Academician Ridge (c, d: 380 m, core 94-11; e: 280 m, core 96-60; f, g: 280 m, core 96-110) and the northern basin (a, b: 895 m, core 94-10).

3.6. Maloe More

Cores 94-12 and 96-52 and peeper 1 porewater profiles from Maloe More were investigated. The upper part of core 94-12 consisted of diatomaceous ooze. Below 7 cm, it was replaced by olive-gray clay mixed with alevrite and single grains of fine sand. Diatomic material disappeared gradually with increasing depth, and more alevrites and sands, including single grains of gravel, occurred together with low porosities of 15–25% (data not shown). Our data show that particulate Fe and Mn increased almost linearly with depth. Both metals were accumulated at 9 cm (Fig. 6a) and 15 cm (Fig. 6c). These observations confirmed earlier characterizations by Patrikeeva (1959), who also reported an increase of particulate Fe between 10 and 20 cm sediment depth for many stations in Maloe More. Former accumulation of Fe and Mn may have been buried by a sudden input of a substantial amount of terrigenous material since a large turbidite was clearly visible in the upper part of core 96-47, which was sampled close to core 96-52. The presence of dissolved Mn and Fe in the porewater (Fig. 6b and d) indicated that these accumulates underwent dissolution. Hence, the Maloe More profiles represented a situation where a buried crust was dissolving and reprecipitating close to the sediment–water interface. In both cores, a small Mn enrichment at the core top coincided with disap-

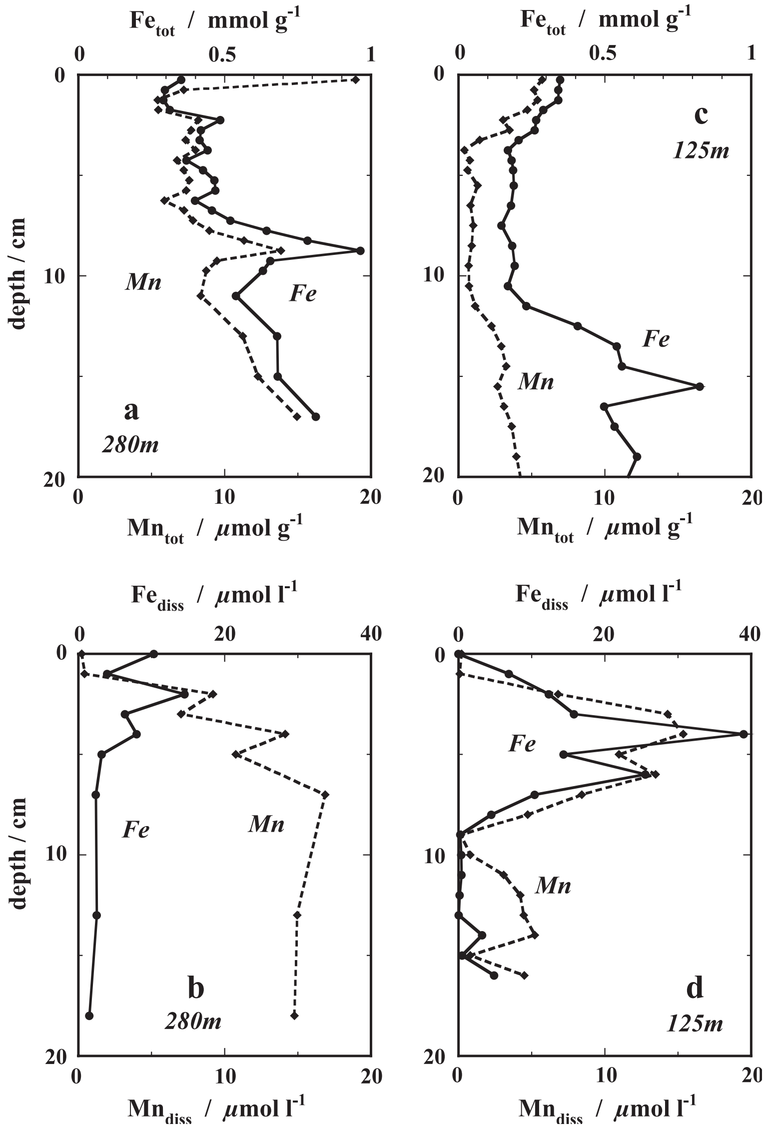

Fig. 6. Sediment profiles of particulate and porewater concentrations of Fe and Mn in the cores from Maloe More (a, b: 280 m, core 94-12; c, d: 125 m, core 96-52).

pearing Mn concentrations in the porewater. The accumulation time for these patterns corresponded to 3–8 years for Mn, and 10–85 years for Fe, respectively (Table 2). The sulfate porewater gradient of −1.8 µmol l^{-1} cm^{-1} was the lowest of all cores (Table 3). There was still porewater sulfate detectable at the depth of 18 cm (Fig. 2b), indicating low content of C_{org} in the sediment.

4. Discussion

4.1. Typology of Fe/Mn enrichments

The results obtained show that two types of Fe and Mn diagenesis may be distinguished in Lake Baikal. The first type was observed in the areas of comparatively rapid (0.24–0.8 mm $year^{-1}$; Table 1) sedimentation rates: near the Selenga Delta, in the southern and central basins. Only surface enrichments were found in these regions of the lake. The oxidized zone of the sediment was confined to the upper 2–4 cm. Sulfate gradients in the porewater were quite large (−13 to −53 μmol l^{-1} cm^{-1}; Table 3), indicating intense mineralization processes close to the sediment–water interface. The Mn and Fe accumulation in the surface sediment was characterized by moderate enrichment factors in the range of 2–16 and 1.2–3, respectively, compared to the background concentration of deeper cores (Table 3). The estimated accumulation times for the solid Mn oxides are in the range of 15–460 years and correspond well with the sediment age of 15–170 years at a depth of 2–4 cm (Table 2).

In contrast, the second type is represented by Fe and Mn trapped into massive enriched layers within the sediment in the northern basin and Academician Ridge, the lake regions with low sedimentation rates of 0.14 and 0.02 mm $year^{-1}$, respectively (Table 1). The oxidized zone in these regions extended over the upper 15–25 cm. The Fe and Mn peaks were broadened and covered the space between the position of the old and position of the new redox boundary (Fig. 5a and c), indicating that the shift of the redox boundary may have been somewhat slower compared to the sedimentation rate. This may be due to the lack of active C_{org}, which ranged from 1.3% to 1.8% in these sediments (Granina et al., 2000). Correspondingly, the sulfate gradients in the porewater were significantly smaller (−3.5 to −6.4 μmol l^{-1} cm^{-1}) compared to the regions of high sedimentation rates (Table 3). This indicated much slower sulfate reduction rates within the sediment. Whether SO_4^{2-} consumption was due to mineralization of C_{org} or anaerobic methane oxidation cannot be decided due to the lack of reliable CH_4 data in the porewaters of Lake Baikal. The accumulation of Mn and Fe occurred below the bottom surface, at the redox interface within the sediment, and large enrichment factors of 10–100 were calculated for these Fe and Mn layers. Assuming steady-state conditions, the estimated accumulation times were on the order of 600–9000 years. This time frame corresponded more or less with the sediment ages near the Mn maximum, which were of 700–5000 years (Table 2).

Several factors might account for the dramatic differences in the Fe and Mn accumulation in these lakes' areas. Partial loss of Fe^{2+} and Mn^{2+} diffusing from the porewater to the overlying lake water could occur in the surface zones near the Selenga Delta. However, this cannot be of great importance since, according to Martin et al. (1998), the near-bottom waters are constantly enriched in oxygen everywhere in the lake, including that area. Part of the iron may be taken within the anoxic sediments for the formation of authigenic sulfides. This is confirmed by the absence of Fe enrichments in the surface sediments at some shallow sites (stations 94-13, 94-05, and 94-07; Table 2) where the Mn enrichments were found. There are black spots and strips of hydrotroilite within the reduced sediments at these sites. On the other hand, the redox fronts within the sediment act as effective barriers for Fe^{2+} and Mn^{2+} in the lake areas characterized by slow sedimentation. The sedimentation rate and the associated diffusion rates in the porewaters could act as important driving forces for the contrasting typology of Fe/Mn layers.

4.2. Influence of sedimentation rates and sulfate reduction

A direct relation between the rates of sedimentation and sulfate reduction is well established in the marine systems (Berner, 1980; Canfield, 1993). Higher sedimentation rates at the ocean margins and in upwelling zones transport a large fraction of bioavailable organic matter to the sediment–water interface. Porewater measurements and the $^{35}SO_4^{2-}$ tracer technique both typically reveal high sulfate reduction rates. An analogous behavior is evident when we compare the different sedimentation regimes in Lake Baikal. Based on the data in Table 4, the turnover rates in terms of electron equivalents are plotted in Fig. 7a as a function of the sedimentation rate. Sulfate reduction estimated from porewater profiles increases linearly with the sedimentation rate (R^2=0.88). On the other hand, the combined electron turnover of iron and manganese reduction calculated from the Fe^{2+} and Mn^{2+} fluxes remains rather independent of the rate of sediment accumulation (R^2=0.08). Sulfate reduction surpasses iron and manganese reduction by a significant margin in the high accumulation zones near the Selenga Delta. With almost 1 mmol e^- m^{-2} day^{-1},

Table 4
Fluxes of electrons at the reduction of Fe, Mn, and SO_4^{2-} calculated from the porewater concentration gradients of dissolved Fe(II), Mn(II), and SO_4^{2-}

Region	e^- transfer$_{(Fe,\ Mn)}$ [μmol e^- m^{-2} day^{-1}]	e^- transfer$_{(SO_4)}$ [μmol e^- m^{-2} day^{-1}]	$e^-_{(SO_4)}$/ $e^-_{(Fe,\ Mn)}$
Near Selenga Delta	130	950	7.3
Southern Baikal	145	620	4.3
Central Baikal	220	550	2.5
North Baikal	220	265	1.2
Academician Ridge	110	145	1.4

the sulfate flux is seven times higher than the combined Mn and Fe reduction fluxes (Fig. 7a). In the regions with slow sedimentation, such as the Academician Ridge and the northern basin, Fe^{2+} and Mn^{2+} fluxes in the sedimentary layers enriched in Fe and Mn are of similar magnitude or slightly lower than the sulfate flux from the overlying water towards the lower end of the layer. These observations could imply that sulfide released by sulfate reduction acts as a major reducing agent for the massive Fe/Mn layers in Academician Ridge and Northern Baikal. The corresponding mechanism, where HS^- acts as mobile electron mediator in the reduction process, is outlined in Fig. 8 and can be summarized as follows: fermentation of organic carbon limits the sulfate reduction process (Jakobsen and Postma, 1999). The production of sulfide acts as a rate-limiting step for the reduction of Fe/Mn oxides. Reduced sulfur precipitates quantitatively as iron sulfide, while the excess Fe^{2+} and Mn^{2+} ions diffuse upwards to the oxic–anoxic boundary. The penetration depth of O_2 determines the position of the upper boundary of the Fe/Mn layer. Martin et al. (1998) determined deep O_2 penetration of more than the measured range of 5 cm in sediments from Academician Ridge, which supports our observations.

These remarkably constant diffusive fluxes of iron and manganese in the different sediment areas of Lake Baikal (Table 2) are in sharp contrast to the total amount of oxides present in the Fe/Mn sedimentary layers. Fig. 7b shows an exponential decrease in the Mn reservoir of the enriched layers as a function of sedimentation rate. The figure reflects the difference in time scales for the accumulation of Mn layers. The

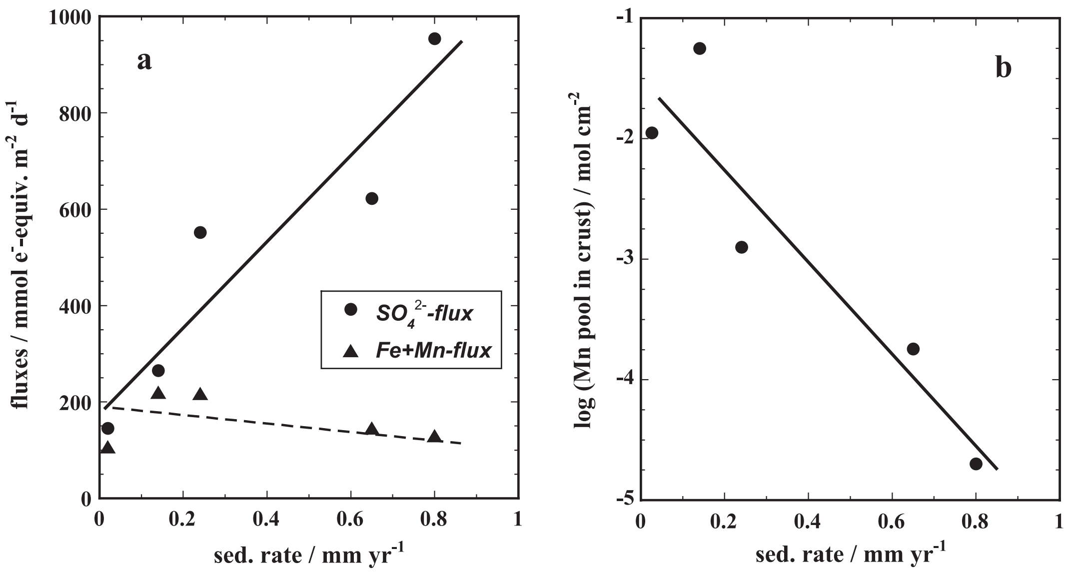

Fig. 7. (a) Diffusive fluxes of SO_4^{2-} and (Fe + Mn), expressed in millimoles electron equivalents per square meter per day, depend linearly on the sedimentation rates of the various locations of the lake. (b) Mn content accumulated in the Mn layers increases exponentially with decreasing sedimentation rates.

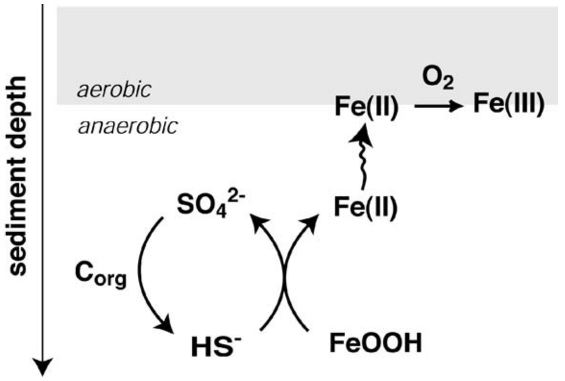

Fig. 8. Mediation of redox processes in the presence of enriched Fe and Mn layers in sediments.

enriched Fe and Mn layers in Academician Ridge and Northern Baikal are accumulated over centuries, even millennia; the surface enrichments near the Selenga Delta, in the southern and central basins, are formed within years to hundreds of years (Table 2). Fig. 7b displays a three-order-of-magnitude difference in the Mn pool of these enrichments. This corresponds well with the rather constant supply of reduced metal ions to the layers and the factor of 1000 difference in their formation time. However, the question remains as to which mechanism is triggering metal accumulation within the sediments.

The comparison of metal accumulation and diffusion rates in Table 2 provides an answer: the mass accumulation rate of particulate Mn to the sediment is typically 10–50 times lower than the corresponding diffusive fluxes of porewater Mn in the (type two) regions with low sedimentation rates. In the regions with higher sedimentation rates (type one), mass accumulation rates tend to be somewhat higher than diffusive fluxes. This difference indicates that in the areas of relatively fast sedimentation (type 1 diagenesis), a large fraction of settling Mn oxides is not transformed by rapid diagenetic processes, but accumulates in dispersed form. In contrast, the Mn accumulation and diffusion rates in the regions of slow sedimentation (type 2 diagenesis) are significantly higher than diffusive fluxes, even higher than the amount transported to the sediment, thus indicating recycling of former Mn depositions. In this case, there is enough time for the enriched layer to dissolve and reprecipitate. In addition, in the second type of diagenesis, an activity of specific microorganisms might contribute to higher Mn accumulation since it is well known that diagenetic accumulation of Fe and Mn in lacustrine sediments is of biogenic character. Recently, it was revealed that specific Fe and Mn oxidizing bacteria, identified as genus *Leptothrix* and genus *Galionella*, exist in Baikal sediments (Granina et al., in press). Moreover, both their abundance and pattern of distribution are closely related to the content of particulate and porewater Fe and Mn, which are in turn controlled by the redox conditions.

A critical comparison of accumulation time and sediment age in Table 2 provides additional support for the hypothesis of complete redox turnover at the areas of slow sedimentation (type 2 diagenesis) and almost unaltered burial at the sites of relatively fast sedimentation (type 1 diagenesis). The sediment age of the enriched layer is typically found to be younger than the calculated accumulation time. This supports the hypothesis of a constant redox cycling and an upward movement, where the metals move into younger sediment layers and thereby accumulate more metals. In summary, settling iron and manganese at the sites of relatively fast sedimentation are rapidly buried, whereas the slow sedimentation regime is characterized by slowly dissolving and reprecipitating Fe/Mn layers, which survive long enough to accumulate almost pure autochthonous oxide phases.

5. Conclusions

This study compares the remobilization and accumulation of iron and manganese in six contrasting sedimentary environments of Lake Baikal, in which the bulk sedimentation rate varied by a factor of 40 from about 0.8 mm year^{-1} near the Selenga Delta to 0.02 mm year^{-1} at Academician Ridge.

The results obtained allow for the distinction of two types of Fe and Mn diagenesis in Lake Baikal. The first type is characterized by only minor Fe/Mn enrichments near the sediment–water interface observed in the regions of relatively high sedimentation rates in the area near the Selenga Delta, and in the central and southern basins. Massive sedimentary layers enriched in Fe and Mn within the upper 15–25 cm of the sediments are typical for the second type of diagenesis. They are localized near the redox interface within the sediments, whereas there are no (or rather minor) Fe and Mn enrichments near the sediment–water interface. This type of Fe and Mn accumulation was found exclusively at Academician Ridge and Northern Baikal, which are characterized by slow sedimentation rates and deep sulfate penetration depths in the porewaters.

The calculated accumulation times for the enriched layers ranged from a few years to hundreds of years in the first case (type 1 diagenesis) and to several thousand years in the second case (type 2 diagenesis). These values were in general agreement with the age of the accumulation zones. Fe and Mn dynamics at sites with high sedimentation rates is dominated by allochthonous input, which is only partially dissolved close to the sediment surface. In contrast, the massive Fe/Mn layers at sites of slow sedimentation are of autochthonous origin. Their slow dissolution and reprecipitation allow for vertical movement of the crusts, keeping a constant position with respect to the sediment surface and preventing the burial as long as the sedimentation regime is constant.

Our results suggest that changes in the sediment regime could produce buried Fe/Mn layers, which might serve as proxy indicators. Deike et al. (1997) analyzed such older layers with ages up to 65,000 years and found evidence for a gradual transformation into vivianite and siliceous mineral phases. Our study supports their hypothesis that such buried layers might be indicative of periods of low sedimentation rates. Comparative sediment trap studies in the southern and northern parts of Lake Baikal are currently underway to provide additional evidence for such a direct link between Fe and Mn dynamics in the sediment and mass accumulation rates in the water column.

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