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Rare earth elements in waters from the Yuzhno-Sakhalinsky mud volcano, Far East of Russia

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Abstract. For the first time, data have been obtained on the concentrations of REE in the subsurface fluids of the Yuzhno-Sakhalinsky mud volcano, as well as in the spring at the foot of this volcano. It has been demonstrated that the REE concentrations in the waters of the studied volcano are significantly higher than in the waters of the mud volcanoes of Junggar Basin. It has been ascertained that the total concentration of REE in mud volcanic waters does not depend on their mineralization, yet it correlates with the concentration of Al. This is probably caused by the sorption of REE on the fine particles of clay suspension. The obtained ranges of REE have a high positive Eu anomaly, which is likely to be an artifact due to the relatively high concentration of Ba in the studied waters.

1. Introduction

Rare-earth elements (REE) are in essence a group of elements with similar chemical properties. On the one hand, slight changes in the compositions of REE in geological processes make it possible to identify the sources of the original substance. On the other hand, certain changes in the chemical properties of REE gradually increase over time along with the growth of the nuclear charge. Therefore, under certain conditions, a significant separation (fractionation) of light and heavy REE occurs. This can give us an idea of the physical and chemical characteristics of the ongoing natural processes.

In recent years, the peculiarities of REE response in natural waters have been extensively studied. This interest was prompted by the possible utilization of REE as indicators of various hydrogeological and geochemical processes. However, the concentrations of REE in natural waters are extremely low and can total to a few ng/l, or, at most, tens of ng/l. Massive countrywide studies in this area have become possible owing to the improvement of the tools and methods of chemical analysis. The modern analytical equipment is sufficiently sensitive to establish even the lowest concentrations of elements.

Hydrogeochemical studies of mud volcanoes have been carried out for decades. However, they hardly touch upon the issues of the geochemical properties of REE. In this respect we can only point out the study [1], where data on the concentrations of REE in six samples from the mud volcanoes of Junggar Basin (China) were presented. Those were weakly alkaline waters (pH ranging from 7.4 to 9.2) with a mineralization degree from 5 to 13 g/l, their main components being Na (1.7–4.4 g/l), Cl (1.1–6.4 g/l) and HCO_3 (0.6–4.3 g/l). The total concentration of REE in these waters was in the range between 0.012 and 0.677 $\mu\text{g/l}$.



The objective of the present study is to explore the occurrence of REE, as well as the peculiarities of their fractionation, in the waters of the Yuzhno-Sakhalinsky mud volcano. The sampling of the volcano was performed in 2011, so chronologically it is the first scientific study of this kind for this volcano.

2. Materials and methods

Sakhalin Island is the only region in the Russian Far East that hosts surface mud volcanoes. The Yuzhno-Sakhalinsky mud volcano is located in the southern part of Sakhalin Island, approximately 18 km NW of Yuzhno-Sakhalinsk. The waters of this volcano are weakly alkaline with a mineralization degree from 18 to 23 g/l. The concentrations of the main components are predominantly in the following ranges: Na – from 5.5 to 6.5 g/l, HCO_3 – from 10 to 12 g/l, Cl – from 3.8 to 4.2 g/l. A more detailed hydrogeochemical description of the volcano is given in the works [2, 3].

The sampling of sediment-and-water mixtures was performed on 2nd June, 2011, from 7 gryphons and pools of the Yuzhno-Sakhalinsky mud volcano. Besides, one sample was taken from the freshwater spring (mineralization < 500 mg/l) at the foot of the volcano. In the course of the sample preparation for chemical analysis, most of the sediments, or mud, were removed from the samples by means of sedimentation. Following that, the water was separated from the remaining clay suspended matter using the “white ribbon” paper porous filter. The content of REE in the water samples was determined through the use of inductively-coupled plasma mass spectrometry (the ICP-MS method) at the Far East Geological Institute, Far East Branch of the Russian Academy of Science (Vladivostok).

Since the concentrations of different REE differ drastically, they are usually controlled with the help of established standards, for the minimization of the aforementioned differences. In this case, the standardization was conducted in reference to the Russian Platform Shale Composite (RPSC) [4]. The Europium anomaly Eu/Eu^* was calculated as a ratio of the doubled standardized concentration of Eu to the sum of standardized concentrations of the adjacent elements – Sm and Gd. The ceric anomaly Ce/Ce^* was calculated in a similar manner. For a comparative analysis of the levels of concentration and distribution of REE, clarkes of REE in the river waters from the study [5] were used.

3. Results and discussion

The total content of REE in the waters of the Yuzhno-Sakhalinsky mud volcano varies in the range between 1.6 and 7 $\mu\text{g/l}$. This figure is by one or two orders greater than the analogous parameter in the waters of the mud volcanoes of Junggar Basin. At the same time, the larger portion of REE is accounted for by La – in most samples in was in the range between 50 and 65 wt. %. Due to this, on the REE spectra a high negative Ce anomaly can be observed – Ce/Ce^* being from 0.06 to 0.56 (figure 1). The REE spectra are quite even – without any pronounced tendencies towards depletion of, or enrichment with heavy REE as opposed to light ones. Yet, nominally the ratio of the standardized concentration of La to the standardized concentration of Yb for the majority of samples is far higher than one. A high positive Eu anomaly is also observed – Eu/Eu^* being from 12 to 28.

The REE concentrations in the water from the spring in the vicinity of the Yuzhno-Sakhalinsky mud volcano are much lower than in the waters from the gryphons and pools of this volcano. However, the REE spectrum in the water from the spring, on the whole, follows the pattern of the REE spectra in mud volcanic waters, i.e. there is a high content of La and a positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 4.8$) to be noted. At the same time, there is a slight tendency towards the enrichment of the water from the spring with heavy REE, which is not to be observed for mud volcanic waters. The REE spectrum in the spring water also possesses certain

differences from the REE spectrum in the river water (figure 1). The latter is characterized by higher REE concentrations and a negative Eu anomaly.

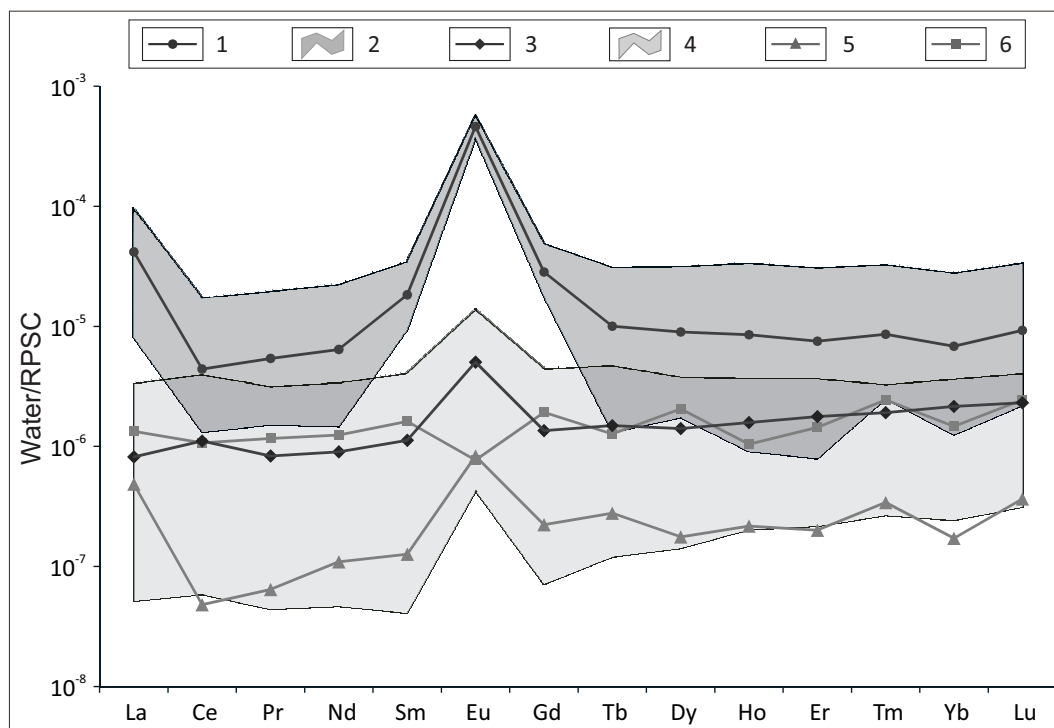


Figure 1. Distribution spectra of REE concentrations in natural waters, standardized with regard to Russian Platform Shale Composite: 1, 2 – average concentrations and range of REE variation in waters of Yuzhno-Sakhalinsky mud volcano; 3, 4 – concentrations and range of REE variation in waters of mud volcanoes of Junggar Basin; 5 – REE concentrations in water from spring at the foot of Yuzhno-Sakhalinsky mud volcano; 6 – REE clarkes in river water (according to study [5]).

The REE spectra in the mud volcanic waters of Junggar Basin bear a certain resemblance to the REE spectra obtained in the course of the present study. They are also rather even and have a strongly pronounced positive Eu anomaly. Yet, these spectra have a significant difference – the presence of a slight positive Ce anomaly. The positive Eu anomaly is accounted for in the study [1] by dissolution of plagioclases, the composition of which normally includes high concentrations of Eu. In our case, we are inclined to attribute this anomaly to other factors. In the study [6], it was demonstrated that in the chemical analysis of natural waters with the ISP-MS method, an overestimation of Eu concentrations can take place due to spectral interference. This occurs in the setting of a high barium load, which is determined as a Ba/Eu ratio. As it follows from the study [6], the critical values of barium loading totaled approximately 1000. In our samples (both from the mud volcano and the spring) the Ba/Eu ratio is in the range between 6500 and 10000. Therefore, the Eu concentrations in our samples should be regarded as overestimated. This casts doubt on the presence of the Eu anomaly under discussion, because it is very likely to have been artificially created during the chemical analysis of the samples by means of the ISP-MS method. It should also be noted that in the waters of the mud volcanoes of Junggar Basin, no measurements of Ba concentration were taken [1].

The concentrations of REE in the waters of different gryphons and pools of the Yuzhno-Sakhalinsky mud volcano differ drastically – sometimes by one order of magnitude. At the

same time, the mineralization of the waters of the gryphons and pools of this volcano varies within fairly narrow limits. In those exact samples, mineralization was not actually measured, but it can be inferred by the measurements of Na concentration, which is the main cation in mud volcanic waters. Our findings show that the total content of REE does not depend on the concentration of Na (figure 2). At the same time, the sum of REE demonstrates a statistically significant correlation with the concentration of Al (figure 2). Therefore, it can be said that a large portion of REE is sorbed on the fine-particle clay solids, which are present in the aqueous solution. We should also note that the concentration of light REE is more dependent on the concentration of Al – the correlation factor goes down with an increase of the atomic number of the chemical element. It is likely that the higher than normal content of La in our samples is associated with this very cause.

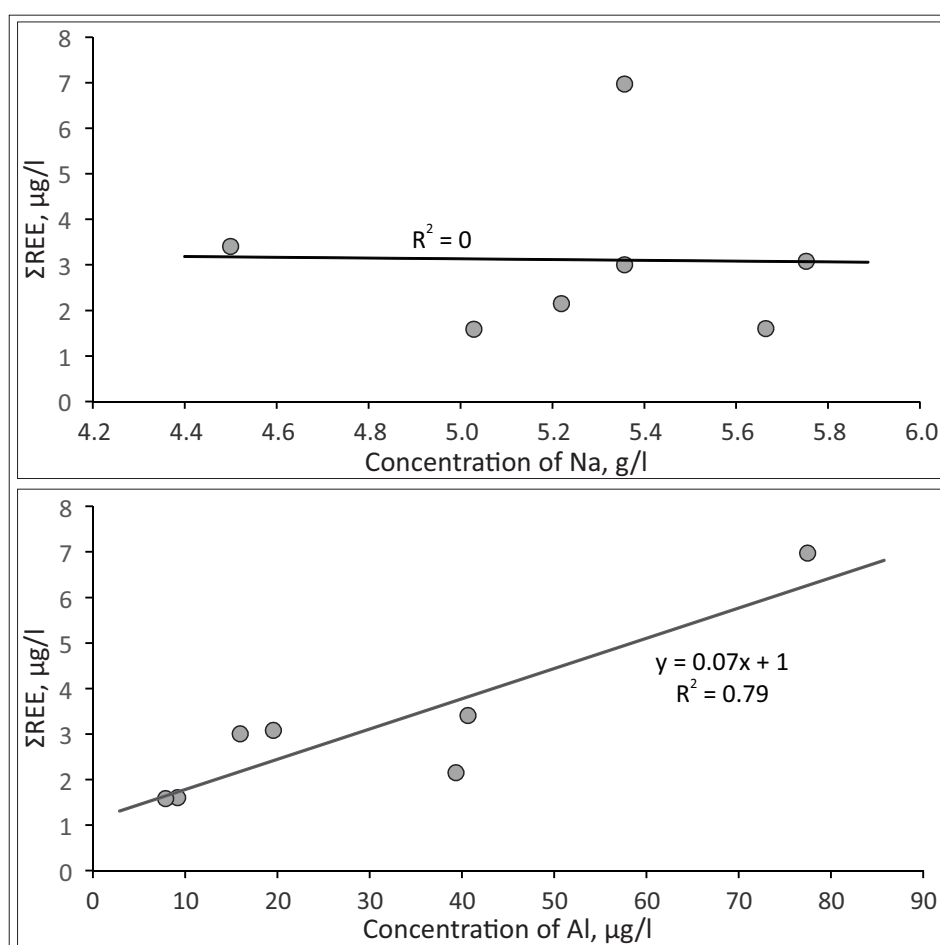


Figure 2. Ratio of total REE to concentrations of Na (above) and Al (below) in waters of Yuzhno-Sakhalinsky mud volcano.

4. Conclusion

In the course of the present study, the concentrations of REE in the subsurface waters from 7 gryphons and pools of the Yuzhno-Sakhalinsky mud volcano were determined. In addition, another sample from the spring at the foot of the volcano was analyzed. The concentrations of REE in the waters of the studied volcano are quite high – by one or two orders higher than in

the waters of the mud volcanoes of Junggar Basin. This can be accounted for by the sorption of a large portion of REE on the finely-dispersed clay particles, because the concentrations of REE in our samples correlate with the concentration of Al. At the same time, the strongest correlation is observed for light REE. On the constructed spectra of REE one can clearly see an uncharacteristically high content of La in the samples, which results in low values of Ce/Ce^* . It is likely that, of all the REE, La is to a larger extent sorbed on the clay suspended solids. At the same time, there is no correlation between the concentrations of REE and the mineralization of mud volcanic waters. On the constructed REE spectra one can also clearly see a positive Eu anomaly. Yet, it is most likely to have been caused by spectral interference occurring at a relatively high concentration of Ba in the aqueous solution. The REE concentrations in the water from the spring are quite low – approximately by one order lower as compared to the REE clarkes in river waters. The REE spectrum in the spring water, on the whole, follows the pattern of the REE spectra in the waters of the Yuzhno-Sakhalinsky mud volcano.

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