

Microscale mineralization pathways in surface sediments: A chemical sensor study in Lake Baikal

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Abstract

We used an array of ion-selective electrodes (oxygen [O₂], hydrogen [H⁺], carbonate [CO₃²⁻], calcium [Ca²⁺], ammonium [NH₄⁺], and nitrate [NO₃⁻]) with a micromanipulator to study mineralization processes in the surface sediments in Lake Baikal. Concentration profiles at submillimeter resolution were measured in sediment cores from four depths (160–1,400 m) in the South Basin. Oxidation rates of organic carbon (C) estimated from O₂ and NO₃⁻ profiles measured in March and July 2001 ranged between 2.2 and 4.9 mmol C m⁻² d⁻¹. The characteristic shape of the O₂ profiles allowed separation of oxidation of organic carbon from reoxidation of reduced compounds at the oxic–anoxic boundary. Of the benthic carbon turnover, 60–75% was metabolized through oxic respiration and 11–28% through anoxic mineralization. The remainder (12–14%) was due to denitrification. Carbon dioxide (CO₂) profiles calculated from O₂ agreed well with those from pH and CO₃²⁻, supporting the concept that oxic respiration was the prevailing mineralization pathway. Alkalinity balance calculated from flux rates of reduced compounds and bicarbonate (HCO₃⁻) calculated from pH and CO₃²⁻ profiles showed that the sediment was a sink for alkalinity. The flux rates in the range of 0.13–1.0 mmol m⁻² d⁻¹ were caused by buffering the hydrogen ions (H⁺) generated from reoxidation processes of reduced compounds. Potential dark CO₂ assimilation by chemoautotrophic bacteria in the sediment was 0.03–0.1 mmol C m⁻² d⁻¹. Because of the long O₂ exposure time of 25–2,500 yr, however, only 3–14% of the initially settled organic carbon was finally buried in the sediments, forming the paleolimnological record of Lake Baikal.

Lake Baikal in Eastern Siberia (Russia) is the world's largest lake by volume, holds ~20% of the global freshwater (23,015 km³) and is the deepest (1,637 m) and most probably the oldest (20–50 Myr) lake on earth. Besides this, its unique ecosystem harbors over 1,000 endemic plant and animal species. In recent years, Lake Baikal has become a key site for paleoclimatic research. The approximately 7-km-thick layer of sediments represents the longest continuous record on the Eurasian continent. The lake remained free of permanent ice sheets throughout the Pleistocene epoch (e.g., Kashiwaya et al. 2001).

Part of the accumulated sediment material stored in this archive consists of diatom ooze and refractory organic material that initially settled on the sediment surface and was exposed to dissolution and degradation processes. Organic mineralization processes are most intense in the surface layer of the sediment containing freshly settled organic matter, which has not been degraded on the way

through the oxygen-rich water column. Oxygen saturation exceeds 80% in the entire water column throughout the year. The high oxygen concentration of the bottom water in this cold, strongly oligotrophic lake is a result of rapid deep water renewal (Weiss et al. 1991; Hohmann et al. 1997; Ravens et al. 2000) and low new production (~15–21 g C m⁻² yr⁻¹, Müller et al. 2005). These low deposition rates of particulate organic carbon (POM) lead to oxygen penetration depths into the sediment exceeding 50 mm in some locations (Martin et al. 1998). Oxic conditions favor mineralization of aged and more refractory organic material because of the formation of oxygen radicals capable of oxidizing refractory organic compounds (Canfield 1994; Kristensen and Holmer 2001). Therefore, sedimentary organic matter that has been exposed to oxygen for a long time might be already highly metabolized when exposed to anoxic conditions where lower metabolic activity might help to preserve the remaining fraction of organics. Characterization of mineralization processes occurring in the oxic sediment zone is, therefore, essential for the interpretation of the composition pattern of deeper sediment layers used for paleolimnological studies and for the quantification of turnover rates of deposited organic matter in this extremely deep and oxygen-rich lake.

Turnover rates and pathways of organic carbon oxidation were often investigated with benthic chambers (Friedl et al. 1998), pore-water samplers (Urban et al. 1997), or microsensors (Viollier et al. 2003). Measurements with benthic chambers provide total flux rates of solutes into or out of the sediment, but do not give insights in their vertical distribution and thus do not localize zones of different metabolic activities. Deployment of diffusion plates introduced by Hesslein (1976) allowed pore-water sampling

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in vertical resolutions of typically 0.5 to 1 cm. This resolution is, however, insufficient to cope with the steep gradients at the sediment–water interface in limnic systems (e.g., Urban et al. 1997). Recently applied polyacrylamide gel probes (diffusive equilibration in thin films [DET] and diffusive gradients in thin films [DGT], e.g., Fones et al. 2001), allow the diffusive sampling of pore water at high resolution (0.1–1 mm), but this method requires fast retrieval to prevent reequilibration, which is difficult to achieve in a deep lake. Electrochemical microsensors, however, fulfill the demand for highly resolved concentration profiles at the sediment–water interface and are an analytical tool that is not intrusive and thus hardly influences the gradients of substrates and metabolites (e.g., Kühl and Revsbech 2001). Numerous studies with electrochemical microsensors addressed biogeochemical issues in marine sediments (Viollier et al. 2003). Among the few high-resolution studies in freshwater sediments, microelectrodes for NO_3^- (e.g., De Beer and Sweerts 1989), NH_4^+ (e.g., De Beer et al. 1991), H_2S (e.g., Kühl et al. 1998), or a combination of O_2 , NH_4^+ , NO_3^- , Ca^{2+} , pH, CO_3^{2-} , or S^{2-} (e.g., Sweerts et al. 1991; Müller et al. 1998) have been applied so far. Müller et al. (2002) introduced a profiling lander system equipped with a large array of ion-selective electrodes for in situ measurements directly at the lake bottom. Related to Lake Baikal, Martin et al. (1993a,b) reported the first oxygen measurements in the sediments and provided an overview of measured oxygen penetration depths at several sites in the period from 1991–1994 (Martin et al. 1998). However, to our best knowledge no quantitative study is available on recent sedimentary mineralization processes of deposited organic material in Lake Baikal. Because of the relevance of the oxic sediment layer for the sedimentary record, we focused our research on processes occurring in the surface sediments. The objectives of this study were (1) to quantify the contribution of oxic respiration on organic matter mineralization, (2) to determine process rates of oxic and chemoautotrophic pathways, (3) to evaluate the carbonate buffer system of the recent sediment, and (4) to assess implications on the paleolimnological record of the deeper sediments of Lake Baikal.

Material and methods

Study and sampling sites—Lake Baikal located in the great Baikal Rift Zone of eastern Siberia consists of three main basins divided by underwater sills: the southern (maximum depth 1,432 m), central (1,637 m), and the northern basin (897 m). The slopes are generally very steep because of the tectonic origin of the lake. Lake Baikal has more than 300 inflows and one outflow (Angara), which is situated on the northwestern shore of the South Basin, and the mean hydrological residence time is approximately 330 yr (Falkner et al. 1991). During the cold period in winter, the lake is covered by an ice layer of 50–150 cm. Ice break-up in the southern basin starts in May, and the lake is typically ice-free from June to November.

Our sampling sites marked in Fig. 1 were chosen at similar locations for sediment analyses and sediment trap

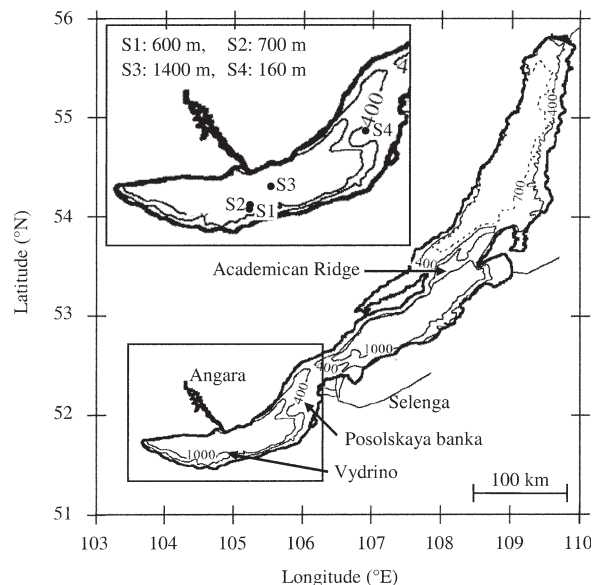


Fig. 1. Map of Lake Baikal showing the sampling sites of the South Basin (enlarged area).

moorings. Particle flux, POM deposition, and sediment chemistry are presented elsewhere by Müller et al. (2005). The sites were located in the South Basin at three different water depths from the Vydrino shoulder (600 m) to the deepest site (1,400 m) and the Posolskaya banka (160 m), an underwater hill south of the delta formed by the Selenga River, the lake's largest inflow. During two expeditions sediment cores were taken in March 2001 from the ice and in July 2001 from the RV *Vereshagin*. The exact geographical coordinates, water depth, and sampling date of all sites are listed in Table 1.

Preparation of PVC-based liquid-membrane ion-selective electrodes—Miniaturized ion-selective electrodes for NH_4^+ , NO_3^- , Ca^{2+} , CO_3^{2-} , and H^+ were prepared as described in detail by Müller et al. (1998). Briefly, 10- μL plastic pipette tips with a tip diameter of about 0.6 mm were used as electrode bodies. Approximately 1 μL of membrane solution was drawn up resulting in a 0.5-mm thick membrane after evaporation. The membrane was conditioned with inner filling solution for 1 d. A chlorinated silver wire (Ag/AgCl) was used as internal reference, and an Ag/AgCl double junction cell (Metrohm Ltd.) served as the reference electrode.

Experimental setup—A sensor rack was equipped with 14 electrodes for NH_4^+ , NO_3^- , Ca^{2+} , CO_3^{2-} , and pH. The sensor slots were arranged 5 mm apart in a square of 4 × 4 cm. The large number of slots allowed multiple determination of each parameter, providing insight into the spatial heterogeneity at small scales and allowing cross-checking of profiles. The sensor rack was mounted to a computer-controlled micromanipulator (Newport), which moved the sensors vertically in step sizes of 0.1–0.3 mm. The reference electrode remained immobile in the water above the sediment. At each sediment depth, five replicate measurements were conducted with each electrode at time

Table 1. Sampling locations in the South Basin of Lake Baikal (see Fig. 1) and measurement program.

Site Longitude (°E), Latitude (°N)	Location (Fig. 1)	Water depth (m)	Sampling date (2001)	Measured parameters (number of profiles)	Measuring place and date
104.908, 51.600	Vydrino (S1)	600	16 Mar	O ₂ (4), NH ₄ ⁺ (6), Ca ²⁺ (7), H ⁺ (8), CO ₃ ²⁻ (5)	On ice, 16 Mar
104.900, 51.617	Vydrino (S2)	700	16 Mar	O ₂ (2), NH ₄ ⁺ (2), Ca ²⁺ (2), H ⁺ (4), CO ₃ ²⁻ (2)	On ice, 16 Mar
104.783, 51.693	Near mooring (S3)	1,400	16 Mar	O ₂ (4), NH ₄ ⁺ (2), Ca ²⁺ (4), H ⁺ (4), CO ₃ ²⁻ (2)	On ice/Listvijanka, 16/17 Mar
105.860, 52.077	Posolskaya banka (S4)	160	10 Jul	O ₂ (3), NH ₄ ⁺ (1), NO ₃ ⁻ (5), Ca ²⁺ (3), H ⁺ (6), CO ₃ ²⁻ (3)	Listvijanka, 13 Jul
104.913, 51.617	Vydrino (S1)	600	12 Jul	O ₂ (2), NH ₄ ⁺ (5), NO ₃ ⁻ (4), H ⁺ (6), CO ₃ ²⁻ (4)	Listvijanka, 13 Jul
105.023, 51.709	Near mooring (S3)	1,400	12 Jul	O ₂ (2), NH ₄ ⁺ (4), NO ₃ ⁻ (4), H ⁺ (6), CO ₃ ²⁻ (4)	Listvijanka, 13 Jul

intervals of 4 s. An impedance converter transformed the electrode signals (potentials) into low ohmic signals, which were recorded and visualized online with a data acquisition program (LabView, National Instruments). In addition, two Clark-type oxygen microelectrodes with a guard cathode (OX25-glass sensor, Unisense Ltd.) were placed at a distance of 15 mm from the sensor rack and spaced 15 mm from each other. These sensors were connected to a self-made picoammeter, and the resulting signal was recorded online with the same LabView program.

During the March expedition, measurements were conducted on-site on ice, and the electrical power was generated using a sine wave inverter (Elektro Automatik), transforming 24 V (DC) from two car batteries into 220 V (AC). The lake acted as a stable ground by connecting the water from an ice hole with our equipment. To eliminate electrostatic noise, we used a grounded Faraday cage to encase the potentiometric measurement setup. Coaxial cables were used for the signal transfer.

Sensor calibration and data validation—Before the actual field measurements, all ion-selective sensors were tested in the laboratory with reference solutions for several hours to eliminate faulty electrodes that showed a strong signal drift or a large deviation from nernstian response. The electrodes finally used to measure pore-water profiles were calibrated again on-site with three solutions of different ion activities in the range of at least one logarithmic unit and close to the concentration expected in the sediment cores. A stable signal was generally achieved within a couple of minutes after changing the calibration solution. The signal response for one logarithmic unit in the activity of the measuring ion (slope) was close to a nernstian response (~ 55.2 mV charge⁻¹ at 5°C) for all sensors. In detail, the H⁺ sensors showed slopes of 53.1 to 55.1 mV (except one with 44.6 mV), the Ca²⁺ sensors 27.3 to 30.4 mV, the NH₄⁺ sensors 53.5 to 57.9 mV, the NO₃⁻ sensors -56.4 to -52.8 mV, and the CO₃²⁻ sensors -27.6 to -20.5 mV.

Signal drift during calibration was small and thus in most cases no correction was necessary. However, a few NH₄⁺ profiles during the July expedition showed a contin-

uous signal drift in the water above the sediment as well as in the sediment itself, which was therefore corrected.

The slope of the sensors was reproducible when moving from calibration solutions to the experimental setup; however, a shift in the absolute electrical potential did occur in some cases. To improve the accuracy of the electrode measurements, we adjusted the profiles to the absolute concentration in the overlying water in case of deviations (see, e.g., Müller et al. 2002). Therefore, water above the sediment of all cores was collected, its pH was measured and conserved with chloroform (CHCl₃) (0.2%), and transported to our lab at Eawag for further chemical analyses. Concentrations of NH₄⁺ and NO₃⁻ were determined photometrically, cations and anions by ion chromatography, and alkalinity by acid titration, to correct for potential shifts. Finally, pH profiles were shifted to 7.4 by -13.1 to 36.8 mV, Ca²⁺ to 0.4 mmol L⁻¹ by -1.0 to 2.8 mV, CO₃²⁻ to 0.7 μ mol L⁻¹ by -10.0 to 11.2 mV (except one by 43 mV), and NO₃⁻ to 9.5 μ mol L⁻¹ by 20.9 to 62.8 mV. The concentration of NH₄⁺ in the lake water was near the detection limit of the sensors (~ 1 μ mol L⁻¹) and, therefore, profile shifts varied strongly and were rather imprecise. Detection limits were not determined in particular, but in Lake Baikal, with water of low ionic strength, these might be around 1 μ mol L⁻¹ and lower for CO₃²⁻ and Ca²⁺ (see Müller et al. 1998).

Electrode measurements of NH₄⁺ and NO₃⁻ showed interferences by other ions. Profiles of NH₄⁺ were corrected for the interference of potassium ion (K⁺), and those of NO₃⁻ for HCO₃⁻ and chloride (Cl⁻) by applying the extended Nikolsky–Eisenmann equation (Bakker et al. 1994; Müller et al. 1998). For K⁺ (~ 25 μ mol L⁻¹) and Cl⁻ (~ 12 μ mol L⁻¹, Falkner et al. 1991) a conservative behavior in the sediment was assumed. Profiles of HCO₃⁻, however, are a result of diagenetic processes and influence the shape of the NO₃⁻ profiles. The selectivity coefficient is $10^{-2.2}$ (or $10^{-2.6}$) (see Müller et al. 1998) and, thus, changes in the HCO₃⁻ concentration of 100 μ mol L⁻¹ affected the NO₃⁻ concentration by 0.25 to 0.63 μ mol L⁻¹. All other measured parameters were not influenced by interfering ions. The O₂ microelectrodes were calibrated linearly by readings in the overlying water and in the anoxic part of the

sediment. Oxygen content of the water above the sediments was determined by Winkler titration.

Data acquisition and data processing—During the March expedition, sediment cores were collected with a gravity corer (Kelts et al. 1986) and PVC liners (6.3 cm diameter) along a transect from 600 m (Vydrino Shoulder) and 700 m, and from the deepest site in the South Basin at 1,400 m depth (Fig. 1). Our measurement facilities were installed in a Russian mobile lab, which was positioned next to the Vydrino site. Thus, concentration profiles of cores from 600- and 700-m depth were measured on-site directly after core retrieval. The temperature of these cores did not differ from in situ conditions during measurements (because of the low air temperature). However, the missing flow velocity of the overlying water in the cores may have reduced the transport of solutes in and out of the sediment but most probably did not affect the profiles during the short exposure times. Before measuring each sediment core, we carefully cut them so that they had a layer of around 5 cm of in situ water above the sediment and 25 cm of undisturbed sediment. At the 1,400 m site, limitations of time and power supply allowed the measurements of O₂ profiles only, and a complete set of profiles were recorded in Listvijanka with a second core from 1,400 m within 20 h. This core was transported with a water column of about 1 m above the sediment, which effectively protected the sediment surface from disturbance.

During the July cruise on board the RV *Vereshagin*, sediment cores were taken with at least 1 m of overlying water from Posolskaya banka (160 m), Vydrino shoulder (600 m), and the center of the South Basin (1,400 m). Cores were wrapped in aluminum foil to protect them from light and warming, and stored vertically (however, a slight temperature increase of some cores cannot be ruled out). Measurements of two stations were performed within 1 day and one within 3 days after retrieval in the lab in Listvijanka. Because turnover rates are typically low in nutrient-poor systems, the storage might not have a strong impact on pore-water profiles. Table 1 summarizes the parameters and number of profiles measured at each site as well as place and date of measurements. In July 2001, the number of profiles was reduced for several parameters because of the malfunctioning of some electrodes.

The possibility of biological sediment mixing (bioturbation) could not be dismissed in Lake Baikal but is more limited at greater depths (Martin et al. 2005), hence, molecular diffusion is the main transport mechanism. Areal fluxes (mmol m⁻² d⁻¹) were calculated from concentration profiles applying Fick's first law for sediments (Berner 1980)

$$J_s = -\frac{D_0}{F} \frac{dC}{dx}, \quad (1)$$

where J_s is the flux into or out of the sediment and F stands for the formation factor, which represents the influence of particles on sedimentary diffusion and changes with depths. At the sediment–water interface F was 1.2, calculated from porosity, $\phi = 0.92$ (similar for all sites, Müller et al. 2005), applying the empirical relation $F = \phi^{-1.81}$ from Maerki et al. (2004). The ratio dC/dx is the concentration gradient at

specific depths or at the sediment–water interface (mmol m⁻⁴), and D_0 is the molecular diffusion coefficient (m² d⁻¹) in pure water at 5°C. Furrer and Wehrli (1996) provided the following coefficients: O₂ (1.08×10^{-4} m² d⁻¹), Ca²⁺ (0.39×10^{-4} m² d⁻¹), NH₄⁺ (1.02×10^{-4} m² d⁻¹), NO₃⁻ (1.02×10^{-4} m² d⁻¹), CO₃²⁻ (0.46×10^{-4} m² d⁻¹), HCO₃⁻ (0.56×10^{-4} m² d⁻¹), and H₂CO₃ (0.91×10^{-4} m² d⁻¹).

Results

Oxygen—The concentration of O₂ in the water above the sediment measured in March 2001 was around 0.40 mmol L⁻¹ at all stations, and thus was close to saturation at 3.5°C. In July 2001, however, O₂ concentrations were lower and between 0.29 and 0.35 mmol L⁻¹ (Fig. 2). The shape of O₂ pore-water concentration profiles showed similar patterns at all stations. They consisted typically of two zones of O₂ consumption, indicated by bent profiles: the first within the top 5 to 10 mm (upper zone) and the second at the oxic–anoxic boundary (lower zone). This pattern was most pronounced in the March profiles (Fig. 2); however, determination of consumption rates with the model of Berg et al. (1998) also showed clearly two main consumption zones in the upper and lower zone of the July profiles (Fig. 2). The flux of O₂ at the sediment–water interface (J_1) reflects the depth-integrated consumption rates over the complete profile. Averaged O₂ fluxes across the sediment surface were highest in March at 600 and 700 m with 5.1 and 3.6 mmol m⁻² d⁻¹, respectively, and were generally lower in July with 2.2 to 2.8 mmol m⁻² d⁻¹ (Table 2). Thereby, a fraction of 60 and 77% was consumed in the upper zone in March and only ~35% in a comparable depth interval in July, reflecting a lower intensity of oxidation processes in the surface compartment. The flux rates of O₂ diffusing into the lower zone (J_2) were ~1 mmol m⁻² d⁻¹ (20–33% of J_1) and ~0.4 mmol m⁻² d⁻¹ (13–18% of J_1) in March and July, respectively (Table 2).

Oxygen penetration depths ranged from 15–27 mm and were lowest at the shallowest site (160 m) measured in July 2001 (Fig. 2), but no relation to sampling date or water depth was observed.

pH—The pH of the bottom water was around 7.4 at all stations in March and July 2001. Pore-water profiles were of parabolic shape with a steep decrease just below the sediment surface and reached values lower than 7 at 25-mm sediment depth (Fig. 2). The pH decreased continuously with depth until O₂ was depleted and remained quite constant below. Steepest pH gradients were determined near the sediment surface at 700 m in March and at 160 m in July 2001 with 0.2 pH units mm⁻¹. The pH data were used in combination with the CO₃²⁻ profiles to quantify the buffer system of inorganic carbon in the sediment pore water.

Carbonate—Carbonate concentration in the water overlying the sediment was around 0.75 μmol L⁻¹ at all sites. The profiles of CO₃²⁻ followed the shape of the pH profiles except for the sites at 700 m in March and 160 m in July

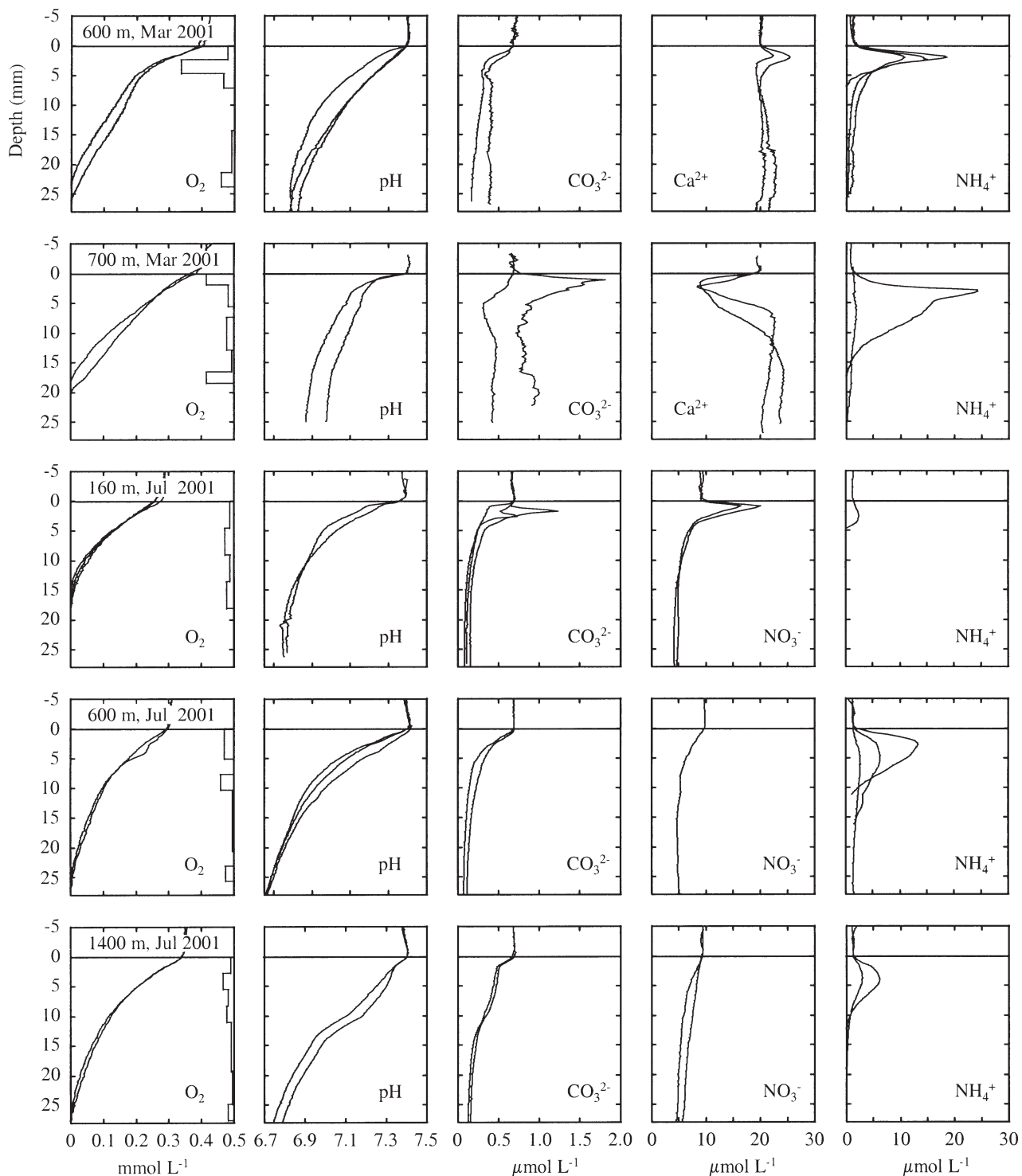


Fig. 2. Selected concentration profiles of O₂, pH, CO₃²⁻, Ca²⁺, NO₃⁻, and NH₄⁺ at different depths measured in March and July 2001. Bars in the O₂ profiles show zones and intensity of O₂ consumption (highest rate was 1.12 mol m⁻³ d⁻¹ at 600 m, March 2001).

2001, where distinct peaks were detected just below the sediment surface. Although the detected CO₃²⁻ concentrations were very low, strong interferences with concentrations of other anions present in Lake Baikal are unlikely (e.g., Müller et al. 1998). The shape of the CO₃²⁻ profiles is

therefore a result of features in pH and alkalinity caused by early diagenetic processes.

Bicarbonate and carbonic acid—No ion-selective electrode is available so far to detect HCO₃⁻ with sufficient

Table 2. Summary of O_2 , NO_3^- , and NH_4^+ flux rates and the total mineralization rate of organic carbon (R_{ox}) at each site in $mmol\ m^{-2}\ d^{-1}$.

	O_2		NO_3^-	NH_4^+	C_{org}
	J_1	J_2	J_1	J_1	R_{ox}
March 2001					
600 m	-5.1 ± 0.8	-1.0 ± 0.1	nd	0.60 ± 0.2	4.9 ± 0.7
700 m	-3.6 ± 0.2	-1.2 ± 0.0	nd	0.46 ± 0.6	3.4 ± 0.2
July 2001					
160 m	-2.6 ± 0.4	-0.42 ± 0.1	0.8 ± 0.2	0.04	2.5 ± 0.4
600 m	-2.2 ± 0.5	-0.41 ± 0.1	-0.072	0.16 ± 0.1	2.1 ± 0.5
1,400 m	-2.8 ± 0.3	-0.37 ± 0.1	-0.047	0.10 ± 0.1	2.7 ± 0.3

J_1 and J_2 stand for the flux rate at the sediment–water interface and at the oxic–anoxic boundary, respectively (see Fig. 3). Negative values indicate fluxes from the water into the sediment, and nd stands for not determined. The number of measurements was $n = 1$ –3, according to Fig. 2.

selectivity in limnic systems. Hence, we calculated concentration profiles of HCO_3^- and carbonic acid ($H_2CO_3^*$) from simultaneously measured CO_3^{2-} and H^+ activities ($pK_1 = 6.52$ and $pK_2 = 10.56$ at $5^\circ C$, Stumm and Morgan 1996). Reference concentrations of HCO_3^- and $H_2CO_3^*$ in the water overlying the sediments were 1.1 and 0.14 $mmol\ L^{-1}$, respectively.

Bicarbonate profiles at 160, 600, and 1,400 m from the July expedition in Fig. 5 were calculated with the averaged measurements from two to three independent sensors for pH and CO_3^{2-} . The standard deviations of HCO_3^- data reflect mainly spatial heterogeneities in these sediments and were relatively small (<30%) compared with the March data (not shown). Apart from individual patterns in the uppermost

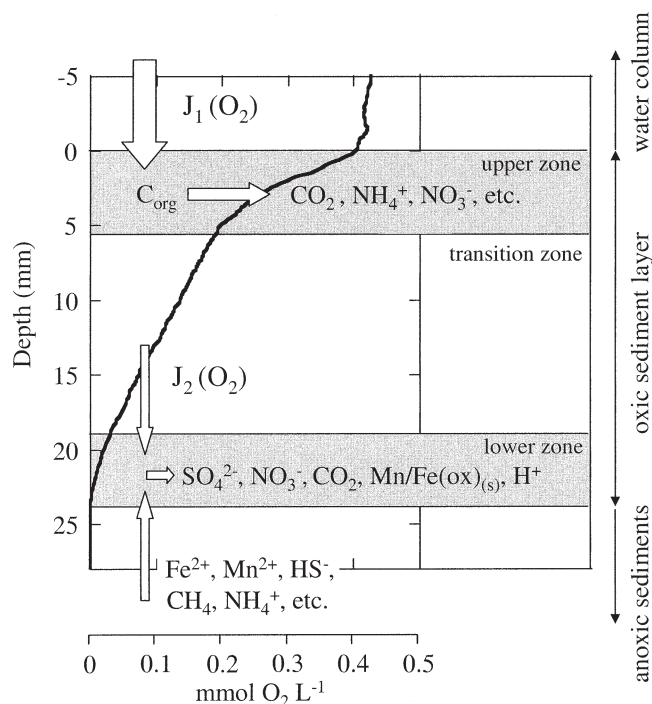


Fig. 3. Two-layer concept of O_2 consumption.

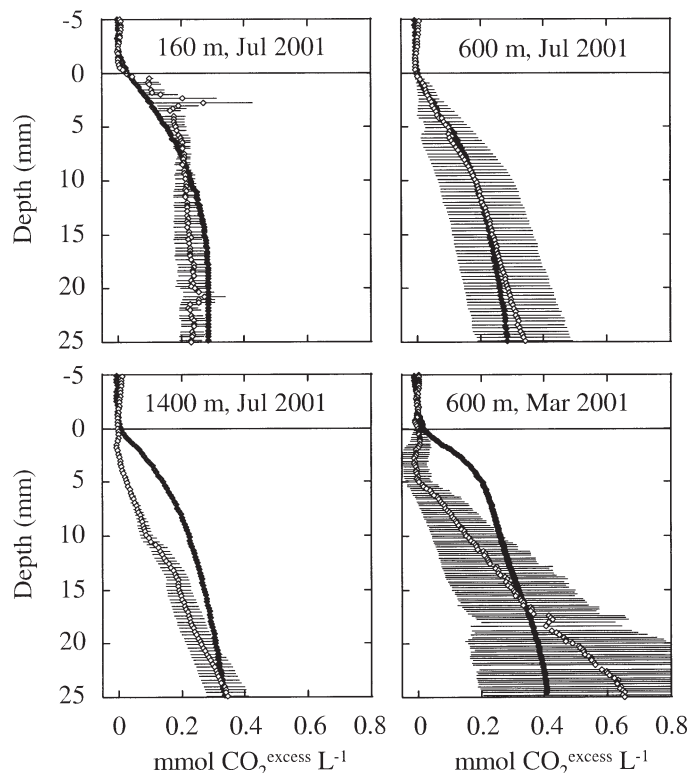


Fig. 4. Profiles of CO_2^{excess} calculated from pH and CO_3^{2-} data (open symbols) and from O_2 measurements (closed symbols) at four sampling sites.

4 mm, the concentration of HCO_3^- decreased slightly with depth. Large subsurface peaks of up to 4 $mmol\ L^{-1}$ HCO_3^- occurred at 160 m in July and were most pronounced at 700 m in March 2001. Profiles of $H_2CO_3^*$ from July and from selected March data (omitting the CO_3^{2-} data of high peak concentration at 700 m) generally showed a continuous increase with depth (see Fig. 4).

Calcium—Calcium concentrations in the overlying water were generally close to 0.40 $mmol\ L^{-1}$. Pore water profiles measured in March 2001 displayed distinct peaks to higher and to lower concentrations at 600 and 700 m, respectively (Fig. 2). Below the peaks, the Ca^{2+} concentration remained constant at the same level as above the sediment. A Ca^{2+} minimum was also found in July at 160 m but was not as pronounced as in March at 700-m depth (data not shown). The excellent reproducibility with multiple sensors documented Ca^{2+} releasing processes as well as Ca^{2+} consuming processes at different locations in the South Basin of Lake Baikal, although calculations of $\{Ca^{2+}\} \times \{CO_3^{2-}\}$ showed saturations in the bottom and sediment pore water of less than 5% with respect to calcite. Peak concentrations of one ion were mainly compensated for by the opposing peak concentrations of the other ion. However, our findings might be an indication of unknown carbonate processes occurring in these sediments during ice cover.

Nitrate—Profiles of NO_3^- were only measured during the July 2001 expedition and showed a concentration

decrease in the oxic zone, which may indicate coexistence of heterotrophic oxic respirators and denitrifiers. Nitrate decreased from $\sim 9.5 \mu\text{mol L}^{-1}$ in the water above the sediment to $\sim 5 \mu\text{mol L}^{-1}$ within the oxic sediment layer. At this low NO_3^- concentration, such sensor measurements are strongly affected by millimolar HCO_3^- concentration. Nevertheless, the HCO_3^- gradient explains only a fraction of the observed NO_3^- decrease. Below 10-mm depth, the concentration of $5 \mu\text{mol L}^{-1}$ remained constant down to 25 mm. Nitrate fluxes into the sediment were between 0.072 and $0.047 \text{ mmol m}^{-2} \text{ d}^{-1}$ at 600 and 1,400 m, respectively (Table 2).

In contrast, distinct peaks of NO_3^- with concentrations of almost $20 \mu\text{mol L}^{-1}$ were found in the sediment from 160 m and also in a second profiling run with the sediment core from 600 m (data not shown). Such peaks, however, overestimate strongly benthic nitrogen mineralization on a basinwide annual average (see Müller et al. 2005).

Ammonium—Distinct peaks of NH_4^+ were found right below the sediment surface in all sediment cores. They were more pronounced in March with peak concentrations of around $20 \mu\text{mol L}^{-1}$. The flux rates of NH_4^+ out of the sediment were $0.5\text{--}0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ in March and ranged between 0.04 and $0.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ in July (Table 2).

High variability of NH_4^+ profiles were found with repeated measurements within 2 hours (same electrodes, same core, and same experimental setup). For instance, peak concentrations were 10 times higher in the second profiling run ($>100 \mu\text{mol L}^{-1}$, data not shown) than previously measured (600 m, March 2001). Comparable large peaks of NH_4^+ were detected in cores at 1,400 m in March and earlier in Lake Baikal in cores sampled at shallow nearshore sites in 1994 (data not shown). Sub-surface NH_4^+ peaks have also been found in marine sediment cores from great water depth (Glud et al. 1994; Lohse et al. 1998). The authors attributed this phenomenon to the probable lysis of bacteria caused by decompression and temperature change during core recovery and considered these peaks to be artifacts and in such cases NO_3^- peaks as well. Decompression effects have certainly affected our pore-water profiles from the deepest sites; however, they might be less important for the shallower sites and may partly reflect micro niches of high benthic activity (e.g., Lewandowski et al. 2002).

Oxidation of organic carbon—Total organic carbon oxidation rate, R_{ox} , can be established by summing denitrification (C_{denit}), and oxic (C_{ox}) and anoxic (C_{anox}) mineralization (Eq. 2). In extended oxic sediments, the flux of O_2 across the sediment–water interface, $J_1(\text{O}_2)$, combines oxic and anoxic respiration and also includes nitrification of liberated NH_4^+ . The concentration of NO_3^- in the sediment, however, did not increase, indicating subsequent carbon oxidation by the NO_3^- produced. Therefore, we assumed denitrification to be fueled by nitrification and by NO_3^- from the water column. The nitrification rate was estimated from the flux rate $J_1(\text{O}_2)$ and the C : N ratio of POM. Neglecting burial of reduced electron acceptors precipitated as iron sulfide (FeS) and manganese sulfide

(MnS), the carbon oxidation rate is given as

$$R_{\text{ox}} = C_{\text{ox}} + C_{\text{denit}} + C_{\text{anox}} = aJ_1(\text{O}_2) + 1.25J_1(\text{NO}_3^-), \quad (2)$$

where $a \approx 0.94$ is the C : O_2 ratio of 11.25 : 12 calculated for the oxidation of POM (C : N = 10, Müller et al. 2005) consuming 12 O_2 per 10 C and subsequent denitrification releasing 1.25 C per NO_3^- (Froelich et al. 1979).

To estimate the carbon oxidation from the NO_3^- flux, we considered the NO_3^- profiles measured at 600 and 1,400 m (Fig. 2) to be more reasonable in terms of mass balance calculations (Müller et al. 2005) compared with profiles showing distinct peaks below the sediment surface, and we assumed similar profiles also at sites where we did not measure NO_3^- . Therefore, denitrification fueled by the water column amounts to $0.06\text{--}0.09 \text{ mmol C m}^{-2} \text{ d}^{-1}$, which is around 10–28% of the total denitrification rate ($0.23\text{--}0.62 \text{ mmol C m}^{-2} \text{ d}^{-1}$). This fraction may even be smaller considering the interference of the NO_3^- -sensor profile by HCO_3^- of decreasing concentration in the sediment of Lake Baikal.

Overall, R_{ox} was estimated between $2.1\text{--}4.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ at our sampling sites (Table 2).

Discussion

Annual carbon mineralization and oxygen exposure time—Only $1.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$ of the total annual primary production of 10 mol C m^{-2} (Moskalenko and Votintsev 1972) are exported from the epilimnion of the South Basin to deeper water layers whereby 1.2 mol C finally settle to the sediment surface as determined by sediment trap data (Müller et al. 2005). Considering a net burial rate of $0.22 \text{ mol C m}^{-2} \text{ yr}^{-1}$ determined from sediment core analysis, the benthic mineralization rate of organic carbon is $\sim 1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ or $2.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Müller et al. 2005). A comparison with our direct assessments of the benthic mineralization based on O_2 pore-water profiles reveals excellent agreement for the average of the two expeditions ($3.2 \text{ mmol m}^{-2} \text{ d}^{-1}$), supporting the reliability of both approaches for the evaluation of annual benthic mineralization rates in spite of seasonal and spatial variability of O_2 profiles. In systems such as Lake Baikal, where the sedimentation rate of organic matter is low and the concentration of oxidants in the bottom water high, sedimentary mineralization rates are limited by the availability of substrate rather than by the supply of electron acceptors. Consequently, the penetration depth of O_2 in the South Basin ranged from 1.7 to 2.7 cm, confirming earlier results by Martin et al. (1998). These authors reported penetration depths from a few millimeters in the Selenga Delta region to more than 5 cm at Academician Ridge, an underwater sill dividing the North from the Central Basin. As a consequence of such deep oxygen penetration and low sedimentation rates in Lake Baikal, sedimentary organic material is exposed to oxygen for decades. For example, the annual sedimentation rate in the South Basin of Lake Baikal is $\sim 0.65 \text{ mm yr}^{-1}$ (Edgington et al. 1991), leading to an oxygen exposure time of 25–40 yr. The much lower sedimentation rates at

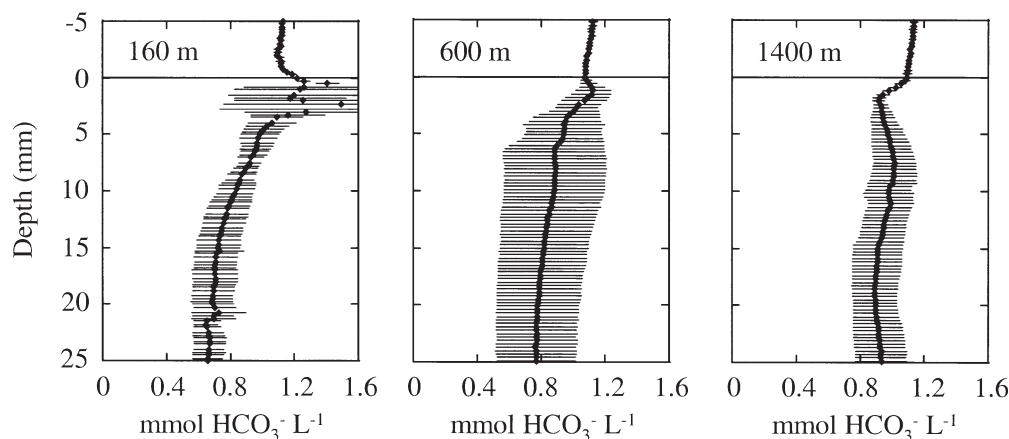


Fig. 5. Profiles of HCO_3^- calculated with pH and CO_3^{2-} data at the three sites sampled in July 2001.

Academician Ridge ($\sim 0.02 \text{ mm yr}^{-1}$, Vologina et al. 2000) and deeper O_2 penetration even correspond to $\sim 2,500 \text{ yr}$. This contrasts with most deep lakes in Europe, where the calculated theoretical exposure time ranges from a few years in oligotrophic to weeks in eutrophic lakes with oxic hypolimnia.

The oxygen exposure time seems to be the key factor in the organic carbon preservation in marine sediment, which is a major issue in the global carbon cycle. For continental margin sediments, Hartnett et al. (1998) established a relation between oxygen exposure time and the burial efficiency of organic carbon, corresponding to the percentage of buried organic carbon with respect to the settling flux. We calculated low burial efficiencies of $\sim 16\%$ for the South Basin and $\sim 3\%$ for Academician Ridge using published O_2 profiles (Martin et al. 1998), a sedimentation rate of 0.02 mm yr^{-1} , a porosity of 0.8, and an organic carbon content of 2% (Müller et al. 2005) for the latter site. Burial efficiencies were lower with longer O_2 exposure time at these two sites in Lake Baikal in agreement with the relation of Hartnett et al. (1998), suggesting similar mechanisms of organic carbon preservation in marine and lake sediments.

Two-layer concept of sedimentary O_2 consumption—Microelectrode measurements revealed two zones in the sediments of Lake Baikal with intense O_2 consumption spatially separated from each other by a 10–15-mm thick layer of much lower reactivity (Figs. 2 and 3). Our multiparameter approach indicated that in these sediments heterotrophic oxic respiration was clearly separated from chemoautotrophic oxidation of reduced compounds: In the upper zone localized right below the sediment surface (Fig. 3), oxic respiration of organic matter was the dominant O_2 -consuming process. Here, the release of NH_4^+ and CO_2 , which lowered the pH, was traced as well as occasional formation of NO_3^- (Fig. 2). Oxic respiration may also be the prevailing process in the adjacent transition zone below, but at a much lower rate, suggesting the prevalence of refractory organic matter. However, in the lower zone, intense reoxidation of reduced compounds was dominant. In a previous study on Lake Baikal it was shown

that Fe^{2+} and Mn^{2+} originating from anaerobic mineralization of organic matter in deeper sediments were reoxidized at the oxic–anoxic boundary (Granina et al. 2004). Intense O_2 consumption at the lower end of the oxic sediment has also been reported in earlier studies on marine sediments, which proposed that there was oxidation of reduced compound, although additional data were not provided (Gundersen and Jørgensen 1991; Glud et al. 1994). Such reoxidation processes generate acidity (Table 3) that lowers the pH. A closer look at the pH profiles revealed a change in slope detected in the lower zone (Fig. 2), indicating a close relation between O_2 consumption and the production of acidity. Oxidation of Fe^{2+} and Mn^{2+} to immobile oxides and hydroxides enriched Fe and Mn at the oxic–anoxic boundary, accumulating distinct layers of Fe and Mn oxides (Deike et al. 1997; Müller et al. 2002; Granina et al. 2004).

The importance of oxic respiration—In the sediments of Lake Baikal, the oxic respiration pathway accounted for 60–75% of the total benthic carbon mineralization (Table 4). A dominance of the oxic mineralization pathway was also reported for marine sediments such as the N. W. European Continental Margin (Lohse et al. 1998) or the continental slope off West Africa (Wenzhöfer et al. 2001), where both regions are characterized by low benthic mineralization rates ($< 4.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$) and high O_2 concentrations in the bottom water exceeding $180 \mu\text{mol L}^{-1}$ (Table 4). Over the continental slope and rise off Central California (Reimers et al. 1992) and on the continental margins of northwest Mexico and Washington State (Hartnett and Devol 2003) aerobic carbon oxidation was favored if benthic mineralization rates were low and O_2 concentration of the bottom water higher than $40 \mu\text{mol L}^{-1}$. Reimers et al. (1992) assigned more than 90% of the O_2 uptake to oxic respiration, which amounted to 69–76% of the total benthic mineralization ($1\text{--}2 \text{ mmol C m}^{-2} \text{ d}^{-1}$) at such sites. In contrast, anoxic respiration processes were dominant with benthic turnover rates higher than $8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ although the O_2 content of the bottom water exceeded 75% of saturation (e.g., Canfield et al. 1993; Glud et al. 1998; Kostka et al. 1999, Table 4). Here, the role of O_2 was rather to oxidize

Table 3. Oxidation processes and potential dark CO₂ fixation at the oxic-anoxic boundary in the sediment of the South Basin.

Substrate	Flux rate (mmol m ⁻² d ⁻¹)	Oxidation process	Excess of H ⁺ / reoxidized substrate	Alkalinity change due to the excess of H ⁺ (mmol m ⁻² d ⁻¹)	O ₂ consumption (mmol m ⁻² d ⁻¹)	Yield factor	Potential dark CO ₂ fixation (mmol m ⁻² d ⁻¹)
Fe ²⁺	0.034*	4Fe ²⁺ +8HCO ₃ ⁻ +O ₂ → 4FeOOH+8CO ₂ +2H ₂ O	0	0	0.0085	<0.01 [¶]	<0.001
Mn ²⁺	0.056*	2Mn ²⁺ +4HCO ₃ ⁻ +O ₂ → 2MnO ₂ +4CO ₂ +2H ₂ O	0	0	0.028	<0.01 [¶]	<0.001
H ₂ S/HS ⁻	~0.05 [†]	1/2 H ₂ S (1/2 HS ⁻)+O ₂ → 1/2 SO ₄ ²⁻ +H ⁺ (1/2 H ⁺)	1.5 (pH≈pK ₁)	0.08	0.1	0.11–0.58 [#]	0.005–0.025
NH ₄ ⁺	~0.05 [‡]	1/2 NH ₄ ⁺ +1/2 HCO ₃ ⁻ +O ₂ → 1/2 NO ₃ ⁻ +1/2 CO ₂ +1/2 H ₂ O+1/2 H ⁺	1	0.05	0.1	0.03–0.11**	0.001–0.004
CH ₄	~0.23 [§]	1/2 CH ₄ +O ₂ →1/2 CO ₂ +H ₂ O	0	0	0.45 0.7	0.10–0.14 ^{††}	0.023–0.09 0.03–0.11
Total				0.13			

* Granina et al. (2004).

† Calculated average from published (Granina et al. 2004) and unpublished SO₄²⁻ pore-water data.‡ Estimated from the NH₄⁺ gradients below the oxic sediment layer from pore-water profiles used by Müller et al. (2005) ranging between 0.02 and 0.08 mmol m⁻² d⁻¹.§ Estimated from O₂ balance of the lower zone.

|| Calculated average from March and July data (see Table 2).

¶ Yield factor for Fe and Mn oxidation were estimated from the energy used to build up 1 mol C-biomass (~3500 kJ, Heijnen et al. 1992) and the released Gibbs free energy of reoxidation process (Stumm and Morgan 1996) at standard conditions.

Kelly (1989); Jørgensen et al. (1991); Heijnen and van Dijken (1992).

** Glover (1985); Heijnen and van Dijken (1992); Painter (1970); Belser (1984).

†† Higgins et al. (1981); Shishkina and Trotsenko (1986).

reduced inorganic compounds than organic matter. To our best knowledge only one study in freshwater sediments was available that investigated the benthic mineralization pathways of organic carbon in the presence of a high O₂ content in the water above the sediment (Sweerts et al. 1991). However, that sediment has been characterized with high carbon turnover rates mainly through anoxic degradation pathways (Table 4).

Although marine and freshwater sediments are different ecosystems, similarities in organic matter mineralization in terms of rates and pathways are apparent (Table 4). Deposition of POM and the availability of O₂ are key factors that determine the metabolic pathway. Oxic respiration seems to be favored only in systems with sufficient O₂ supply and low POM deposition. Comparing the studies of Table 4, we may provide an upper limit for such rates on the order of ~6 mmol C m⁻² d⁻¹. Higher POM deposition may favor anoxic mineralization pathways. Thus, oxic respiration is the dominant mineralization pathway for all of Lake Baikal except at places of high allochthonous input such as the mouths of the main inflows (Selenga, Barguzin, and Upper Angara). Today's low sedimentation rate is a crucial parameter for the functioning of the entire ecosystem of Lake Baikal, but an increase due to anthropogenic pollution may change mineralization processes and rates, and probably threatens the fragile ecosystem in general.

Oxidation of reduced compounds by chemoautotrophic processes—As pointed out in the analysis of O₂ and pH profiles, reoxidation processes of reduced compounds lead to intense O₂ consumption at the oxic-anoxic boundary with 0.4–1.1 (average ~0.7) mmol O₂ m⁻² d⁻¹, corresponding to 13–33% (average ~20%) of the total O₂ flux rate (Table 2). This consumption rate should therefore be balanced by the flux rates of end products from anaerobic degradation processes, in particular Fe²⁺, Mn²⁺, HS⁻, NH₄⁺, and CH₄. In our electrode profiles, an increase of NH₄⁺ was not detected in the first few millimeters below the oxic sediment layer. Hence, NH₄⁺ fluxes into the oxic zone, which are directly related to total anaerobic mineralization, were estimated using pore-water data from dialysis samplers and filtration of sediment core sections used for the study of Müller et al. (2005). They were on average ~0.05 mmol m⁻² d⁻¹ (Table 3) and agreed well with the expected release from anaerobic mineralization of organic matter (C : N = 10). Fluxes of S(–II) were estimated from published (Granina et al. 2004) and unpublished pore-water sulfate (SO₄²⁻) data. The same authors reported flux rates of Fe²⁺ and Mn²⁺. A summary of flux rates, the reoxidation processes, and the potential rate of O₂ consumption for each compound is presented in Table 3.

The oxidation of Fe²⁺ and Mn²⁺ with ~0.04 mmol O₂ m⁻² d⁻¹ was less important compared with the oxidation of NH₄⁺ and HS⁻, which consume 0.1 mmol O₂ m⁻² d⁻¹ each. Despite substantial uncertainties, the flux rates of Fe²⁺, Mn²⁺, HS⁻, and NH₄⁺ explain only one-third of the O₂ consumption at the oxic-anoxic boundary, suggesting that the oxidation of methane (CH₄) may be an important process. According to the O₂ balance, the oxidation rate of CH₄ in the lower zone is

Table 4. Portioning of the mineralization pathways of organic matter degradation of marine and freshwater sediments with high bottom water O₂ content (>180 μmol L⁻¹).

	Depth (m)	Total benthic mineralization (mmol C m ⁻² d ⁻¹)	Oxic respiration (%)	Denitrification (%)	Anoxic pathways (%)
Marine sediments					
Eastern Skagerrak (Denmark and Norway) (Canfield et al. 1993)	190–695	10–16	4–17	<6	>88
N.W. European Continental Margin (Goban Spur) (Lohse et al. 1998)	208–4450	1.0–4.3	>70	<10	<20
Young Sound, NE Greenland (Rysgaard et al. 1998; Glud et al. 2000)	20–63	8–20	20–38	2–4	62–80
Fjords on Svalbard and coast of northern Norway (Kostka et al. 1999)	115–329	11–24	5–14	2–3	83–92
Continental slope off West Africa (Wenzhöfer et al. 2001)	1251–2185	0.3–3.5*	>55*	~15*	<30*
Freshwater sediments					
Lake Vechten The Netherlands (Sweerts et al. 1991)	12	29†	~20†	~5†	~75†
Lake Baikal (South Basin) (this study)	160–1400	2.1–4.9	60–75	12–14	11–28

* Denitrification was estimated from their O₂ data and Redfield stoichiometry assuming coupled nitrification–denitrification and anoxic mineralization from sulfate reduction rates.

† Denitrification was estimated to be similar to the NH₄⁺ oxidation in the sediment (e.g., Canfield et al. 1993).

probably at least 0.23 mmol m⁻² d⁻¹ (Table 3). Burial of reduced compounds such as FeS is not included in this redox balance; such processes would increase the estimated value of CH₄ oxidation.

The potential dark CO₂ fixation was estimated from the flux rate of reduced compounds (substrates) and yield factors, the molar ratio between CO₂ fixation, and substrate oxidation. Yield factors were obtained in studies on pure cultures or from thermodynamic calculations (see Table 3). The potential dark CO₂ assimilation is on the order of 0.03–0.1 mmol C m⁻² d⁻¹. Compared with the total primary production in the photic zone (~27 mmol C m⁻² d⁻¹) or the new production exported from the epilimnion (~5 mmol C m⁻² d⁻¹) the estimated potential dark CO₂ fixation accounts for a few percent at maximum. In the sediment layer with intense chemoautotrophic processes, the relevant deposition of organic carbon from photosynthesis is only ~1.2 mmol C m⁻² d⁻¹ as estimated from the sediment burial rate (~0.6 mmol m⁻² d⁻¹, Müller et al. 2005) and anoxic carbon degradation (~0.6 mmol C m⁻² d⁻¹, Table 4). Therefore, the potential dark assimilation corresponds to a maximum of 8% of the sediment flux. In addition, heterotrophic bacteria may also incorporate CO₂, and thus possibly enhance the dark CO₂ fixation rate significantly (e.g., Zopfi et al. 2001). However, we presume that this new biomass underlies relatively high turnover rates with negligible effects on the paleolimnological record of organic carbon in Lake Baikal.

Alternative assessment of mineralization rates—An alternative approach to assessing benthic mineralization of organic carbon addresses the release of dissolved inorganic carbon (e.g., Anderson et al. 1986). In the sediments of Lake Baikal, where oxic respiration is the favored mineralization pathway and calcite dissolution is absent (Falkner et al. 1991), mineralized inorganic carbon is mainly released as CO₂. Hence, flux rates from concentra-

tion profiles of CO₂ provide directly an estimate on benthic mineralization rate. We define CO₂^{excess} as

$$\text{CO}_2^{\text{excess}}(z) = \text{CO}_2^{\text{meas}}(z) - \text{CO}_2^{\text{lake}}, \quad (3)$$

where CO₂^{meas}_{2(z)} stands for the concentration of CO₂ in the pore water with sediment depth *z* and CO₂^{lake} for the concentration of CO₂ in the bottom water. Consequently, CO₂^{lake} also reflects the concentration in the pore water in the absence of any biogeochemical activity in the sediment.

Our experimental approach combining pH, CO₃²⁻, and O₂ electrodes allows us to derive profiles of CO₂^{excess} from two independent data sets: First, from pH and CO₃²⁻ data subtracting the constant background concentration, CO₂^{lake}, and secondly, from O₂ profiles. Eighty-three percent of O₂ is directly converted to CO₂ through the oxic mineralization pathway (C : N = 10) and, therefore, CO₂^{excess} with sediment depth *z* can be calculated as:

$$\text{CO}_2^{\text{excess}}(z) = 0.83(\text{O}_{2,\text{bw}} - \text{O}_{2(z)})D_{s,\text{O}_2}/D_{s,\text{CO}_2}, \quad (4)$$

where O_{2,bw} stands for the O₂ concentration in the bottom water. The ratio of the sedimentary diffusion coefficients allows a direct comparison with CO₂^{excess} profiles derived from pH and CO₃²⁻ data.

These independently derived CO₂^{excess} profiles allow the quality control of electrode measurements and underline their accurate functioning at low concentration as well. The excellent agreement as exemplified by the July 2001 data at 160 and 600 m (Fig. 4) confirms oxic mineralization as the prevailing diagenetic pathway and documents the absence of a buffer system for CO₂. Accurate CO₂^{excess} flux rate quantification might be strongly affected by calculation of uncertainties as a result of this indirect approach.

In contradiction to the July 2001 data at 160 and 600 m, a constant concentration of H₂CO₃^{*} in the top ~5 mm was

obtained in the March cores at 600 m and also in the July cores from 1,400 m (Fig. 4). The pH gradient below the sediment surface at these sites was smaller than at the other sites (Fig. 2). This may indicate a loss of dissolved CO_2 due to unknown processes.

Alkalinity balance at the oxic–anoxic boundary—Reoxidation processes of reduced compounds at the oxic–anoxic boundary (Fig. 3, lower zone) consume O_2 following the reaction stoichiometries summarized in Table 3. The diffusive transport of Fe^{2+} , Mn^{2+} , and NH_4^+ from deeper sediments to the redox boundary is accompanied by a corresponding upward diffusion of HCO_3^- (\approx alkalinity), balancing the transport of the positively charged cations (Table 3). The reoxidation process liberates 2 H^+ for each equivalent of Fe^{2+} and Mn^{2+} and consumes alkalinity transforming bicarbonate into carbonic acid. Nitrification and sulfide oxidation, however, generate an excess of 1–2 H^+ per equivalent of oxidized substrate compared with the coupled flux of HCO_3^- (Table 3). In the absence of acid-driven carbonate dissolution, this acidity is buffered by the alkalinity at the redox boundary, corresponding to an alkalinity sink within the sediment. Quantitatively, the net change of alkalinity by the reoxidation processes in the lower zone was estimated to be approximately $0.13 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 3). This consumption rate of alkalinity is balanced by the downward flux of HCO_3^- from the transition zone and the lake water above the sediment, respectively.

Profiles of HCO_3^- for the July data are presented in Fig. 5. Despite the large uncertainty caused mainly by spatial variability, a decrease with sediment depth is apparent, indicating an alkalinity sink at the oxic–anoxic boundary with intense reoxidation processes of reduced compounds. Quantitative estimations on flux rates from these concentration profiles ranged roughly from 0.37 to $1.0 \text{ mmol m}^{-2} \text{ d}^{-1}$. Compared with the total change of alkalinity (Table 3) estimated with data of insufficient 1-cm vertical resolution (Urban et al. 1997), the flux rates from HCO_3^- profiles are somewhat higher but are on the same order of magnitude.

Both, the alkalinity balance and the microsensor measurements revealed the oxic–anoxic boundary in the sediments of Lake Baikal as a sink of alkalinity. For a more precise and comprehensive analysis directly measured CH_4 and CO_2 profiles would be highly valuable.

Ion-selective electrodes were applied for pore-water measurements at the submillimeter scale in sediment cores from the South Basin of Lake Baikal. Resolving the steep concentration gradients in the top 25 mm enabled accurate quantification of benthic turnover rates. Simultaneous determination of O_2 , pH, and CO_3^{2-} pore-water profiles opened new perspectives for describing organic carbon mineralization and the fate of O_2 in the sediment. Hence, oxic respiration is shown to be the prevailing mineralization pathway as revealed by the characteristic shape of O_2 profiles and confirmed by the calculated profiles of $\text{CO}_2^{\text{excess}}$ from pH and CO_3^{2-} . This approach is favored in carbonate-poor sediments, where the reaction of CO_2 in calcite dissolution is negligible. However, we also recommend the application of a similar approach in calcite-rich

sediments where calcite dissolution can be quantified with Ca^{2+} electrodes at submillimeter vertical resolution (e.g., Wenzhöfer et al. 2001; Müller et al. 2003).

Reduced compounds from anoxic mineralization were reoxidized at the oxic–anoxic boundary, and the rate of O_2 consumption was used as a measure of total anoxic mineralization. Here, reoxidation processes generated H^+ , which was buffered by an alkalinity flux from the lake to the anoxic zone within the sediment. The quantitative assessment of an alkalinity balance for the redox boundary confirmed the pathways and rates of reoxidation processes.

The intense reoxidation processes at the oxic–anoxic boundary by chemoautotrophic bacteria drive a potential dark assimilation of CO_2 . The estimated CO_2 fixation was not significant compared with the settling flux of organic carbon from photosynthesis and thus, hardly affects the paleolimnological signals of organic matter.

The advantage of low potential dark assimilation of CO_2 for paleolimnological studies as a result of the small contribution of anaerobic mineralization is counterbalanced by low carbon burial efficiencies due to the long O_2 exposure time. Transfer functions of biogenic proxies for climatic conditions must therefore include the serious effects of oxic diagenesis.

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