Mineral and geochemical composition of the Onega Ice Lake sediments

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Abstract An analysis of the mineral-geochemical composition and structure of the Holocene–Pleistocene bottom sediments was performed on Lake Polevskoye, a small lake in the northern Lake Onega area in Russian Karelia, which is considered representative to describe the Late Weichselian Onega Ice Lake sediments. The analysis was accomplished using modern analytical methods, including scanning electron microscopy and ICP-MS, which allowed us to interpret their genesis in a new light. It is assumed that the distribution of rare earth elements (REE) in the bottom sediments of the recent Lake Onega and in the sediments of Onega Ice Lake will improve our understanding of the history of sedimentogenesis. It is apparent in the distribution of REE, their composition and data on the geochemical and mineral composition of the Holocene bottom sediments of Lake Onega and Lake Polevskoye (varved clays) that in their composition of terrigenous matter the material introduced from the north-western part of the catchment area is mainly composed of Archaean and Early Proterozoic crystalline complexes. However, the values of several indicator ratios of elements in the lower part of the of varved clays with shungite interlayers indicate the presence of mixing of clastic material from two sources of different geochemical origin: the north-western part of the catchment area (source of shungite rocks) and the south-eastern part of the catchment area (Phanerozoic sedimentary rocks of the Russian Platform).

Keywords • Onega Ice Lake • Lake Polevskoye • bottom sediments • varved clays • geochemistry • mineralogy • rare earth elements • scanning electron microscopy

INTRODUCTION

The basin of Lake Onega, Europe’s second largest lake with an area of 9720 km² and a catchment area of about 53,100 km² (Filatov 2010), is located among the crystalline rocks of the Baltic Shield and the Vendian-Phanerozoic sedimentary rocks of the Russian Platform. The lake is 248 km long, with the greatest width of 96 km and maximum depth of 120 m, with an average of 30 m. The lake basin is of tectonic origin and modified by the Pleistocene glaciers (Biske 1971). Crystalline rocks of the catchment area are partially covered with interglacial, continental and marine sediments of the Pleistocene age (Glushanin et al. 2011), which are intensively eroded. The geological structure and evolution of the lake and its catchment area have been discussed in many publications (Biske 1971; Demidov 2006; Subetto 2009). At the end of the Quaternary period, the Onega basin of the lake has undergone significant changes associated with the degradation of the late Cretaceous Scandinavian ice cover and the development of a vast melt
reservoir – Onega Ice Lake (OIL). At the bottom of the glacial cold lake, due to the presence of moraine material which has been eroded and transferred by the melt waters of the glacier, varved clay accumulated (Demidov 1997).

Research into the formation of bottom sediments (BS) in Lake Onega studied their granulometric composition and set the age of sediments, which allowed the time of formation of the lake basin in the Onega basin to be determined as being about 13,000 years ago (Biske et al. 1971; Semenovich 1973; Saarnisto, Saarinen 2001; Demidov 2005). Previously, in the study of glacial clays formed in OIL, the existence of a widely extended marker interval of pink varved clays was found, which can be used for correlation-stratigraphic and paleogeographic interpretations (Demidov 2004). Knowledge of the mineral and geochemical composition of bottom sediments of OIL is fragmentary and mainly based on analytical data on rock-forming elements. However, these data were mainly obtained over 70–80 years and cover only the upper Holocene horizons (Biske 1971; Kvasov et al. 1976).

The aim of the current study was to investigate the mineralogical-geochemical composition and distribution of rare earth elements in the BS of the recent Lake Onega and OIL, and an analysis of their inherent REE systematics in order to contribute to the understanding of sediment formation.

MATERIALS AND METHODS

The data obtained on the lithostratigraphy of the BS of Lake Polevskoye in the northern Lake Onega area is considered to be representative of the description of OIL sediments (Fig. 1).

Varved clays are exposed on lake shores because of the lowering of the glacial lake level; these exposed varved clays have been used for dating the local deglaciation in the northern Lake Onega area (Demidov 1997). During the Late Weichselian era, Lake Polevskoye was a part of a large OIL. The overlapping sediment cores from Lake Polevskoye were obtained by the Russian corer (length 1 m; diameter 7 cm) from the lake ice in 2017. The core was subsampled at in tervals of 1–2 cm, and the samples were studied using a set of geological, geochemical, petrographical and mineralogical methods at the multi-element isotopic research centre of the Siberian Branch of the Russian Accademy of Sciences in Novosibirsk. Major (Al, Fe, Ca, Mg, K and Na) and trace (Cd, Pb, Cu, Zn, Mn, Cr, Ni, Co, V, Hg, Be, Ba, Sr and Li) elements in the bottom sediments were determined by atomic absorption with the use of flame and electrothermal atomisation (Solaar M6, Thermo Electron Corporation). The mineral composition of the sediments was determined by powder X-ray diffraction and IR spectroscopy. The samples were studied with an ARL X’TRA diffractometer (CuKα radiation). The morphology, phase and chemical compositions of some minerals in the sediments were studied using a MIRA 3 Tescan scanning electron microscope. ICP-MS analysis was carried out on an ELEMENT high-resolution mass spectrometer (Finnigan MAT, Germany). The chemical features of the BS (loss on ignition +550°C, zone sequence, Corg, Ptotal, Fe, Mn, Eh and pH) were studied at the hydro-geochemistry, hydro-geology and paleolimnology laboratories of the Karelian Research Centre of the Russian Academy of Sciences in accordance with Boeva (2009).

RESULTS

The uppermost part (4.5 m) of the Lake Polevskoye sediment sequence is composed of Holocene gyttja (LOI 32%) (1 in Fig. 2) which is replaced downwards by a massive homogeneous gray-green mud-clay (2 in Fig. 2) down to 6.2 m. At the transition from gyttja to clay, on contact there is a thin sand-silt layer of a few cm (3 in Fig. 2). These
sediments are overlaid by the varved clays which have accumulated in Onega Ice Lake (LOI 98%) (4–8 in Fig. 2).

The main section of varved clay has a greenish-grey colour and is dominated by clay and silt fractions. Quartz and feldspars prevail among the terrigenous minerals in all bottom sediments (alkali feldspar and average plagioclase and, to a lesser extent, potassium feldspars). Muscovite, biotite, pyroxenes and amphiboles, epidote and accessory minerals can be found in micro quantities, along with anatase, ilmenite, magnetite, titanite, zircon, haematite, and others. The authigenic minerals are generally represented by opal and chaledony, forming diatom walls; there are also some sheet Fe silicates and aluminium silicates.

Dolomite is added to this set of minerals at the bottom of the core (below 11 m). The power of 2 layers – varve (tapes) – decreases from 10–15 mm in the lower part (varved clay with shungite) to 1–2 mm in the upper part of the section. The aforementioned “pink horizon” has been reported in varved clays of OIL as well as in small lakes of the Zaonezhye Peninsula (Saarnisto, Saarinen 2001; Demidov 2006). In the varved clay section of Lake Polevskoye, the “pink horizon” (30 cm) has a very sharp lower contact at a depth of 10.37 m and a gradual upper boundary at a depth of 10.08 m. (Fig. 3).

Annual varves consist of 2 layers. In summer, the lake receives unsorted material forming a sandy-dusty summer layer; during the cold season, under the ice cover, glacial mud precipitates forming a clayey winter layer. However, according to SEM images (Fig. 2, B) in the varves of the “pink horizon” of Lake Polevskoye, three layers within individual varves could be seen. American scientists describe the presence of such a micro-layer (intra annual rhythmites) in a number of publications about glacial varves (Ridge et al. 2012). They explained the occurrence of the intra-annual rhythmites that indicate the beginning of the melt season when the melting initially starts, meaning that it is not continuous; this might be because of some melting pulses or occasional melting events at the beginning of the melt season. From our point of view, the emergence of a layer can be explained by the presence of strong winds at the beginning of the freezing of OIL; also, the ice may be repeatedly broken, so possible revenue particles are aleurito-pelite dimensions of wind-blown (larger than in winter, but much smaller than in summer). In spring, this interlayer is formed during the melting of lake ice from the accumulated aeolian dust.

The lowest portion (12.05–13.0 m) of varved clays is presented by varves with beige to light pinkish-brown winter layers and black summer layers that are rich in shungite material. A black colour-ed (pyrolusite, shungite) interlayer and bright green and honey colours (vivianite-siderite, rhodochrosite) are abundant among the massive homogeneous grey silty-clay layers and also in the silty clay interlayers associated with the winter layers within individual varves (Fig. 4).

We performed detailed studies of the mineral, geochemical composition and structural characteristics of the sheet iron silicates and aluminosilicates in the bottom sediments of Lake Polevskoye and Lake Onega. According to the results of X-ray diffraction analysis, the association of clay minerals in samples from the depth of 10.10–10.14, 10.37–10.42 and 10.42–10.46 meters are represented by mixed layered illite-smectites, chlorite-smectites, micas (muscovite, illite, biotite), chlorites, and kaolinite (Fig. 5).
The method of modelling X-ray diffraction profiles reveals important features of layered phases (Fig. 6).

The diffraction lines of mica 001 are not modelled by one component, which indicates the presence in the samples of just three of its species. One well-crystallized dioctahedral mica polytype 2M1 with a high interlayer potassium content (1–0.9 fu) and an average octahedral iron content (0.2–0.4 fu) (Table 1).

The model spectrum is characterised by narrow intense diffraction peaks 001; the average domain size along the Z axis is 25 layers. We identify this phase as muscovite. The second is also a well-crystallised trioctahedral mica, with a more intense diffraction peak of 001 – Fe-biotite – 1M. Another variant is a highly dispersed dioctahedral mica phase, with an average domain size of 14 layers; the K content in the interlayers is 0.4–0.5 fu, and the octahedral Fe is 0.5–0.7 fu. This forms a wide base of diffraction lines of mica in experimental spectra, which we identified as being illite. A number of papers have been devoted to the classification of micaceous minerals in sedimentary deposits (Kossovskaya, Drits 1971, 1975; Drits, Kossovskaya 1991). According to the recommendations of the Nomenclature Committee (Bailey et al. 1984), we use the term “illite” as a group name for all highly dispersed micaceous minerals in which the amount of swelling smectite interlayers does not exceed 15% (Drits, Kossovskaya 1991).

A similar result was obtained for chlorite, the diffraction lines of which also have an excessive width in the region of low intensity. To recreate the characteristic profile geometry, in addition to the well-crystallised trioctahedral Fe-chlorite with an iron content of 1.9–2.6 fu per cell and domain sizes of 19 layers, modelling offers a dispersed chlorite-like phase with 8-layer domains, with an Fe content of 0.4–0.8 fu and 3–5% smectite layers. This phase will be called chlorite-smectite.
DISCUSSION

According to the data from the article of academician Kuzmin M.I., knowledge of changes in the content of clay minerals within the bottom sediments of Lake Baikal is a crucial tool for climate reconstructions (Kuzmin et al. 2014). Clay minerals, like
biogenic silica, are a good indicator of paleoclimatic environmental changes. The number of smectite layers in illite-smectite increased during the interglacials and reached a maximum in the Late Holocene (Kuzmin et al. 2014).

A comparison of average contents of elements in the bottom sediments which are selected at various depths of the columns of varved clays from different depths of Lake Polevskoye and Lake Onega (C4) (normalised by concentrations in clay and shells of the Russian Platform; Vinogradov 1962) did not show any significant differences (Fig. 8).

In Holocene bottom sediments of Lake Onega and Lake Polevskoye, higher concentrations of Mn, Cd, Mo, Na, and Zn are observed compared to those in the clays of the Russian Platform (Vinogradov 1962) (Fig. 9 A). These values of elevated concentrations can be explained by their elevated concentrations in catchment rocks (dolerite basalts, crystalline schist rocks of the Baltic shield, shungite rocks), relative to the contents in the clays of the Russian Platform (displays high concentrations of Cd, Mo, Na, and Zn in shungite rock, which are dominated in the catchment area) (Fig. 9 B). In contrast, a higher concentration of Mn in lake sediments remains under discussion, as does the question of the source of manganese in recent BS.

Data on rare earth elements (REE) are increasingly used for the reconstruction of formation conditions and the evolution of various geological strata and processes. The content of REE in the BS of Lake Polevskoye at different depths (gyttja, homogeneous clay, varved clay layers, “pink horizon”, clays above and below the “pink horizon”, and varved clay with shungite layers) and their distribution pattern are shown in Fig. 10. In comparison, the content of REE in the modern BS of Lake Onega (excluded data from the Petrozavodsk Bay of Lake Onega, as the distribution in it is clearly different from other areas of the lake), in varved clays of Baltic Ice Lake (Kunzendorf, Valius 2004), and in the clays of the Russian Platform (Migdisov et al. 1994) are presented in Fig. 10.

The average REE content in BS of different ages do not differ significantly, except for gyttja in which the REE concentration is much lower due to dilution with organic matter. The general character of REE distribution in the BS of Lake Polevskoye has no difference compared to the BS of Lake Onega (Table 3). In the layers of varved clay with shungite interlayers — ∑REE are ranges from 142 to 148 g/t (∑LREE/HREE from 3.2 to 3.5); in varved clay within the "pink
horizon” – ∑REE from ~180 to ~256 g/t (4.6–5.2); in homogeneous clays above the varved clay interval – ∑REE from ~130 to ~176 g/t (4.5–5.1); in gyttja – ∑REE from ~51 to ~54 g/t (3.5–3.8); in modern BS of Lake Onega – ∑REE from ~84 to ~136 g/t (3.6–5.6); in modern BS of the Petrozavodsk Bay of Lake Onega – ∑REE from ~242 to ~439 g/t (15–26), which corresponds to the continental lithogenesis. The bottom sediments are characterised by low ratio LREE/HREE values (< 4) and lack of distinct negative Eu anomaly (Eu/Eu* > 0.85–0.90), except layers of varved clay with shungite interlayers. The spectra of varved clays with shungite are similar to the REE spectra of clayey rocks in the cover of ancient platforms, such as the Russian Platform (Fig. 10) (Ronov, Migdisov 1996). The PAAS normalised REE distribution in BS of Lake Polevskoye and Lake Onega are characterised by rather low angle slightly MREE oriented shape and the following peculiarities. A weak negative (Ce/Ce*) PAAS (0.89–0.92), except for the Petrozavodsk Bay BS of Lake Onega (2.56–4.33) and varying values (Eu/Eu*) PAAS: a significant negative value for gyttja (0.56), mild negative for the upper intervals of varved clay (0.92–0.99), and clearly manifested positive for varved clays with interlayers of shungite (1.66; 1.32) and slightly positive for the “pink horizon” (1.1). A positive Ce anomaly in the Petrozavodsk Bay BS of Lake Onega indicates that BS are formed under recovery conditions. The general feature of BS in most of the layers indicates the expressed similarity with the distribution of REE in crystalline rocks of Archaean and Proterozoic of the Baltic Crystalline Shield. The BS of Lake Onega are characterised by the size Nd (t) from −21.98 to −25.90, which also corresponds to the model age of crystalline rocks of Archaea and Proterozoic Baltic Shield.

CONCLUSIONS

In general, the distribution of REE, their composition and data about geochemical and mineralogical composition of recent bottom sediments in Lake Onega and bottom sediments of Lake Polevskoye are formed by the terrigenous material of the north-western territories of the catchment area, which is mainly composed of Archaean and Early Proterozoic crystalline complexes. The values of several indicator ratios of REE in the lowermost layers of varved clay with shungite interlayers indicate the presence of mixing of elastic material from two sources of different geochemical origin: the north-western part of the catchment area (source of shungite rocks) and the

Fig. 10 The PAAS normalized spectra (Taylor, Maklenann 1988) of REE distribution in bottom sediments. Lake Polevskoye, Holocene sediments: (1) gyttja, (2) massive homogeneous grey silty clay; Late Pleistocene sediments: (3) varved clays above “pink horizon”, (4) varved clay of “pink horizon”, (5) varved clays below “pink horizon”, (6) pinkish-brown varve with black interlayers of shungite; (7) recent bottom sediments of the Lake Onega; (8) varved clays of the Baltic Ice Lake; (9) clay of the Russian Platform (Migdisov 1994)

Table 3 Content of REE and their indicator ratios in representative samples of bottom sediments of Lake Onega from different areas and Lake Polevskoye from different depths

<table>
<thead>
<tr>
<th>Sample</th>
<th>∑REE g/t</th>
<th>∑LREE/HREE</th>
<th>(Ce/Ce*)</th>
<th>(Eu/Eu*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern BS, Lake Onega</td>
<td>142–148</td>
<td>3.2–3.5</td>
<td>0.89–0.92</td>
<td>0.91–0.98</td>
</tr>
<tr>
<td>Modern BS of the Petrozavodsk Bay, Lake Onega</td>
<td>242–439</td>
<td>15–26</td>
<td>2.56–4.33</td>
<td>0.92–0.97</td>
</tr>
<tr>
<td>Gyttja, Lake Polevskoye</td>
<td>51–54</td>
<td>3.5–3.8</td>
<td>0.94</td>
<td>0.56</td>
</tr>
<tr>
<td>Massive homogeneous grey silty clay, Lake Polevskoye</td>
<td>122–168</td>
<td>4.1–5.2</td>
<td>0.78–0.91</td>
<td>0.93–0.96</td>
</tr>
<tr>
<td>Massive homogeneous grey silty clay, Lake Onega</td>
<td>130–176</td>
<td>4.5–5.1</td>
<td>0.88–0.95</td>
<td>0.91–0.99</td>
</tr>
<tr>
<td>Varved clay within the “pink horizon”, Lake Polevskoye</td>
<td>180–256</td>
<td>4.6–5.2</td>
<td>0.93–0.98</td>
<td>1.10</td>
</tr>
<tr>
<td>Varved clay with shungite interlayers, Lake Polevskoye</td>
<td>142–148</td>
<td>3.2–3.5</td>
<td>0.91–0.96</td>
<td>1.66</td>
</tr>
<tr>
<td>Varved clay with shungite interlayers, Lake Onega</td>
<td>138–144</td>
<td>3.1–3.3</td>
<td>0.92–0.97</td>
<td>1.32</td>
</tr>
</tbody>
</table>
south-eastern part of the catchment area (composed of Phanerozoic sedimentary rocks, Russian Platform). The “pink horizon” is a transition interval, where the characteristics of element ratios indicate that the bottom sediments of this interval were probably formed in warmer and more turbulent water conditions with increased oxygen content.

ACKNOWLEDGEMENTS

The study was supported by the Russian Scientific Fund project number 18-17-00176. Authors express sincere thanks to the anonymous reviewers for their constructive comments and suggestions what allowed to improve the quality of this article. The authors sincerely thank anonymous reviewers for critical reading and helpful comments.

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