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Geochemistry of Early Diagenesis in Sediments of Russian Arctic Glacial Lakes (Norilo–Pyasinskaya Water System)

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Abstract: The Russian Arctic region is lacking in studies on geochemical changes reflecting early sediment diagenesis in lake environments. The paper presents new data on the compositions of bottom sediments and sediment pore water from two lakes of the Norilo–Pyasinskaya water system in Arctic Siberia. Lakes Pyasino and Melkoye occupy basins left by glaciers that originated from the Putorana Plateau during the Last Glacial Maximum (LGM). Clayey sediments were continuously deposited in the lakes, and the depositional environment has changed only slightly for the last ca. 20 ka. Two sediment cores with lengths of 4.0 and 3.2 m were collected in Lakes Pyasino and Melkoye, respectively, with a *Livingstone*-type piston *corer* providing undisturbed, stratigraphically consistent sedimentary sequences. Their analyses revealed a change from oxidized to reduced conditions at a depth of ~10 cm. The concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+, as well as the HCO_3^-/Ca^{2+} ratio in pore water, showed a depthward increase indicating the progressive degradation of organic matter. Another trend was the gradual decrease in SO_4^{2-} alongside increasing HCO_3^-/SO_4^{2-} caused by bacterial sulfate reduction, although this was rather weak, judging by the low concentrations of S (II) bound to Fe-sulfides, H_2S, etc. Additionally, the microbial digestion of organic matter caused a release of its mobile components, which led to the enrichment of the water in NO_3^-, PO_4^{3-}, and DOC. Most of the analyzed elements (Al, B, Ba, Co, Cu, Mo, Ni, Si, Sr, V, and Zn) reach higher concentrations in the pore water than in the lake water above the water-sediment boundary, which is evidence of diagenetic processes. As a result of redox change, immobile Fe (III) and Mn (IV) natural oxides were reduced to mobile Fe (II) and Mn (II) species and migrated from the solid phase to the pore water, and eventually precipitated as authigenic Fe sulfides and Mn carbonates. The results are useful for better understanding the early diagenesis processes in different geographical settings over the huge Eurasian continent.

Keywords: pore water; lake sediments; authigenic minerals; diagenesis; major and trace elements; geochemistry; Russian Arctic

1. Introduction

Data on the diagenesis of soft-bottom sediments have implications for the patterns of their consolidation and transformation to sedimentary rocks. The diagenesis of sediments in continental settings of freshwater and saline lakes, as well as highland and lowland bogs, differs from that in oceans and seas [1–15]. In continental environments, it often occurs at low SO_4^{2-} concentrations and high dissolved organic carbon (DOC) and involves different pore water transformations [16–18].

The compositionally homogeneous sediments of glacial Arctic lakes deposited at slow rates during the Holocene constitute a good model of continental diagenesis. Such lakes are rather deep, and the chemistry of the lake waters and their sources are almost invariable over time, which enhances the visibility of diagenetic effects in pore water reflected in the precipitation of authigenic minerals. Unlike the sediments of high-latitude lakes, those of temperate zones are highly heterogeneous [14,15]. The diagenesis of sediments in such lakes is hard to discriminate from processes associated with the transformation of water through the lake's history or with changes in deposition environments [19,20]. Specifically, discriminating diagenetic minerals from those precipitated from lake waters, e.g., calcite formed at greater water mineralization, may be problematic. It is also hard to identify the cases in which lake level changes have an effect on water chemistry.

The chemistry of bottom sediments in continental lakes of the Russian Arctic has been poorly investigated, while the early diagenesis issue still remains unknown [21,22]. Comprehensive studies of the Norilka–Pyasina system of lakes and rivers only began in the 1990s. The bottom sediments and pore (interstitial) water were first analyzed in 1991–1994 in cores from the large lakes Pyasino and Lama in the vicinity of Norilsk city, as well as in those from Purino lakes north of Norilsk [23,24]. Those studies were mainly aimed at environmental monitoring and pollution detection, with a special focus on Cu, Ni, Cr, Co, Cd, Pb, Zn, Fe, and Mn concentrations, without regard to diagenesis. Most of the other investigations in the region concerned the monitoring of natural waters [25–27].

The early diagenesis of bottom sediments in continental lakes of the Russian Arctic is among the key problems of theoretical and practical value. We are trying to bridge the knowledge gap by applying the methods of marine diagenesis studies to Arctic lakes [6–9,18,28] in order to gain insight into postdepositional processes in the sediments and pore water of continental environments. In this respect, the targets were:

(i) The distribution and migration patterns of Fe, Mn, and S as tracers of diagenesis, and the related trace elements (Cu, Zn, Ni, Mo, Co).

(ii) The mechanisms of pore water transformation under early diagenesis and the distribution of dissolved components: Major ions, biogenic compounds, and transition elements.

(iii) The precipitation of authigenic minerals in early diagenesis, and the role of organic matter in the process.

2. Physiographic Background and Methods

2.1. Physiographic Background

Lakes Pyasino and Melkoye are located in the unique Arctic region at the southwestern margin of the Putorana Plateau in a forest-tundra landscape [29]. The lakes are transient and are connected by the Norilka River and discharged into the Arctic Ocean by the Pyasina River (Figure 1). The surface topography was sculptured mostly by Pleistocene glaciers, which moved from the Putorana local center of glaciation, ploughed the existing valleys, and controlled the deposition. The glacial processes periodically destroyed the previous deposits and landforms, and the modern valleys thus bear the imprint of the latest Late Pleistocene glaciation. When retreating, the glaciers left three major terminal moraines that dam the glacial lakes Pyasino, Melkoye, and Lama [30]. Those regional events have poor geochronological constraints, but presumably occurred during the Sartanian glacial epoch, the last glacial maximum (LGM), and subsequent deglaciation from approximately 20 ka BP to the beginning of the modern Holocene warming at 11.7 ka BP. The three lakes apparently formed successively, from Pyasino to Lama [31], and became exorheic. The lakes were much larger and deeper in the past but have been shrinking as erosion has lowered the drainage threshold. The modern-level variations of the lakes are controlled by the rivers that collect atmospheric precipitation waters from the catchment. The lake level falls notably in the autumn, especially in Pyasino [32], when shallow-water sediments are periodically exposed above the lake level [21].
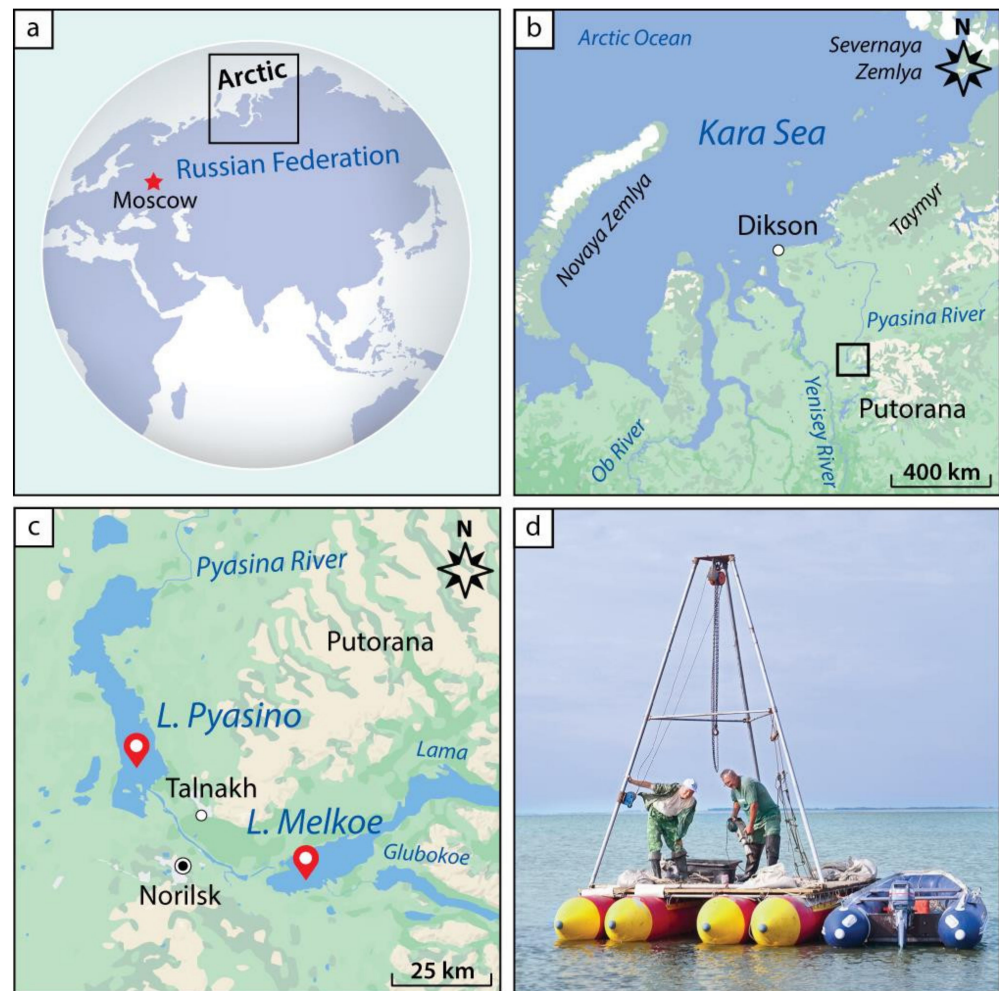
Figure 1. Overview and detailed maps of the study area (**a–c**); drilling rig (**d**).

Lake Pyasino is located in the offshoots of the Putorana Plateau, approximately 20 km north of Norilsk (Figure 1c). The lake receives many rivers (Norilka, Ambarnaya, Koeva, Bucheko-Yurekh, Shchuchiya, etc.) and discharges into the Kara Sea through the Pyasina River that flows from its northern end (Figure 1b). The Norilka (called also Norilskaya or Talaya) River is its largest tributary that drains a large area of highlands and lakes [27]. The lake extends 70 km from north to south and is up to 15 km wide; it occupies an area of 735 km^2 and its catchment covers 24,000 km^2.

In general, the Pyasino is rather shallow; its average depth is 4 m, and the deepest place in the northern part of the lake is 37 m. The upper bottom sediments are often quartz-feldspar sands [22]. The Norilsk area has numerous mined sulfide Cu-Ni deposits [32], while Lake Pyasino, as the terminal component of the Norilo–Pyasinskaya water system, regulates and accumulates the wastewaters of the Norilsk mining and smelting enterprise, which are contaminated with heavy metals (Cu, Ni) [25,26]. Additional artificial contaminators are hydrocarbons [32].

Lake Melkoye occupies a broad depression at the western edge of the Putorana Plateau, approximately 25 km east of Norilsk (Figure 1c). The lake has a flat bottom and mainly low sides and is locally swampy. Its elevation is 44 m above sea level, the surface area is 270 km^2, and the drainage area is 12,100 km^2. The average lake depth is 3.9 m and is 22 m at the deepest place in the west. The water level variations reach 4.7 m between the highest stand in July and the lowest level in April. The lake recharges mainly from snow and rain and takes in the Glubokaya River flowing into its southern end from Lake Glubokoye. Lake

Melkoye is connected to Lake Lama via an 18 km long arm [33]. The ice-stand season lasts from early October to late June/early July [34].

2.2. Methods

The lake water samples were collected at drilling points by a bathometer from a depth of 0.5–1.0 m. Temperature, pH, and Eh were immediately measured in the samples with an *Anion 4100* ionometer. The water samples for the hydrochemical analysis had not been treated, and for elemental analysis, water was vacuum-filtered through 0.45 μm filters and packed into plastic bottles with the addition of concentrated nitric acid (1 mL/L) for preservation.

The lake sediment samples were collected via vibration drilling using a *Livingstone*-type drive rod piston corer. The drilling rig was mounted on a 5 t load inflated floating platform (Figure 1d) and consisted of lifting equipment and a drill with a set of rods, 30 m in total length. The corer provided continuous recovery of undisturbed cores by 2 m long and 7.5 cm in diameter lots. The total core length was 3.2 m in Lake Melkoye (69.31101° N, 89.10311° E) and 4.0 m in Lake Pyasino (69.65102° N, 87.87651° E).

The recovered cores were measured for pH and Eh with the *Anion 4100* ionometer, wrapped in polyethylene, placed in tight plastic boxes, and transported to the laboratory. The pore water was squeezed from 10-cm core pieces into tight syringes protected from oxygen input [33], following the standard method using a press mold 6 cm in diameter and an *Omec PI.88.00* hydraulic press.

The concentrations of anions in the lake and pore water samples were determined by titrimetry (HCO_3^-) and capillary zone electrophoresis (CZE) (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, F^-). Cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) and major and trace elements (Si, Al, B, Ba, Sr, P, Li, Cr, Ni, Co, Mo, Fe, Mn, Cu, Zn, As, Sb, Ti) were measured by atomic emission spectroscopy with inductively coupled plasma (ICP-AES), on a Thermo Jarrell *IRIS Advantage* ICP-AES spectrometer (Thermo Jarrell Ash Corp., Franklin, MA, United States).

The total dissolved carbon (TDC) and proportions of dissolved inorganic and organic carbon (DIC and DOC, respectively) in water were determined on an Analytik Jena *AG Multi N/C 2100S* analyzer (Analytik Jena GmbH, Jena, Germany). TDC was estimated by the amount of CO_2 released from samples after catalytic oxidation at 950° in the presence of oxygen flux, in a quartz reactor. DIC was estimated by the amount of CO_2 released from samples after digestion in 10% H_3PO_4. DOC was found as the difference between TDC and DIC.

The sediment organic matter (OM) was determined by the loss of ignition in a muffle furnace at 450 °C over four hours.

The concentrations of trace elements in total samples of the sediments were determined by electric arc atomic emission spectral analysis on a *Grand Potok* system consisting of a *Potok* AC generator and a *Grand* spectrometer (VMK-Optoelectronics, Novosibirsk, Russia) with the spill-injection method used to introduce the samples into a plasma arc. The spectra were recorded using an MAES multichannel analyzer, with detection limits at 0.1–1 ppm. The samples were powdered and quartered; three portions of each sample were measured followed by the averaging of the results. Selective dilution (sequential extraction) was used to determine the forms of occurrence of chemical elements in the bottom sediments [34].

The speciation of sulfur in sediment samples, total sulfur (S_{total}), sulfate (S (VI)), and sulfide (S (II)), was studied according to [14] with ICP-AES. S_{total} was determined by high-temperature digestion in HNO_3 under a lid and then by digestion in HCl, which transforms sulfide into sulfate. S (II) was removed from specimens via digestion in diluted HCl and subsequent filtering of the residue, whereby only sulfate sulfur remained. The amount of S (II) was estimated as the difference between S_{total} and S (VI).

The mineralogy of lake sediments was analyzed by the X-ray powder diffraction (XRD) method on a *DRON-4* diffractometer (Cu-Kα radiation), at the Analytical Center for Multielement and Isotope Studies of the Institute of Geology and Mineralogy SB RAS. The grain morphology and element composition were studied in selected samples by scanning

electron microscopy (SEM) on a *Tescan Mira 3 LMU* microscope, according to [35]. The grain size was determined with the *Analysette 22 MicroTec* laser particle sizer.

The *Selektor-C* software package was used for thermodynamic calculations of the occurrence of chemical elements in sediment pore waters and their forms of participation in minerals based on the algorithm of minimizing the Gibbs free energy of a heterogeneous system [36]. The method stems from thermodynamic equilibrium in heterogeneous multi-component systems, with linear mass balance constraints.

The mobility of elements in pore water was estimated via the ratio K_x:

$$K_x = m_x \times 100 / a \times n_x$$

where m_x and n_x are the concentrations of the element x in pore water (mg/L) and sediments (wt.%), respectively, and a is the mineralization (total dissolved solids, TDS), mg/L. The mobility of elements was graded according to K_x as very high ($n \times 10$ to $\times 100$), high (n to $n \times 10$), medium ($0.1n$ to n), low, and very low ($<0.01n$).

3. Results

3.1. Lake Water Chemistry

The water of Lake Pyasino is classified as bicarbonate-sulfate of the calcic-sodic group, and the water of Lake Melkoye as bicarbonate of the calcic group. The lake water samples have oxic-type Eh ranging from +187 to +281 mV, neutral pH (7.6–7.8), and low mineralization of 132 to 163 mg/L TDS (ultrafresh). All cations are slightly higher in Lake Melkoye, while the water of Lake Pyasino contains slightly more Cl^- and F^- (Table 1).

Table 1. pH, Eh, carbon, Si, and major ions in sampled lake water.

Parameter, mg/L	Lake Pyasino	Lake Melkoye
pH	7.58	7.82
Eh, mV	+187	+281
DOC	4.5	1.2
DIC	8.6	4.1
HCO_3^-	67	112
Cl^-	2.7	1.5
NO_3^-	0.18	0.01
F^-	0.25	0.07
PO_4^{3-}	0.01	0.28
SO_4^{2-}	37.8	7.5
Ca^{2+}	15.75	26.4
Mg^{2+}	2.84	8.7
Na^+	4.70	5.4
K^+	0.35	0.76
Si	4.72	3.61
Total ions	132	163

The relatively high concentrations of 38 mg/L SO_4^{2-} in Lake Pyasino (at 67 mg/L HCO_3^-) are due to anthropogenic effects [23,24,27]. The pollution load on the Pyasino ecosystem also shows up in DOC and NO_3^- concentrations (4.5 and 0.18 mg/L, respectively), which exceed those in Lake Melkoye (Table 1).

Major (Si, Al, Fe) and trace (B, Ba, Sr, Mn, Co, Ni, Li, Cu, Zn, Ti, V, Mo, Y, Zr, Ag, Se, La) elements indicate the diversity of the studied Arctic limnic systems. The concentrations of the following elements (Table 2) in Lake Pyasino apparently exposed to pollution reach high values: 25 µg/L Al, 18 µg/L B, 42 µg/L Fe, 4 µg/L Mn, 46 µg/L Zn, and 15 µg/L Ni. The samples from Lake Melkoye (Table 2) are rich in Ba (11 µg/L), Sr (215 µg/L), Zr (0.4 µg/L), Ag (0.2 µg/L), Se (8 µg/L), La (0.2 µg/L), as well as Cu (11 µg/L), Mo (36 µg/L), and V (9 µg/L). The high Cu, Mo, and V concentrations in the Melkoye Lake should be explained

by the general geochemical background of this ore region. Additionally, dissolved silica is slightly higher in the Melkoye near-surface water (Table 1).

Table 2. Elements chemistry of sampled lake water.

Parameter, µg/L	Lake Pyasino	Lake Melkoye
Al	25.02	1.08
B	18.36	5.88
Ba	2.97	11.43
Sr	167.16	214.62
Fe	42.48	13.08
Mn	4.36	0.52
Co	0.18	0.24
Cu	2.7	11.46
Zn	46.32	1.44
Mo	0.42	35.52
Li	0.72	0.48
Ni	15.00	4.44
Ti	0.18	1.68
V	0.63	9.15
Y	0.07	<0.01 *
Zr	<0.01 *	0.36
Ag	<0.01	0.24
Se	<0.01	7.86
La	<0.01	0.24

* Below detection limit.

3.2. Physical Properties of Bottom Sediments

Bottom sediments in Lake Pyasino are compositionally heterogeneous (Figure 2). The terrigenic Holocene grey mud composes the upper 288 cm and glaciogenic late Pleistocene brown mud lies below a sharp boundary between the two units; their ages are substantiated at the end of this subsection. The upper 18 cm is grey-brownish and water-saturated (up to 90–95%). The 232–248 cm interval includes visually prominent dark grey clay with thin organic-rich blackish layers.

The retrieved sediments of Lake Melkoye are homogeneous along the core and are composed of bluish-greyish mud. They correlate with the upper unit of the Lake Pyasino sequence; the sediments of the lower, brown-colored unit are exposed near the shores of Lake Melkoye. The upper 15 cm of the sediments has an extremely high water content, which reaches 85–90% and decreases to 75–80% between 65 and 93 cm, where the mud is very dense. Water saturation increases to ~85% in the 155–179 cm interval of mud with ochreous intercalations, though the underlying bluish-grey mud is denser and drier.

The ages of the two units of the lake sediments, grey and brown, are substantiated by radiocarbon dates and geological correlations. The grey unit is the upper member of the bottom sediments. It showed ages of 3.2–12.6 ^{14}C years; the dates were obtained from a series of 8 additional short cores to the long cores of both lakes. The Melkoye Lake long core revealed ages of 9922 ± 128 years from total organic matter and 8094 ± 114 years from humus fraction (Lab. No. GV-GV03092) at a depth of 250 cm. Therefore, the Holocene age of the grey layer is evident; however, we cannot confidently use the dates because data on the probable old carbon effect is absent. The lower brown unit has a wider distribution than the modern lakes and composes their shores as high as 100 m. This logically reflects an environment of larger lakes from the deglaciation time [37].
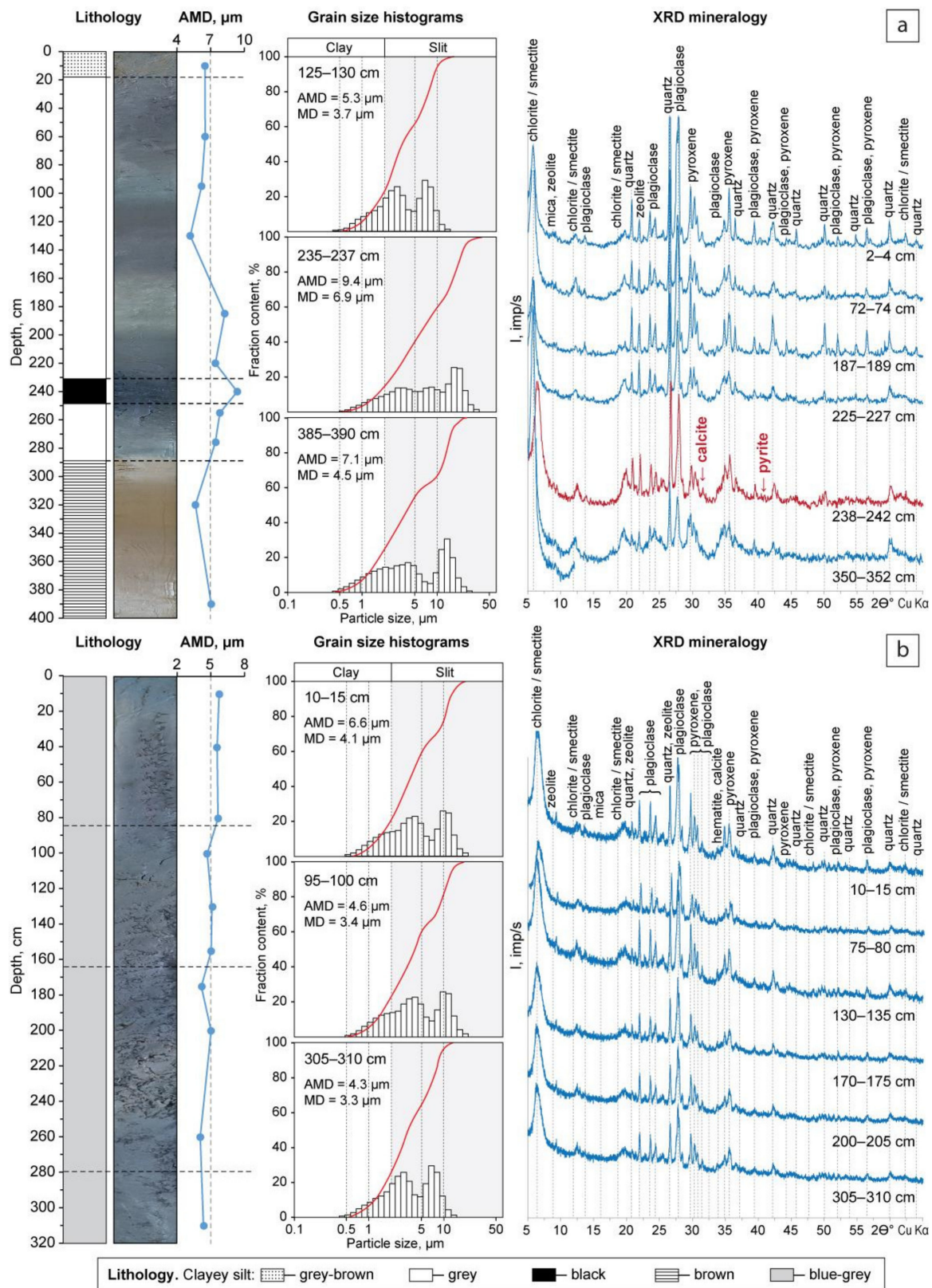
Figure 2. Lithology, grain size, and mineral composition of Pyasino (**a**) and Melkoye (**b**) lakes' sediment cores. AMD—particles arithmetic mean diameter. XRD—X-ray diffractometry.

The grain-size analysis of the Pyasino sediments showed the proportions of a clay fraction of 16–31%, silt of 69–84%, and sand is absent. The arithmetic mean diameter (AMD)

of the particles ranges from 5.3 to 9.4 μm, and the median diameter (MD) ranges from 3.4 to 6.9 μm; therefore, the sediments are generally granulometrically the same. There are minor differences in the following core intervals. The 0–190 cm interval has minimum values: AMD 6.3–6.6 μm and MD 4.4–4.8 μm. The values decrease even more in the 135–144 cm interval: AMD 5.3 μm and MD 3.7 μm. The grain size is higher below a depth of 190 cm: AMD 7.1–9.3 μm and MD 4.5–7.0 μm. The largest grain size is in the black layer at the 232–248 cm interval: AMD 9.3 μm and MD 7.0 μm.

In the Melkoye Lake sediments, clay is 21–27%, silt is 73–79%, and sand is also absent. AMD ranges from 4.1 to 5.7 μm, and MD ranges from 3.2 to 4.1 μm. The sediments have a uniform substance and smaller grain size than in Pyasino.

The samples in both lakes showed distinct bimodal particle distributions along the entirety of the cores except in the 0–30 cm and 232–248 cm (black layer) intervals of the Pyasino core. The histograms' bimodality is stronger in the brown, late-Pleistocene part of the Pyasino core, and weaker in the grey Holocene part. The bimodality suggests variable sources of the particles, being partly fluvial and partly terrigenic.

3.3. Mineralogy of Bottom Sediments

The major minerals in the lake sediments are chlorite/smectite, pyroxene, and plagioclase. The Lake Pyasino sediments have high percentages of chlorite/smectite (with few smectite layers) and progressively lower percentages of pyroxene (augite–diopside), plagioclase, quartz, mica (poorly ordered), and zeolite (Figure 2a). Quartz decreases to trace amounts depthward. Calcite and pyrite appear in minor amounts in the 232–248 cm interval. The sediments of Lake Melkoye are mineralogically homogeneous and contain high percentages of chlorite/smectite (with many smectite layers), low percentages of plagioclase and pyroxene (augite–diopside), and minor amounts of quartz and zeolite (laumontite); traces of hematite and calcite were found at all core depths (Figure 2b). Mica was found in the 130–320 cm interval.

Scanning electron microscopy revealed quartz and aluminosilicates: Plagioclase, feldspar, amphibole, pyroxenes, chlorite, as well as accessory monzonite, rutile, ilmenite, chloritoid, and tourmaline, in the sediments. The 232–248 cm core interval from Lake Pyasino was rich in pyrite, hydrotroilite, kaolinite, and carbonates (Figure 3a–c). Less than 5 μm crystals of pyrite were also found in the pore water filter residue from the Lake Melkoye core in the 30–40 cm interval. The residue left after 0.45 μm filtration of pore water contained amorphous silica (Figure 3d), while the lake water filter residue contained diatoms and sporadic zooplankton particles. A few diatoms were also found in the upper 20 cm of sediments. Other phases revealed in the lake sediments included calcium phosphates, as well as oxides and hydroxides of iron and manganese. Additionally, SEM analyses of the Pyasino sediment samples revealed the presence of Ta and Zr, as well as high concentrations of Cu and Ni.
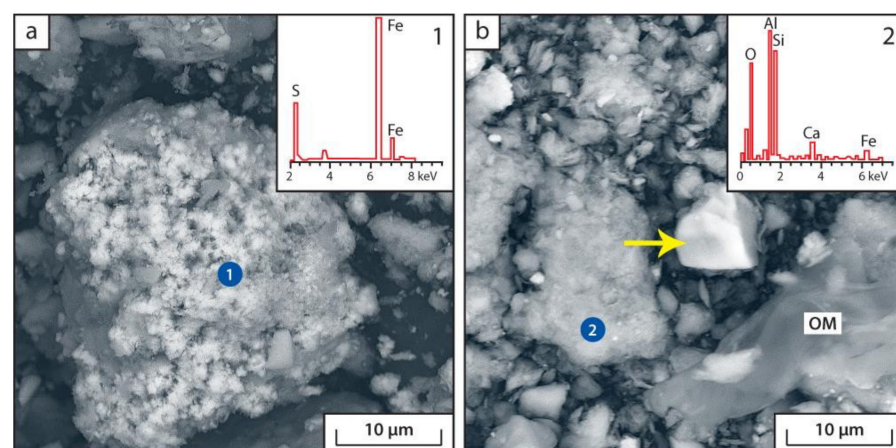

Figure 3. *Cont.*
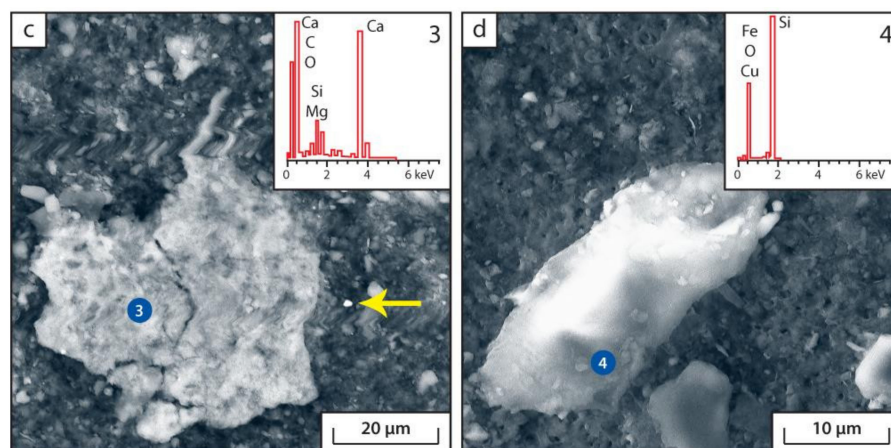
Figure 3. Microphotographs and energy dispersion spectra of authigenic (diagenetic) minerals in bottom sediments (**a**,**b**) and minerals left on 0.45 μm filters after pore water filtration (**c**,**d**). Lake Pyasino: (**a**) Pyrite in organic matrix, 234–238 cm depth; (**b**) kaolinite-? (Al_2O_3 38.9%, SiO_2 45.8%), 210–220 cm depth (the arrow shows terrigenic iron oxide), OM—organic matter; (**c**) calcite, 234–238 cm depth (the arrow shows pyrite crystal). Lake Melkoye: (**d**) Amorphous silica, 20–30 cm depth.

3.4. Chemical Composition of Bottom Sediments

The Pyasino and Melkoye core samples provided information on depth-dependent patterns of organic matter (OM) and elements in the lake sediments (Figure 4). The OM distribution varies gradually along the Pyasino core from 7.5 in the upper 10 cm to 11.6%, with an anomaly of 14.7% in the 232–248 cm interval. The sediments of Lake Melkoye contain slightly less OM than those of Lake Pyasino; it varies smoothly within 7.1%–8.4%, without apparent anomalies.

The downcore element patterns in Lake Pyasino aptly trace the lithological changes (Figure 4a). The grey-brown mud in the upper 18 cm of the lake sediments has rather high concentrations of Mn (0.23%), Ni (336 ppm), and Mo (1.87 ppm). The notably high Ni contents in the shallowest sediments indicate the industry-related pollution the lake ecosystem has been exposed to since the 20th century. The organic-rich dark grey mud between 232 and 248 cm stands out against the main portion of lake sediments in low concentrations of some lithophilic elements (5.7% Al, 37.3% Si, 1.1% Ca, 2.2% Mg, and 0.08% Mn) and higher contents of biophilic elements, such as Cu (300 ppm), Zn (190 ppm), Ba (716 ppm), and Na (0.32%). The light brown mud at the 288–354 cm core depths contains higher Al (14.8%), Ca (2.7%), Mg (5.1%), and Mo (2.4 ppm) on average but lower Na (0.1%), P (188 ppm), and Zn (97 ppm). The general downcore trends in Lake Pyasino are increasing Al, Ca, and Mg and decreasing Si, Na, Fe, P, Cu, and Zn concentrations.

The more lithologically homogeneous Melkoye Lake sediments show more uniform element patterns (Figure 4b). The uppermost mud at 0–15 cm core depths contains rather low concentrations of Al (1.6%), Si (37.3%), Ca (0.82%), Mg (1.5%), Na (1.6%), Mn (0.2%), Cu (169 ppm), Zn (150 ppm), Mo (0.97 ppm), and Ba (107 ppm), but Ba increases to 1375 ppm in the 15–30 cm interval. The lower layers (190–300 cm) have average contents of Al (2.4%), Ca (1%), and Ni (123 ppm) slightly below those of the other core portion. The concentrations of Ca, Cu, and Zn increase down the core. Rather high values of Ni, Cu, Zn, and Co are specific for the Norilsk region, which is a unique province for Cu and Ni sulfide ores. The ores are widely exposed to the surface and are naturally leached [32]. Additionally, extremely high concentrations of Ni, Cu, Zn, Co, Cr, and Mo in the upper parts of the studied cores result from the technogenic load to the region, especially lakes.

The sampled lake sediments generally have low concentrations of total sulfur (Table 3), which mainly occurs as oxidized S_{IV} species, i.e., sulfates. S (II) species such as FeS, H_2S, and other sulfides are found in the lower part of the Pyasino core and are absolutely absent in the Lake Melkoye sediments. This is evidence of a moderate bacterial sulfate reduction, as occurs in most freshwater lakes [14,15]. The reduced sulfur species predominate over the

oxidized ones only within the 233–244 cm interval of the Pyasino core composed of dark grey mud with organic-rich inclusions, where the pore waters contain very low SO_4^{2-}.
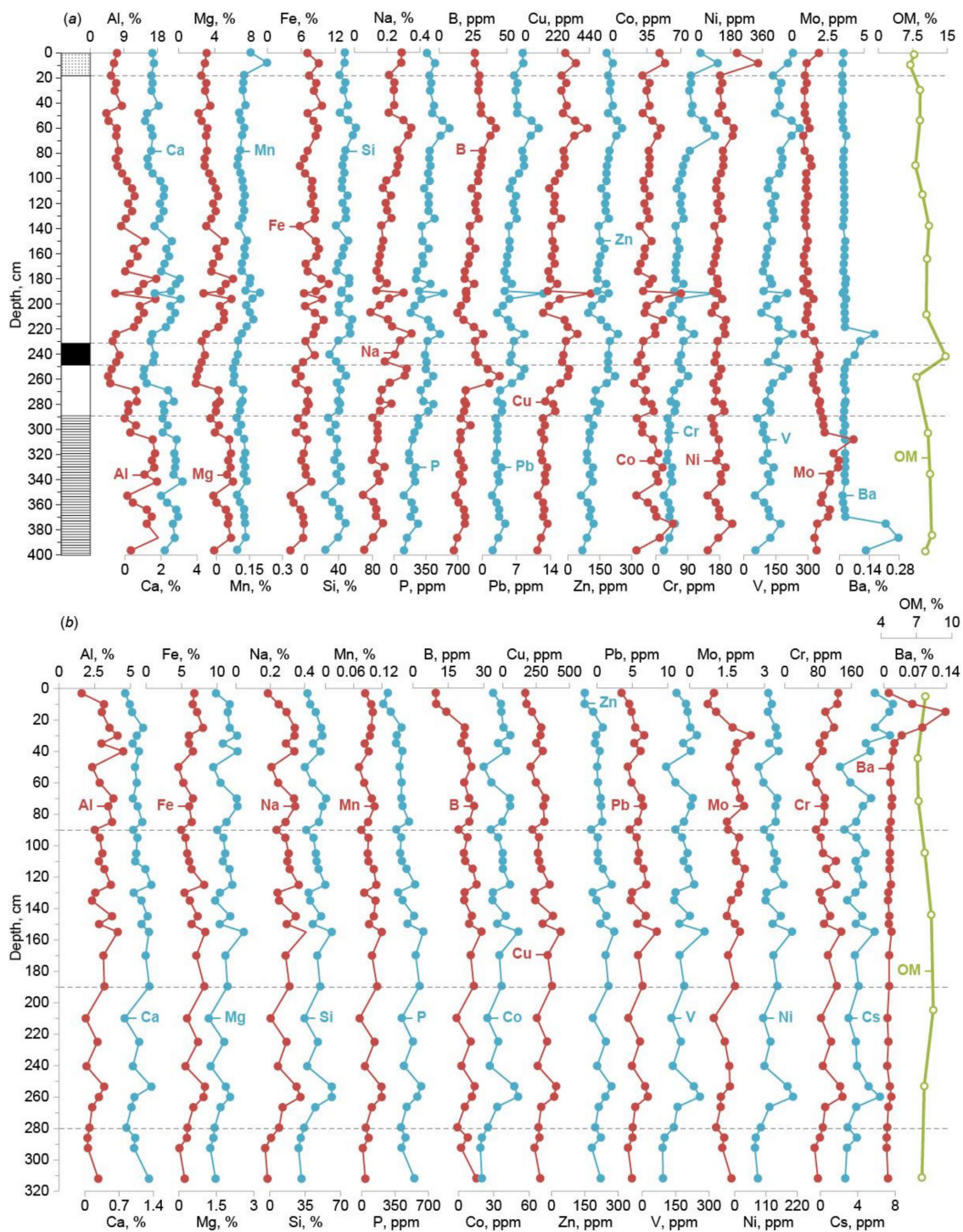

Figure 4. Downcore distribution of organic matter (OM), elements in sediments of Lakes: Pyasino (**a**) and Melkoye (**b**). Legend is the same as in Figure 2.

Table 3. Downcore distribution of S species (wt.%), pH, and Eh (mV) in lake sediments.

Depth, cm	S_{tot}	S (VI)	S (II)	Eh	pH	Depth, cm	S_{tot}	S (VI)	S (II)	Eh	pH
		Lake Pyasino						Lake Melkoye			
6	0.031	0.031	0	−94	7.84	2	0.040	0.040	0	+38	7.41
48	0.029	0.029	0	−149	8.28	12	0.041	0.041	0	−65	7.44
156	0.032	0.031	0.001	−173	8.26	32	0.040	0.040	0	−95	7.45
235	0.100	0.030	0.070	−208	8.33	52	0.045	0.045	0	−133	7.53
264	0.034	0.030	0.004	−189	8.25	172	0.030	0.030	0	−167	8.29
363	0.028	0.028	0	−121	8.43	232	0.029	0.029	0	−119	8.06

3.5. Chemical Composition of Pore Water

Figure 5 illustrates the major-ion chemistry of the sediment pore waters from Lakes Pyasino and Melkoye. The percentage of bicarbonate reaches 86% of all anions on average over the section. The concentration of HCO_3^- increases depthward from 67–112 to 199–297 mg/L already near the core top and further to 335–491 mg/L, which is evidence of progressive downward organic matter degradation. The depthward changes of pH and Eh are, respectively, 7.6–7.8 to 8.1–8.4 average pH and +327 mV to −260 mV Eh. The dramatic Eh decrease may result from microbial sulfate reduction and anaerobic organic matter decay during diagenesis, which accounts for the HCO_3^- increase. The concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) also become higher with depth.
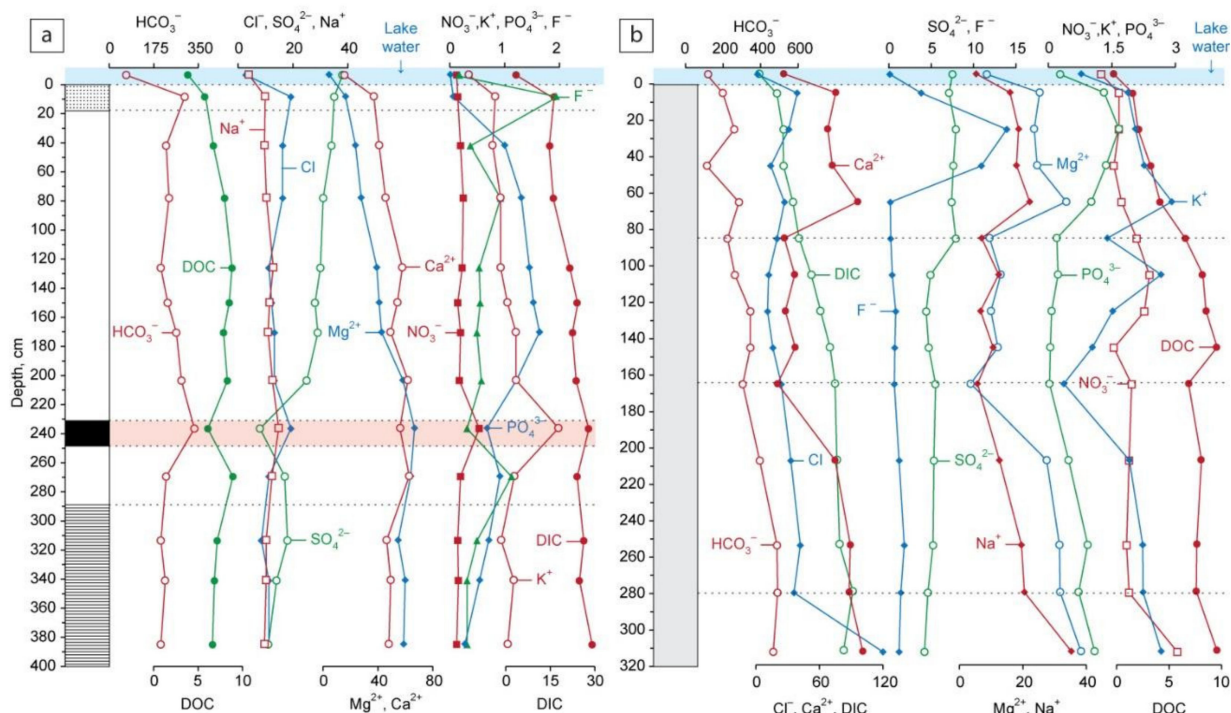

Figure 5. Concentrations of DOC, DIC, and major ions (mg/L) in lake and pore waters, Lake Pyasino (**a**) and Lake Melkoye (**b**). Lithology in Figure 2.

The SO_4^{2-} concentrations in the pore water from both lakes are uniformly distributed in shallow bottom sediments and average approximately 32.5 and 7.3 mg/L, respectively (Figure 5), being approximately the values typical of the lake water (37.8 and 7.5 mg/L, respectively). At greater depths, SO_4^{2-} decreases gradually to 20.8 and 5.2 mg/L, respectively, due to sulfate reduction by bacteria. However, the sulfate-reducing activity is rather low and does not affect the DOC contents in pore water much, except for the dark 232–248 cm

layer in the Pyasino core, where DOC decreases depthward from 7.9 to 5.8 mg/L at decreasing SO_4^{2-}.

The pore water enrichment with biogenic compounds, indicated by NO_3^-, PO_4^{3-} and DOC (Figure 5), results from microbial destruction of organic matter whereby its most mobile components migrate to pore water, the process in which the redox conditions in the sediments become reduced. However, the OM contents in the sampled lake sediments are insufficient to provide any marked gain of biogenic components (but PO_4^{3-}). In addition to organic matter digestion, PO_4^{3-} may increase via the decomposition of P-bearing minerals.

The concentrations of the analyzed elements in pore water most often exceed those in the near-bottom lake water, which reflects diagenetic processes in bottom sediments (Figure 6). In Lake Pyasino, the difference is not very large, except for Ni (Figure 6a). At the 232–248 cm core depths, the concentrations of Al, Mn, Li, and B increase, while Si, Fe, V, Cu, Sr, Mo, and Ni decrease. The Ni concentrations in lake water are markedly higher than in pore water: 0.0150 mg/L compared to 0.0015–0.0055 mg/L (the maximum is 0.0073 mg/L at 200–210 cm depth). The Zn concentrations are 0.046 mg/L in lake water, while in pore water, they are 0.036 mg/L in the upper 10 cm of the core and 0.030–0.002 mg/L below. Manganese shows an increasing depthward trend (0.0242 to 0.0736 mg/L), which is typical of reduced sediments.
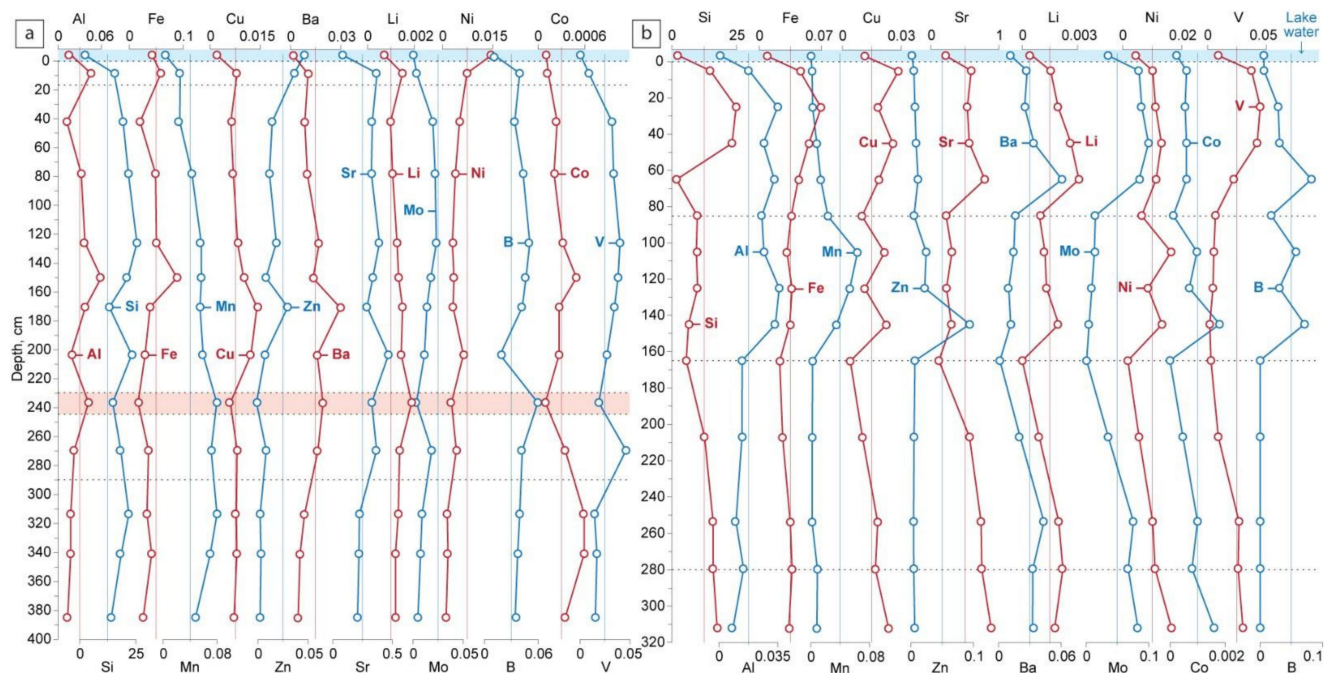

Figure 6. Concentrations of elements (mg/L) in lake and pore waters, Lake Pyasino (**a**) and Lake Melkoye (**b**).

The concentrations of all analyzed elements in the Melkoye samples are higher in pore water than in lake water (Figure 6b). The pore water showed notable differences between the two depth intervals: Increasing Si, Mo, and V at 5 to 85 cm, increasing Mn Ni, and Co, while Sr, Ba, Mo, and V decreased at 85 to 165 cm. The concentrations of Al, Zn, and B decrease downcore, from 165 to 320 cm core depths. Iron increases toward the top from 0.0248 to 0.0635 mg/L, which is six times the lake water value (0.0131 mg/L). Al reaches 0.0244–0.0322 mg/L in the 30 to 165 cm interval.

As the pore water chemistry changes from oxidized to reduced conditions, low-mobile Fe (III) and Mn (IV) convert to mobile Fe (II) and Mn (II) and migrate from the solid phase to pore water.

4. Discussion

The main changes in mineral composition, i.e., the dissolution of minerals and precipitation of authigenic minerals, are directly or indirectly related to organic matter and are driven by the energy of mainly microbiological and chemical processes of its decomposition and mineralization. The critical role of organic matter in early diagenesis was largely discussed regarding the sediments of seas and oceans [1,3,7,9,18,28]. The diagenesis of sediments in Lakes Pyasino and Melkoye is also controlled by the presence of organic matter, which, even being low, already produces a reduced environment in the upper 10–12 cm, with Eh from −65 to −94 mV (see Table 3). The sampled lake sediments lack prominent oxidized layers (except for the top 2 cm in Lake Melkoye), and all reactions occur in anoxic conditions. The Eh values become notably more negative with depth: −119 to −208 mV.

The depth-dependent redox changes in lake sediments record their physicochemical changes. Negative Eh values are primarily due to organic matter decomposition, with bacterial oxygen consumption and the formation of H_2S as a result of sulfate reduction. The depthward pH increase may have several causes: (1) Increasing HCO_3^-, H_2S, and methane production, (2) the reduction of nitrite and nitrate species, and (3) the formation of NH_4^+ [13–15]. Sulfate reduction notably increases alkalinity on account of lower SO_4^{2-} but higher HCO_3^-, which leads to precipitation of $CaCO_3$ and local Ca^{2+} decrease in pore water.

The bacterial sulfate reduction in the sampled lake sediments is rather slow: The SO_4^{2-} concentration in pore water remains almost invariable along the core and is comparable with that in lake water, which is the main source of sulfate inputs in the pore water. The low rate of sulfate reduction is confirmed by the lack of reduced sulfur species in the sediments (Table 3). Sulfates, in limited contents, were found only in the organics-enriched 232–248 cm interval in the Pyasino core and below 84 cm in the Melkoye core. The uniform SO_4^{2-} concentrations in the pore water of water-saturated (90–95% H_2O) top sediments may be maintained by the constant supply from the lake water. The pore water of deeper sediments from Lake Melkoye is depleted in SO_4^{2-}, though SEM detected pyrite crystals in filter residue already at the core top, which is a signature of sulfate reduction. The bacterial sulfate reduction associated with the composition of organic matter is further indicated by the increasing HCO_3^-/SO_4^{2-} ratio (Table 4).

Table 4. Major ion ratios in lake water and sediment pore water.

Depth, cm	Ca^{2+}/Mg^{2+}	Ca^{2+}/Na^-	HCO_3^-/SO_4^{2-}	Na^+/Cl^-	Depth, cm	Ca^{2+}/Mg^{2+}	Ca^{2+}/Na^-	HCO_3^-/SO_4^{2-}	Na^+/Cl^-
		Lake Pyasino					Lake Melkoye		
Lake water	5.55	3.35	1.76	1.74	Lake water	3.05	4.89	14.93	3.60
8	4.21	2.22	8.49	0.88	5	2.99	4.70	28.03	0.41
42	4.79	1.71	6.59	1.49	25	2.89	3.63	32.91	0.61
78	4.94	1.62	7.58	1.75	45	2.95	3.99	14.74	1.29
126	4.91	1.47	6.77	3.58	65	2.86	4.33	38.51	0.83
150	5.23	1.32	8.21	3.43	85	2.85	3.78	28.35	0.36
171	5.01	1.15	9.10	3.30	105	2.83	2.94	53.88	1.04
204	5.40	1.06	11.36	4.49	125	2.83	4.12	78.64	0.62
237	5.21	1.07	41.88	3.52	145	3.08	3.47	73.62	0.67
270	5.56	0.98	13.18	5.83	165	5.86	3.55	55.45	0.24
314	5.05	0.84	11.28	6.63	254	2.84	4.55	93.85	0.47
341	5.38	0.82	15.71	5.46	280	2.78	4.29	106.74	0.57
385	5.60	0.81	18.45	5.36	312	2.64	2.86	111.43	0.30

Therefore, microbially mediated sulfate reduction in SO_4^{2-}-poor freshwater lakes occurs at lower rates than in seas and oceans. The freshwater lakes more often undergo precipitation of carbonates while the pyrite formation is less active [13,16,17]. Thus, diagenesis in low-SO_4^{2-} freshwater continental lakes can be specified as a special non-sulfate type, and sulfate reduction in the sampled Arctic lakes is slow because of low OM in the bottom sediments.

The relative concentrations of major cations in pore water change with depth (Table 4), as a result of leaching and ion exchange in the pore water–sediment system. The depthward mineralization increase and changes in major-ion ratios indicate the diagenetic alteration of lake sediments. Pore water becomes more mineralized due to the increase in Ca^{2+}–HCO_3^- pairs correlated with *r* values up to 0.7 (Table 5), as Ca^{2+} is leached from sediments while carbonate minerals become redissolved, and the concurrent mineralization of organic matter produces HCO_3^-. Thus, organic matter decomposition leads to HCO_3^- increase, with ensuing diagenetic transformation of the chemical composition of pore water.

Table 5. Significant correlation ($\geq$0.65) of major ions, organic carbon (DOC), and inorganic carbon (IC) in pore water of lake sediments.

Lake	HCO_3^-–SO_4^{2-}	Ca^{2+}–HCO_3^-	Ca^{2+}–Mg^{2+}	NO_3^-–DOC	SO_4^{2-}–DOC	DOC–IC	Fe–SO_4^{2-}	Fe–DOC
Pyasino	−0.70	0.74	0.94			0.71	0.65	
Melkoye	−0.85	0.72	0.99	0.69	−0.85	0.86	0.67	−0.75

The major-ion ratios of Ca/Mg and Ca/Na in interstitial water change with depth (Table 4) as a result of leaching and ion exchange in the pore water–sediment system. Ca^{2+} increases depthward, being expulsed from sediments (though it may be low locally). The diagenetic leaching of the mineral part of sediments causes an increase in concentrations of alkali and alkali-earth elements in pore water. However, Mg^{2+}, Na^+, and K^+ can partially move back to the sediment absorption complex due to cationic exchange. This should lead to some decrease in their concentrations in pore waters in local parts of the cores. The leaching and ion exchange processes appear in mobility variations (K_x): Twice higher for Ca but lower for Mg and especially Na and K (Table 6).

Table 6. Mobility (K_x) of elements in lake water and pore water from different core depths.

| Element | Lake Water | 36–48 cm | 144–156 cm | 264–275 cm | 374–385 cm | Lake water | 20–30 cm | 125–127 cm | 300–320 cm |
			Lake Pyasino					Lake Melkoye	
Ca	3.93	6.23	7.59	8.45	8.38	6.10	16.39	17.79	21.87
Mg	0.81	0.68	0.50	0.43	0.46	4.07	3.31	1.02	2.83
Na	27.7	16.3	15.1	13.8	14.0	15.8	5.7	8.3	9.4
K	1.91	0.89	0.23	0.52	0.30	1.80	0.22	0.44	0.29
Al	0.0015	0.007	0.010	0.007	0.003	0.0025	0.0026	0.0030	0.0008
Fe	0.002	0.001	0.003	0.001	0.001	0.0015	0.0023	0.0010	0.0018
Mn	0.037	0.051	0.101	0.156	0.098	0	0	0	0
B	0.0003	0.0003	0.0005	0.0004	0.0008	0.0002	0.0004	0.0006	0
Si	0.070	0.095	0.125	0.143	0.186	0.091	0.129	0.051	0.154
Mo	0.0003	0.0004	0.0042	0.0025	0.0009	0.0206	0.0147	0.0011	0.0145

The rather uniform concentrations of Cl^- and F^- in the interstitial water of the sampled lake sediments (Figure 5) implicitly indicate that the lake water composition remained almost invariable through the Holocene, with the only exception of very high F^- in the upper 10 cm and 40 cm of the Pyasino and Melkoye cores, respectively. The anomaly may be due to the variability of the sediment composition, which is evident for Lake Pyasino and less evident for Lake Melkoye.

Pore water enrichment with respect to biogenic compounds of NO_3^-, PO_4^{3-}, and DOC (Figure 5) in surficial lake sediments (no NO_3^- in Lake Pyasino) results from the microbial destruction of organic carbon, which maintains the migration of the most mobile organic components into interstitial water and the respective reduced conditions in the sediments. The depthward DOC increase indicates that organic matter is subject to mineralization under diagenesis, while the increase in NO_3^- in interstitial water from the Melkoye core may indicate greater numbers of microorganisms that metabolize nitrogen. For instance, greater NO_3^- concentrations in the interstitial water of Lake Melkoye result from the oxidation of ammonia by nitrifiers, while the increase in soluble phosphates PO_4^{3-} in

pore water is due to diagenetic decomposition of P-bearing organic matter, as well as the breakdown of Fe–P complexes in the sediments.

Greater concentrations of Si in pore water (Figure 6) than in lake water may result either from the decomposition of diatom frustules (amorphous silica in diatomite is easily soluble) or from Si leaching from the solid phase. The leaching option is supported by higher mobility (K_x) of Si in pore water than in lake water (Table 6). Locally lower Si concentrations in pore water may be due to SiO_2 precipitation during diagenesis, which is implicitly confirmed by the presence of authigenic silica detected by SEM in the filter residue (Figure 3a).

The diagenetic changes in the major-ion chemistry of interstitial water lead to the precipitation of authigenic minerals: Carbonates, mainly calcite, and iron sulfides. Pyrite was identified by XRD and SEM. Judging by SEM data and sulfur speciation, all iron sulfides found in lake sediments are associated with the diagenesis and metabolism of sulfate-reducing bacteria. The conditions for the formation of diagenetic calcite and pyrite are especially favorable in organic-rich sediments (232–248 cm interval of the Pyasino core), as predicted by thermodynamic modeling (Table 7). The modeling results are supported by the presence of reduced sulfur compounds, mostly FeS and H_2S. Therefore, organic carbon provides most of the energy for the diagenesis and precipitation of authigenic minerals, in the same way as in the marine bottom sediments [1,9,11,18].

Table 7. Simulated percentages (%) of chemical elements in pore water of Lake Pyasino and amount of precipitated equilibrium mineral phases (g).

Element Species/Mineral	60–70 cm	235–240 cm
C		
$H_2CO_3^0$	49.41	11.81
HCO_3^-	34.63	84.22
CO_2^0	15.96	3.83
CO_3^{2-}	0.01	0.15
Fe		
Fe^{2+}	88.56	90.21
$Fe(OH)_2^+$	11.44	1.06
$Fe(OH)_3^0$	0	0.05
$FeHCO_3^+$	0	8.68
Mn		
Mn^{2+}	96.90	99.25
$MnSO_4^0$	3.07	0.74
$MnHCO_3^+$	0.04	0.01
Cu		
Cu^{2+}	17.65	0.00
$CuHCO_3^+$	82.35	100.00
Zn		
Zn^{2+}	36.93	0.00
$ZnHCO_3^+$	63.07	100.00
Ba		
Ba^{2+}	99.99	96.09
$BaCl^+$	0.01	0
$Ba(HCO_3)^+$	0	3.91
As		
AsO_4^{3-}	0.00	0.40
$HAsO_4^{2-}$	100.00	99.60
Mo		
MoO_4^{2-}	99.93	99.95
$HMoO_4^-$	0.07	0.05
Ni		
Ni^{2+}	99.93	99.98
NiF^+	0.07	0.02

Table 7. *Cont.*

Element Species/Mineral	60–70 cm	235–240 cm
	Co	
Co^{2+}	99.80	99.77
$CoCl^+$	0.20	0.23
	V	
HVO_4^{2-}	3.25	25.86
$H_2VO_4^-$	96.75	74.14
	Si	
SiO_2^0	99.89	98.92
$HSiO_3^-$	0.11	1.08
	Minerals	
Kaolinite	1.67×10^{-4}	20.46×10^{-4}
Vivianite	0.01×10^{-4}	0.88×10^{-4}
Calcite	0	912.66×10^{-4}
Pyrite	0	1.20×10^{-4}

The forms of Fe found by selective dissolution showed growth of the sulfide forms (and trace metals Cu, Zn, Ni, Co) in the interval of 232–248 cm (Figure 7). This indicates increased pyritization of the sediments in this interval.
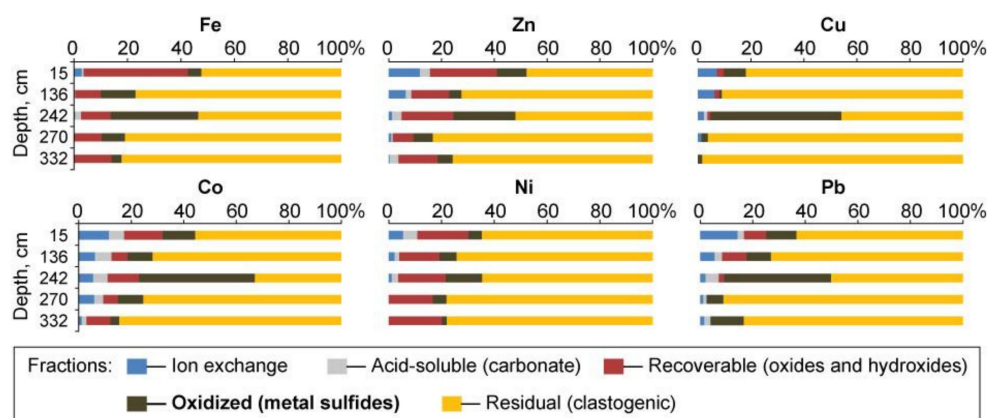

Figure 7. Forms of occurrence of chemical elements in selected depth levels of Lake Pyasino sediments.

Thermodynamic calculations also show that the reductional diagenesis in Arctic lakes may produce clay minerals, e.g., kaolinite (Table 7); such conditions may occur within the 232–248 cm core depths in Lake Pyasino (Figure 3b).

In the diagenesis process, clay minerals, mainly montmorillonite, are converted into mixed-layer montmorillonite–hydromica forms, and chlorite and kaolinite [38].

The diagenesis of bottom sediments is evidenced by the fact that the concentrations of many elements (Fe, Mn, Sr, Ba, B, Cu, Zn. Al, V, B, Mo, Ni, Li, Co) in pore water exceed those of lake water (Figure 6). The relatively high contents of transition elements (especially Fe and Mn) are due mainly to redox changes during diagenesis. As interstitial water changes from oxidized to reduced conditions, Fe (III) and Mn (IV) become reduced to mobile Fe (II) and Mn (II) and migrate into pore water from the solid phase. According to thermodynamic calculations, the reduced Fe (II) and Mn (II) species predominate in the pore water of the sampled lake sediments (Table 7), but the amount of Mn (II) is insufficient for the precipitation of authigenic rhodochrosite. As a result, Mn^{2+} in the pore water of Lake Pyasino sediments increases with depth (Figure 6a), i.e., the deeper sediments become progressively more reduced. In the case of Lake Melkoye, on the contrary, Mn increases locally within the 85 to 145 cm core depth.

The OM contents in the sampled lake sediments are apparently insufficient to maintain any significant Fe enrichment of pore water (especially in Lake Pyasino), while the local

decrease in Fe concentrations may be due to the formation of pyrite. Previously, we showed [14,15] that reactive iron species in organic-rich sediments can migrate to pore water as organic complexes or inorganic Fe (II) bicarbonates, while a part of the organic matter becomes consumed in the reduction of Fe and Mn. The accumulation of Fe^{2+} in the upper 40 cm of the Lake Melkoye sediments provides an explanation that the reduction of Fe (III) in the solid phase, in this case, is faster than the formation of new mineral forms of divalent iron [13,16].

Under the reduced conditions, the pore water of upper sediment layers gains Mo and Cu that has an affinity to sulfur (Figure 6), though Cu, Zn, Ni, Mo, and Co in the pore water may be low locally as they become consumed by the formation of iron sulfides. This is especially evident in the 232–248 cm interval of the Pyasino core where authigenic framboidal pyrite was identified (Figure 3d). Furthermore, SEM data show Ni, Cu, and Zn enrichment at some core depths in both lakes. The chemistry of Cu, Zn, Ni, Mo, and Co distribution in lake sediments may be controlled by redox conditions in lake water and sediments, as well by the processes of sulfate reduction and sulfide formation. As a result, elements migrate from lake water near the water–sediment interface into the pore water and, possibly, become bound in sulfides, e.g., authigenic pyrite.

Factor analysis for sediments of Lake Melkoye showed that Ni, Cu, Zn, and Co form closely related pairs with a correlation close to one (in this case, Mo complicated interpretation, so it was removed from the dataset). The pairs indicate coefficients of 0.6–0.7. An interesting pattern emerged from the cluster analysis: Samples from the highest horizons of the core significantly differ in composition from the deeper ones (Figure 8). Four groups of samples were identified. The upper horizons are not the maximum of these presumably technogenic elements. Their maximum contents are in the middle part of the core, from a depth of 155 cm and below. In the Cu/Ni ratio, the interval of 3–15 cm differs markedly from the rest of the sediment, possibly due to the high watering of the sediment, or the quantity and composition of the organic matter.
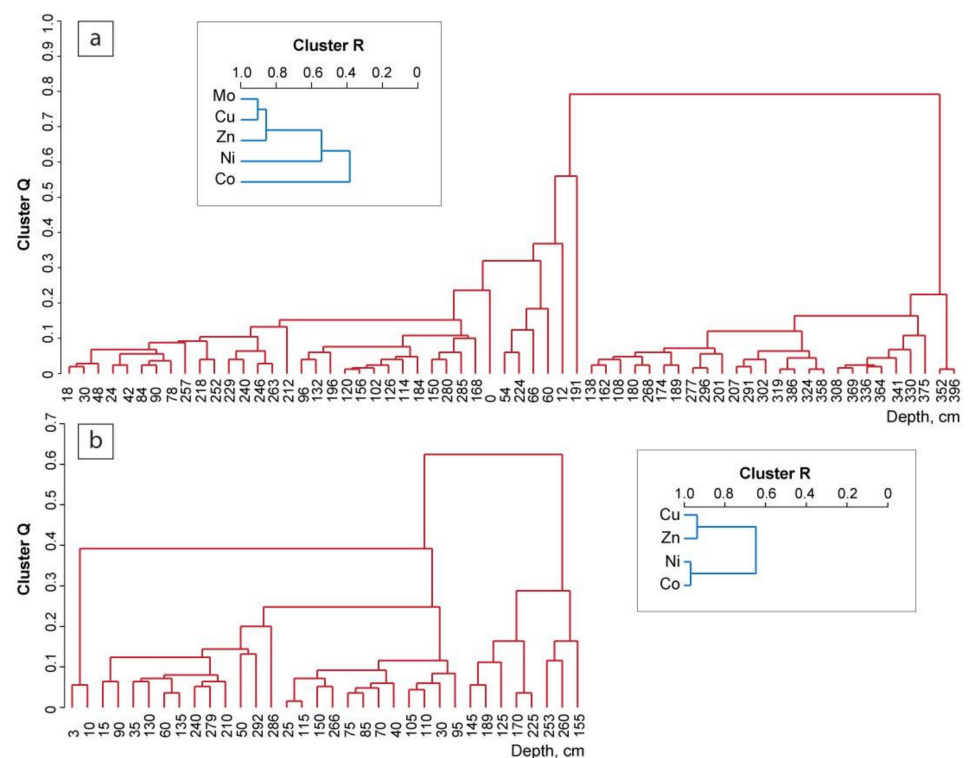

Figure 8. Correlation analysis of presumably technogenic elements in Lakes Pyasino (**a**) and Melkoye (**b**) sediments. R-clustering reflects degree of correlation between contents of the chemical elements. Q-clustering reflects grouping of chemical analyses of sediment samples by depth.

Examining the distribution of Ni, Cu, Zn, Co, and Mo in the sediments of Lake Pyasino showed a weak correlation. Therefore, the clustering of this core is more successful. The dendrogram shows that the upper sediment layers are truly enriched with these elements (Figure 8). It is safe to distinguish three groups along the core: Upper, middle, and lower. By determining the average content of the elements for the whole core and taking these values as evidence, we assume that the high values of Ni, Cu, and Zn in the upper intervals of the Pyasino core are a consequence of the technogenic stress on the lake ecosystem.

5. Conclusions

The pore water of the sampled lake sediments changed compositionally under diagenesis and differs from the lake water, with TDS, HCO_3^-, and Ca^{2+} increasing depthward. Bacterial sulfate reduction in the Arctic freshwater lakes turns out to be less active than in seas and oceans because of low SO_4^{2-} and OM concentrations in the bottom sediments. The SO_4^{2-} depletion is the main feature of freshwater diagenesis, which can be classified as a special non-sulfate type. Diagenesis includes the leaching of alkaline and alkali earth metals from the solid phase but Mg^{2+}, Na^+, and K^+ may partly migrate to sediments through ion exchange reactions, while the sediments lose Ca^{2+}. Compared to lake water, pore water is richer in biogenic compounds (SiO_2, NO_3^-, PO_4^{3-}, and DOC), which are released by the decomposition of organic matter. The ongoing mineralization of organic matter is recorded in increasing DOC down the core. On the other hand, NO_3^- in interstitial water may locally decrease depthward as a result of denitrification. The diagenetic redox changes associated with the mineralization of organic matter influence the physicochemical properties of pore water (Eh < 0), as well as the distribution of transition elements, especially Fe and Mn. The diagenesis of lake sediments also appears in the concentrations of many elements (Fe, Mn, Sr, Ba, B, Cu, Zn. Al, V, B, Mo, Ni, Li, Co) in pore water that exceed those of lake water. The diagenetic changes in the major-ion chemistry of interstitial water also lead to precipitation of authigenic calcite and iron sulfide (pyrite) phases. Higher concentrations of SO_4^{2-}, Zn, and Ni in the interstitial water of the Pyasino core relative to those in the lake water apparently result from anthropogenic loads (pollution).

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