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## Fractionation of rare-earth elements in surface streams of Baransky volcano (Etorofu, Southern Kuriles)

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### Abstract

Baransky is an active volcano, located in southern Kurile arc, on the subduction zone between Okhot and Pacific plates. Being active during the last 50 years, it is still a threat to locals and air transport. Geochemical study of hydrothermal system of Baransky volcano gives us an opportunity to understand processes occurring in volcanic structure. Thermal springs of the Kipyaschiy creek basin were studied for major ions, micro and rare-earth elements. Hydrothermal springs are characterized with  $T = 90\text{--}100^\circ\text{C}$ ,  $\text{pH} = 1.2\text{--}1.9$ ,  $\text{Cl} = 1.8\text{ g/l}$  and  $\text{SO}_4 = 4\text{ g/l}$ . These conditions have a strong influence on water of Kipyaschiy creek. During fluids/surface water interaction we see fractionation of rare-earth element as indicators of changing physico-chemical parameters of the creek. Solfatars are enriched in trivalent Gd and Lu, bivalent Eu, Tm and Yb and depletion in tetravalent Ce, Tb, Dy and trivalent Ho and Er. Hydrothermal fluids are enriched in all REEs with trend to HREE accumulation, but minimum changes in Ce and Gd.

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### 1. Introduction

Baransky is a volcanic complex located in the central part of Etorofu ( $\text{N}45.097^\circ$ ,  $\text{E}148.024^\circ$ ), southern Kuriles (Fig. 1). Caldera Kipyaschiy is superimposed on volcano lifting of Ivan Grozniy ridge, elongated in the north-east direction and includes a number of volcano-tectonic structures and the same modern volcanoes: Rebunshiri, Ivan Grozniy, Dragon, Machekha, Tebenkov, Baransky<sup>4,9</sup>. The Kipyaschiy fault is composed of intensely fractured rocks and various breccias. In the depths of horst structure, there is an active process of volcanic metamorphism, volcano-

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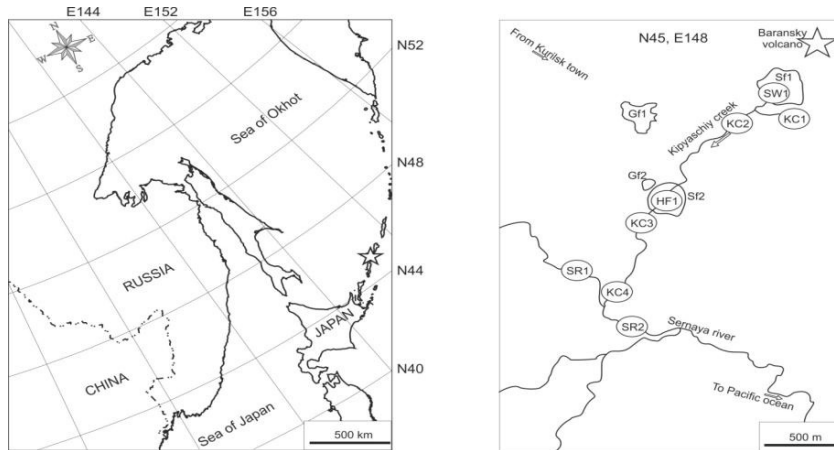


Fig. 1. Location of Baransky volcano (left), schematic map of sampling points (right). Oval – sampling point; Gf1, Gf2 – geothermal fields with geothermal power stations; Sf1, Sf2 – solfataric fields

sedimentary rocks are being influenced by high-temperature (300-350°C), fracture-porous sulfide-carbonate-sulphate and sodium chloride fluids<sup>6</sup>. Previously<sup>2,3</sup> we reported on total hydrothermal flux from Baransky volcano and its influence on the environment. Our goal was understanding conditions, which influence variation of chemical composition of waters forming within active volcanoes<sup>2</sup>. Current work focuses on behaviour and fractionation of rare-earth elements (REE) in waters in natural anomaly as indicator of processes, occurring inside an active volcanic structure.

## 2. Materials, methods and analytical data

Thermal springs were sampled during field work in 2013. We took samples along Kipyaschiy creek. Samples were collected into acid-washed, high-density polyethylene bottles. Water samples were filtered through cellulose filters (0.45  $\mu\text{m}$ ) and then acidified to pH <2 with an ultrapure nitric acid, excluding samples intended for anion analysis. Water temperature, conductivity and pH were measured directly in the field (in situ) to avoid changing parameters. Major elements (Na, K, Ca, Mg and F, Cl,  $\text{SO}_4$ ) were analyzed by liquid chromatography on LC-20, with an analytical error of less than 5%. Al, Fe, Mn, Mg and Sr concentrations were analyzed by AES-ICP on iCAP 6500Duo. Rare-earth elements were measured using -ICP-MS on Element XR.

Hydrochemistry of Kipyaschiy creek was discussed earlier<sup>2</sup>. Data on concentrations of main ions and REEs in waters of Kipyaschiy creek basin are given in Table 1.

## 3. Discussion

Theoretical basis of REE behavior in water depending on the pH, temperature and pressure was studied by many scientists<sup>1,5,9</sup>. Those works proved that even in reducing conditions Eu may be present in the divalent state, in turn pointing to a sufficiently high temperature of the deep reservoir, which results in leaching of rock-forming minerals. Processes of adsorption and complexation in the waters go in opposite directions. Stronger adsorption to particles of minerals reduces the content of lanthanides in solution, while the more stable complexation increases it, caused by increased solubility and mobility of the complexes of rare earth elements in comparison with their ions. Thus, REE study can develop new approach on discussing and understanding processes, occurring inside active volcanic structure.

To discuss the change of concentration of REEs occurring in Kipyaschiy creek and Sernaya river during interaction with hydrothermal fluids, solfatars and mature waters of Baransky volcano, we introduce REE-concentration change 'C1', 'C2', 'C3' and 'C4', where C1 = KC2-KC1; C2 = KC3-KC2; C3 = KC4-KC3; C4 = SR2-SR1. C1, C2, C3, C4 lines reflect change of REEs concentration after influence of solfatars, hydrothermal fluids and thermal creeks onto surface water flows (Fig.2). On the site-1 there is a mixture of upstream of Kipyaschiy creek

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