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Paleoenvironmental reconstruction for mineral groundwater area Marcial Waters (Lake Onega catchment)

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ABSTRACT. Assessment of the conditions for the formation of Marcial waters was carried out on the basis of complex isotope-geochemical studies of water, peat deposits in the area of mineral water discharge and regional climate paleoreconstruction. The dependence of the chemical composition of water and flow rate of wells on weather and climatic conditions was discovered. Variations in the chemical composition of water do not coincide in time with a change in the flow rate of wells due to the mixing of modern waters of infiltration origin and, possibly, meltwater of permafrost. The evolution of the hydrogeological system of ferrous waters after the retreat of the glacial edge from the northwestern coast of Lake Onega is shown. It is shown that a permanent aquifer was formed at the end of the Preboreal time. The distribution of iron and uranium isotopes in the peat core reflects a change in the redox conditions due to climate change and the participation of meltwater in the groundwater flow.

Keywords: ferrous water; isotopic composition, paleoreconstruction, peat, sulfide oxidation

1. Introduction

The first Russian resort "Marcial waters", using sulphate ferrous waters, was organized under Peter I. Discharge of mineral waters takes place in the valley of Lake Gabozero (Onega Paleoproterozoic structure). Groundwater is confined to intermoraine sands and gravels and to fractured schungite-containing, pyritized schists and dolerites. The chemical composition of water is characterized by relative long-term stability. The isotopic composition of water (δ^2H, $\delta^{18}O$) has changed significantly over the past 40 years, losing the signs of nonequilibrium isotope fractionation, apparently due to cryogenic metamorphism. Noble gases ($^3He/^4He$, $^{20}Ne/^4He$) indicate a mixture of "young" groundwater components, containing tritium, and "ancient" groundwater components, containing elevated concentrations of helium. The share of the "ancient" component is gradually decreasing, currently amounting to several percent by volume. Tritium / helium-3 dating gives an age of about 35–45 years for the "young" component. The formation of mineral waters is associated with the sulfide oxidation; however, the details of the process remain debatable. In this paper, the assessment of the conditions for the formation of mineral waters is based on complex isotope-geochemical studies and regional paleoreconstruction of the climate. A peat deposit was investigated on a slope below the mineral water discharge site. It is assumed that the section of the deposit should record changes in the conditions of mobilization of iron in the water-rock system.

2. Material and methods

Monitoring of the geochemical and isotopic composition of water was carried out, as well as observations of the temperature and dynamic regime of groundwater. Field work included the drilling of a peat bog. The chemical composition of water was determined by standard methods (Northern Water Problem Institute KRC RAS), the trace elements by the ICP method (Institute of Geology, KRC RAS). The deuterium and oxygen-18 contents in water were determined using a Picarro L-2120-i laser infrared spectrometer (RC Geomodel and RC RDMI, Science Park of St. Petersburg State University). Radiocarbon dating of the peat deposit was performed by Maksimov E.F. and Petrov A.Yu. (Institute of Earth Sciences, St. Petersburg State University). The chemical composition

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of peat was determined by the XRD method (RC RDMI, Science Park of St. Petersburg State University), and the isotopic composition of uranium (234U / 238U) was determined by the alpha spectrometric method with radiochemical preparation. The composition of noble gases was studied by mass spectrometry (Geological Institute of the KSC RAS).

Maps of the Onega Ice Lake (OIL) for different time periods and modern localization of the mineral water discharge area are compared using a digital elevation model using the Ice6G geophysical model of Earth isostasy (Zobkov et al., 2018).

3. Results and Discussion

The dependence of the chemical composition and flow rate of wells on weather and climatic conditions was discovered. The production rate of all four wells fluctuates synchronously, reaching a minimum in the winter and increasing after the spring flood. Groundwater levels decrease with decreasing precipitation. Variations in the water chemical composition do not coincide in time with a change in well flow rates. Apparently, this is a consequence of the mixing of modern waters of infiltration origin and, possibly, meltwater of extinct permafrost.

The relief evolution model shows that in the Holocene, the Marcial aquifer feeding area located on land, while the Gabozero Lake valley remained under water until the end of the Preboreal time (about 9600–9300 BP), when OIL regressed and the level dropped to 70– 65 m (Demidov, 2005). This is confirmed by the age of the peat 9640 ± 150 years (depth 2.2 m, elevation about 70 m). The peat deposit consists of layers with the inclusion of terrigenous particles and ore crusts, indicating the flow of ferruginous waters. The minimum iron content (4–6%) was observed at a depth of 1.7–2 m (the beginning of warming). Maximum iron concentrations range is 9–22%. The isotopic ratio 234U / 238U = 1.4–2.2 (in terms of activity) indicates the participation of melt water in the groundwater runoff. The inverse relationship between the iron content and uranium isotopes reflects the dependence of the migration rates of iron and uranium on redox conditions.

4. Conclusions

The evolution of groundwater systems during the Quaternary, including the Martial Waters, began after the disappearance of the ice sheet. At the beginning of warming, water filtration was seasonal and occurred only in the active layer. Possibly, there were areas of dry rocks with a negative temperature. At this time, reserves of iron sulfates are formed on the watersheds in the oxidation zone of pyritized shales. The deficit of liquid precipitation and the cold climate contributed to the conservation and accumulation of oxidation products, which was noted for ore deposits in modern permafrost regions (Ptitsyn et al., 2009). A permanent aquifer appears to have formed at the end of the Preboreal time. Reserves of highly soluble sulfates provide a relative constancy of the chemical composition of mineral water.

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