

Fig. Correlation of our local varvo-chronology with chronology of Saarnisto & Saarinen (2001)

THE TRACE ELEMENTS CHEMISTRY OF THE "MARCIAL WATERS" SPRINGS, CENTRAL KARELIA

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The first Russian spa resort "Marcial Waters" is located 54 km to the north of the Petrozavodsk (Republic of Karelia). The variations of trace elements content in ferruginous water from the resort sources are discussed.

"Marcial Waters" springs are confined to the denudation-tectonic valley of the Gabozero Lake (Onega structure). The territory is formed by Paleoproterozoic volcanogenic-sedimentary rocks (graphitic schists, siltstones) and intruded by intrusive gabbro-dolerites (the rock age is estimated at ~1.9 Ga) [Tokarev et al., 2015; Onega Palaeoproterozoic..., 2011]. The rock association has

tectonic dislocations and sulfide mineralization in the contact zones with schist [Svetov et al., 2015]. The complex is covered by Quaternary sandy-argillaceous sediments.

The water mineralization is the result of the surface waters interaction, penetrating into tectonic dislocations zones to volcanic-sedimentary unit and causing oxidation of volcanogenic massive sulfides (VMS) on contact with gabbroids, which is represented mainly by pyrite [Tokarev et al., 2015]. Water discharge is carried out by upward filtration through loose sediments in the Raudargiya stream valley and the Gabozero Lake basin.

Four spouting water springs are located on the resort currently. The spring №4 is represented by high-ferruginous sulfate waters ($\text{Fe}^{2+} \sim 100 \text{ mg/l}$). Other three springs reflects the varying degree of high-ferruginous waters contamination by the sandy horizons waters of Quaternary sediments. As a result, these springs have hydrocarbonate-sulfate composition with lower mineralization and Fe^{2+} content of 10–50 mg/l. Average springs characteristic: pH value range from 6.3 (spr. №4) to 6.0 (spr. №1–3), *Eh* (mB) range from +213 (spr. №4) to +200 (spr. №1–3), total dissolved solids from 0.8 (spr. №4) to 0.24 (spr. №1–3) g/l [Tokarev et al., 2015].

Trace element content in Marcial water was analyzed in June 2015, November 2016 and March 2017. Acidified samples (5% v/v ultrapure HNO_3) were collected in high density polyethylene bottles for analysis. Trace elements were measured by ICP-MS (X-Series 2 Thermo Fisher Scientific) in the analytical laboratory of the IG KarRC RAS. Cation analyses calibration were performed using international standards IV-STOCK-1643. The trace and rare earth element contents were measured directly in solution without pre-concentration and precision was better than 2%.

The carried out research has shown:

1) Marcial springs water contains a wide range of trace elements with concentrations from 0.001 to 200 ppb;

2) The high divalent ferrum concentration in waters, connected with pyrite oxidation process leads to accompanying element transport from magmatic sulfides (VMS). The concentration of this elements has high values: Mn (280–620 ppb), Zn (40–200 ppb), Ni (30–180 ppb), Co (9–40 ppb), As (30–70 ppb), that can be result of interaction between water and polymineral sulfide system (included arsenopyrite, sphalerite, millerite, cobaltite);

3) The springs are characterized by high concentration of Sr (40–70 ppb) and Ba (3–15 ppb) because of interaction between water and silicate minerals (sodium-calcium feldspar) probably; by lower concentration of of Li (9–12 ppb), B (18–28 ppb), P (45–115 ppb), Rb (2–5 ppb), Mo (1–4 ppb), Cu (0.7–3 ppb); <1ppb for Be, Ti, V, Cr, Se, Y; <0.2 ppb for Zr, Nb, Ag, Cd and by lowest concentration of Sn, Sb, Te, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Tl, Bi, Th, U < 0.05 ppb. Presence some of these elements can be explained through its transporting from sulfides and accessory minerals (apatite, monazite and other).

4) The data on water composition for the period 2015–2017 years have shown water stability for Zn, Mn, Ni, As, Ba and variability for Cu, Cr, Mo, Cd, Be, Pb, Sb, Tl, Ag.

5) REE distribution for all springs has a LREE depleted type and various spectrum configurations, that allowed to separate two spectrum types. The first type is corresponds to spring №1, it has lowest REE level, positive Eu ($\text{Eu}/\text{Eu}^* \sim 1.58\text{--}2.46$) and weak negative Ce anomalies ($\text{Ce}/\text{Ce}^* \sim 0.65\text{--}0.76$). The second spectrum type with enrichment in HREE and Eu anomaly absence ($\text{Eu}/\text{Eu}^* \sim 0.63\text{--}0.98$) corresponds to composition of water springs №2, №3, №4.

The studies of trace elements distribution of the Marcial waters springs have shown relatively stable water composition (except for Cu, Cr, Mo, Cd, Be, Pb, Sb, Tl, Ag). Spring water are formed as a result of infiltration waters interaction with ore and silicate minerals, which controlled the chemical composition specificity. In spite of the close pH and *Eh* water values, the REE distribution indicates different mechanisms of their accumulation, that allows to separate two contrasting water types formed as a result of mixing of high-ferruginous waters of the springs №4 with infiltration water differences.

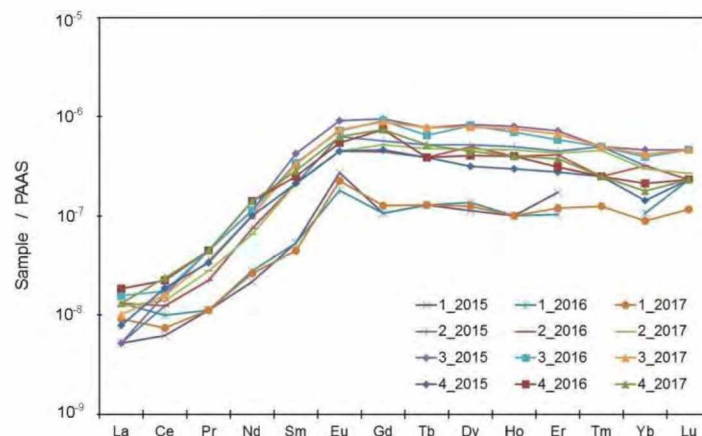


Fig. 1. REE distribution in Marcial water springs normalized to PAAS (Taylor, McLennan, 1985). Legend: 1, 2, 3, 4 – springs number; 2015, 2016, 2017 – sampling years.

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PALAEOCLIMATIC AND PALAEOENVIRONMENTAL CHANGES AT THE LATE PLEISTOCENE–HOLOCENE TRANSITION IN THE SE BALTIC REGION (KALININGRAD DISTRICT, RUSSIA)

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