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BG5.3 **Extreme environments, mud volcanoes and hydrothermal systems on Earth and planetary analogues: biology, stratigraphy, structure, evolution and monitoring of active and fossil settings**

Concentrations and behavior of rare earth elements in mud volcanic waters

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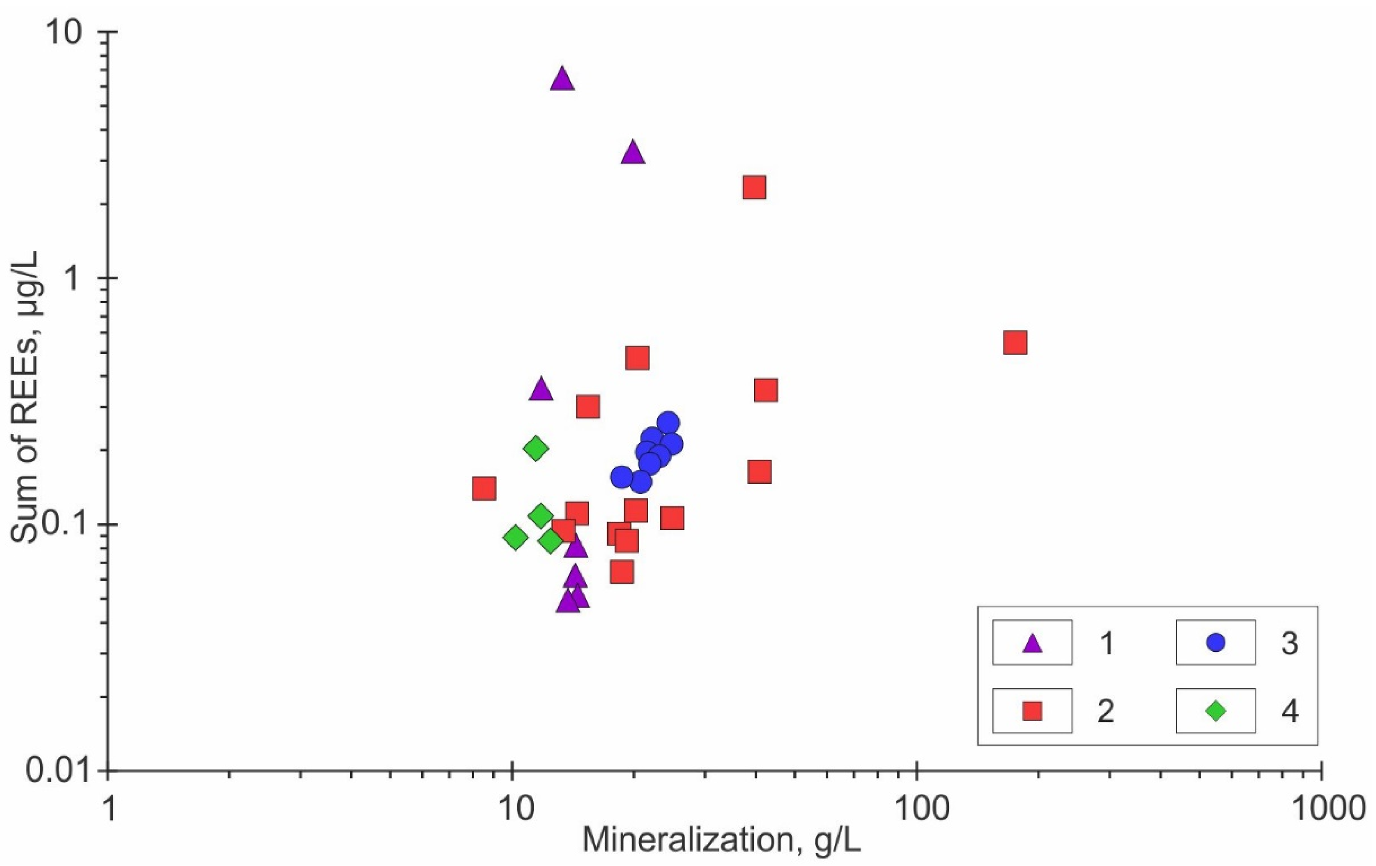
Abstract: *For the first time, data are presented on the distribution of REEs in the waters of mud volcanoes of Sakhalin Island (Russia), the Taman Peninsula (Russia), and Azerbaijan. The spectra of REEs are quite similar for most samples of mud volcanic waters. It has been established that mud volcanic waters with the total REEs concentration less than 0.5 µg/L are enriched with heavy lanthanides and depleted with cerium. On the example of Yuzhno-Sakhalinsk mud volcano it is shown that REEs concentration will be higher in active gryphons.*

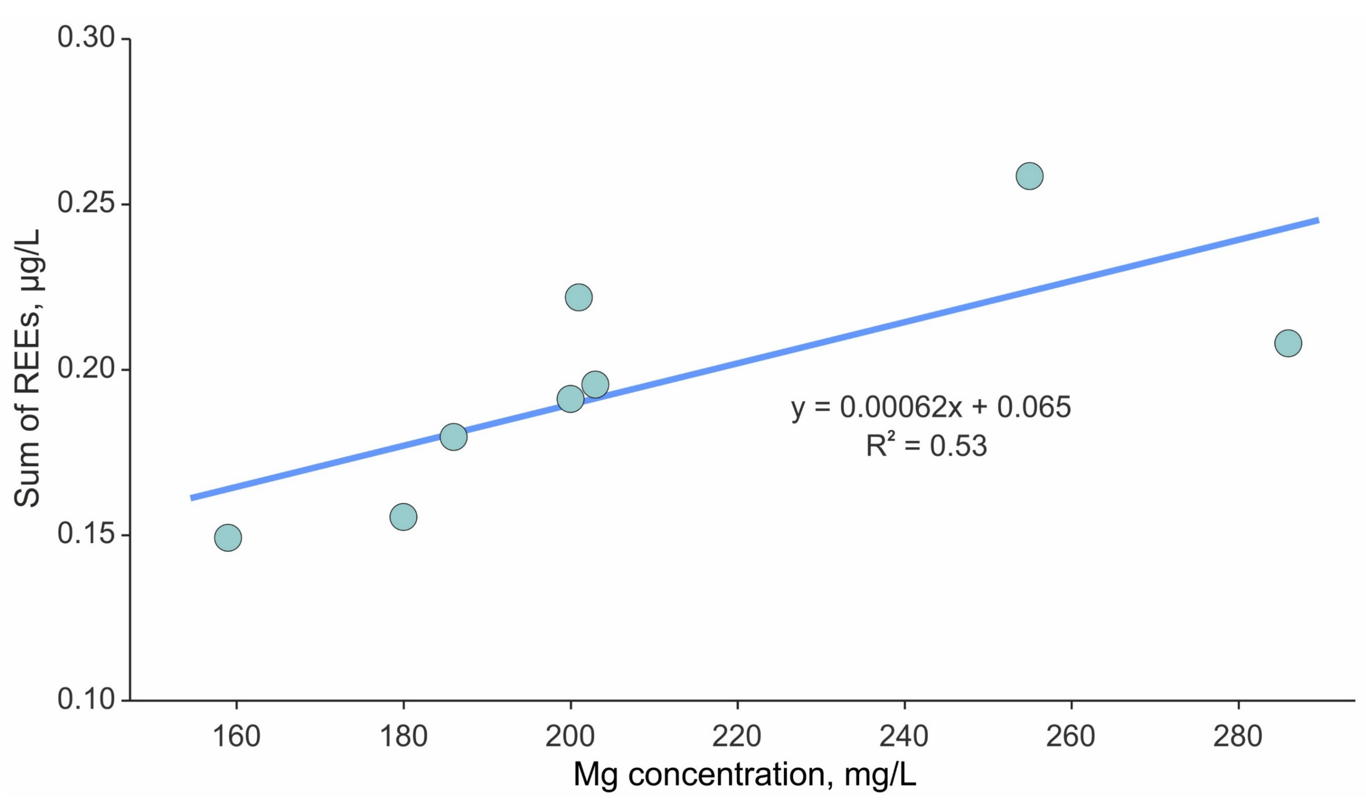
Rare-earth elements (REEs) have similar chemical properties. This defines the identical, at first glance, behavior of REEs in natural processes. Given that the compositions of REEs vary poorly in natural processes, we are able to make a judgement about the REEs compositions of the sources of initial matter. However, the weak differences in the chemical properties of REEs grow with an increase in the nuclear charge from La to Lu. In some natural processes, this resulted in fractionation between light rare-earth elements (LREEs) and heavy rare-earth elements (HREEs). While studying the REEs distribution in seas, rivers, hydrothermal zones, etc., REEs are used as indicators of geochemical processes. At present, the REEs distribution in mud volcanic waters has barely been studied. In this work, the data on the REEs content in the mud volcanic waters from Azerbaijan (Shamakhy-Gobustan, Absheron, Lower Kura) and Russia (Taman Peninsula, Sakhalin Island – Yuzno-Sakhalinsky and Pugachevsky volcanoes) were first reported and analyzed. In total, 33 samples from 20 mud volcanoes were studied. The REEs content was determined by the inductively coupled plasma mass spectrometry (ICP-MS). Basic anions and cations were determined by the ion chromatography. All samples were filtered through a microporous membrane filter with 0.45 µm pore size.

The REEs determination in the waters of mud volcanoes by ICP MS is a difficult analytical task due to spectral and nonspectral interferences. The nonspectral impacts are related to the low ratio between a useful analyte signal (response) and an interfering intensity of noise due to high mineralization of the mud volcanic waters and low REEs contents in the samples. The spectral interferences are conditioned by the overlapping of oxide and hydroxide signals of Ba onto the analytical masses of REEs from Nd to Lu. Owing to this, the determination of Eu is an acute issue. There are significant additional signals from oxide and hydroxide ions of Ba on the analytical masses of Eu. The Ba content in the waters of mud volcanoes is up to 17 mg/L; the Ba/Eu ratio is up to 10^6 (sometimes higher). This results in significant overestimation of the Eu concentration in the samples. The problem of Gd, Sm, and Tb determination is less acute. To correct spectral data, we used the original algorithm described in [3].

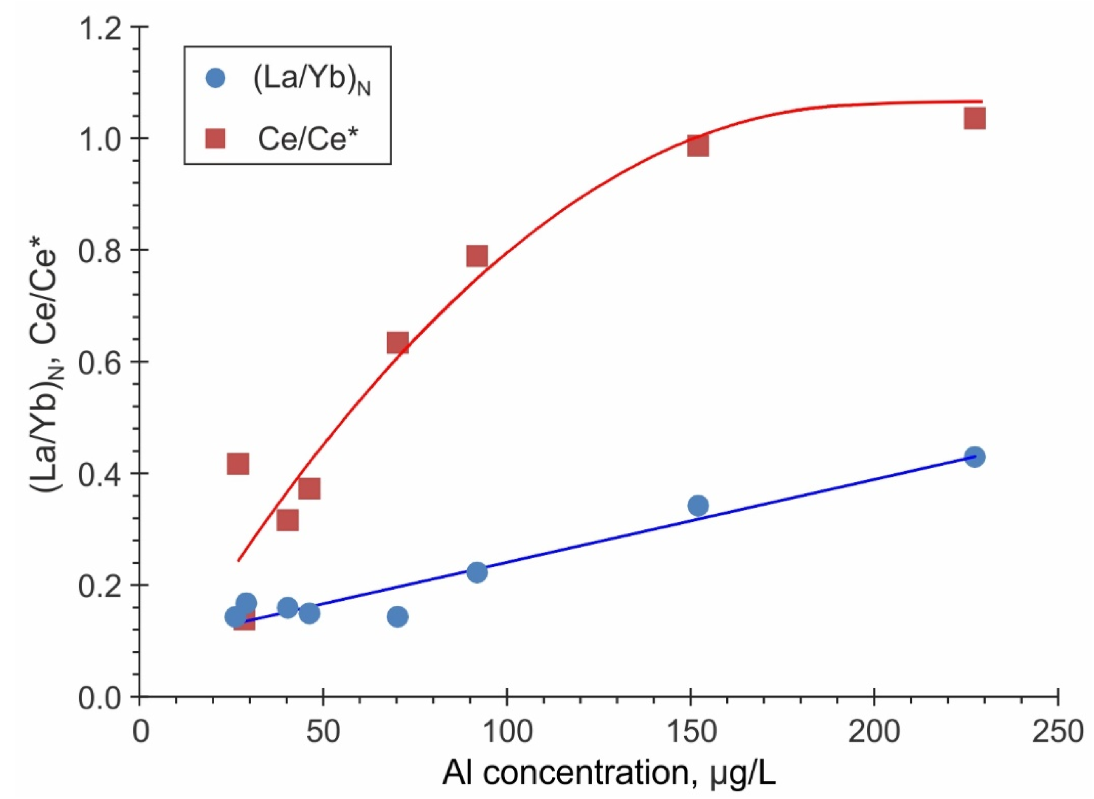


The ratio between the sum of REEs and mineralization for the mud volcanic waters: 1 – Taman Peninsula; 2 – Azerbaijan; 3 – Yuzhno-Sakhalinsky volcano; 4 – Pugachevsky volcano.

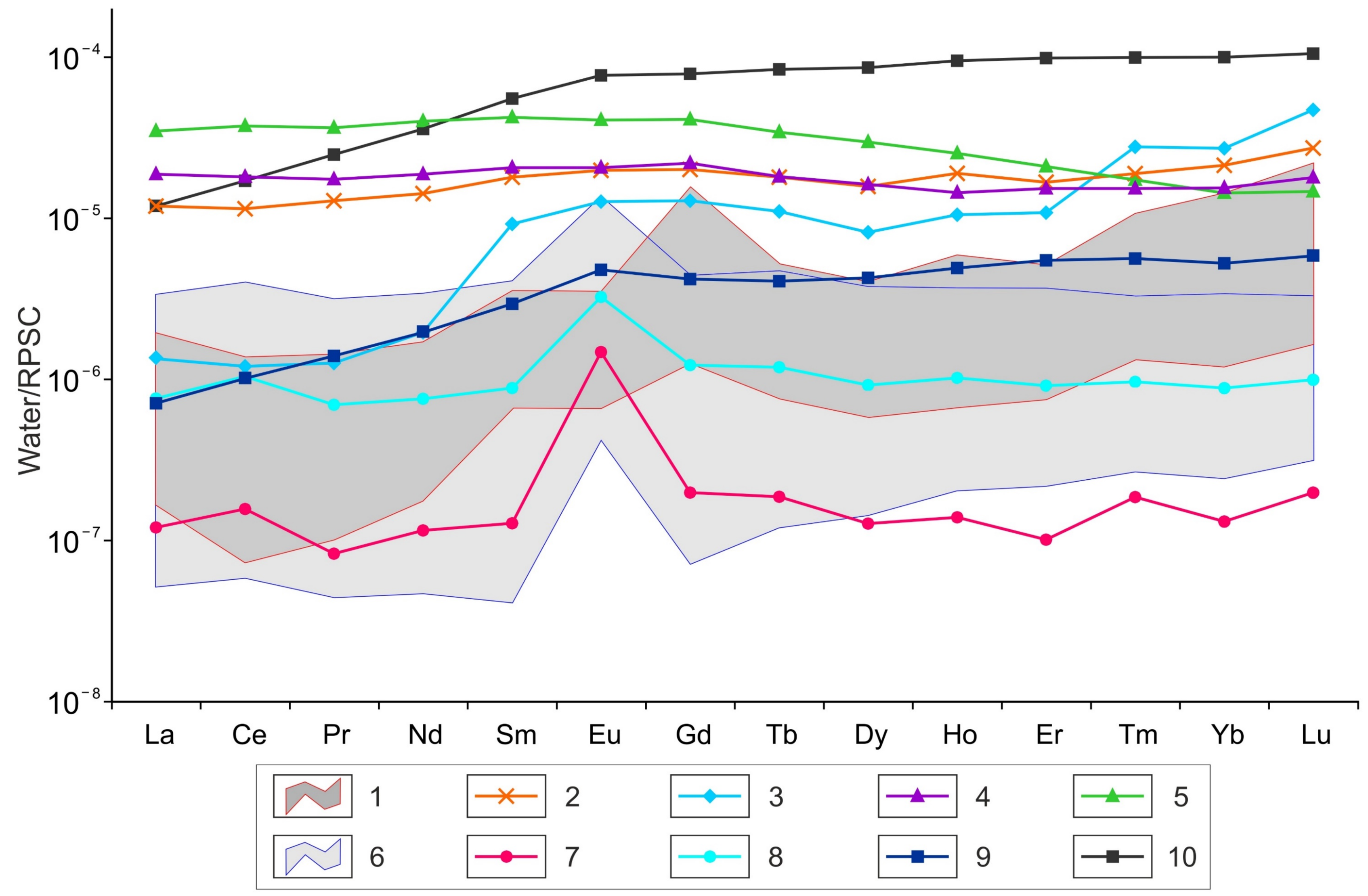
The waters studied are neutral or weakly alkaline; pH ranges from 6.8 to 8.7. Mineralization is generally 10-40 g/L. The sum of REEs commonly ranges from 0.05 to 0.5 µg/L. In some samples, the sum of REEs is up to 6.5 µg/L. Spearman's rank correlation coefficient between the sum of REEs and mineralization is 0.42. This is more than a critical value, which is 0.34 for our sample number and a significance level of 0.05. Therefore, there is a statistically significant positive relation between the sum of REEs and mineralization. However, this relation is rather weak; i.e., mineralization cannot be the key factor determining the REEs content in the mud volcanic waters.



The ratio between the REEs content and chemical composition of waters from gryphons of the Yuzhno-Sakhalinsky mud volcano. A positive correlation between the sum of REEs and the Mg concentration is observed. Similar positive correlations are also observed with the Na and HCO_3 concentrations. At the same time, there is no correlation between the sum of REEs and Cl concentration.



Dependence of the parameters $(La/Yb)_N$ and Ce/Ce* on the Al concentration in water samples from the Yuzhno-Sakhalinsky mud volcano. A special experiment was conducted in which the same samples were filtered through membrane filters with different pore sizes: 0.2 µm, 0.45 µm, 1 µm and 3 µm.



The spectra of REEs for the volcanic waters, normalized to clays of the Russian Platform: 1 – the field of the mud volcanic waters with the sum of REEs < 0.5 µg/L; 2, 3 – the Agdamskii and Neftechala mud volcanoes, Azerbaijan; 4, 5 – the Gora Gnilaya mud volcano, Taman Peninsula; 6 – the field of the mud volcanic waters of Junggar Basin, China [4]; 7, 8 – the Paratunka hydrothermal system, Kamchatka Peninsula [1]; 9, 10 – the Mutnovsky magmatic volcano, Kamchatka Peninsula [2]

The concentrations of REEs in the mud volcanic waters were normalized to the REEs composition in clays of the Russian Platform (RPSC). The spectra of REEs is rather of the same-type for most samples of the mud volcanic waters. The specific range of concentrations is clearly distinguished for the samples with the sum of REEs < 0.5 µg/L. It is obvious that these samples are HREE-rich, with $(La/Yb)_N$ coefficient ranges generally from 0.1 to 0.45. A negative cerium anomaly is characteristic for these samples, and the Ce/Ce* coefficient is most commonly <1; for some samples it is up to 0.1. It is interesting to find that a positive Ce anomaly is found on the spectra of REEs in breccia of mud volcanoes. Ce is likely removed from water and accumulated on fine-grained clayey suspended matter. More uniform spectra are typical of the mud volcanic waters with a high content of REEs. For these waters the $(La/Yb)_N$ coefficient is higher and reaches 2.4. There is no Ce anomaly in these samples, and the Ce/Ce*coefficient is close to 1. The spectra of REEs for waters in magmatic volcanoes of Kamchatka Peninsula [1, 2] and the mud volcanic waters of Junggar Basin [4] are shown for comparison. The waters of magmatic volcanoes showed a different profile of the REE distribution. The spectra of REEs for the mud volcanoes of Junggar Basin have positive cerium and europium anomalies in contrast to our results. In [4], there are no data on the Ba concentration in the mud volcanic waters. Thus, we are not able to make a judgement concerning its influence on determination of the Eu concentration or to estimate the validity of the europium anomaly mentioned.

In 2015, on the Yuzhno-Sakhalinsk mud volcano, along with the sampling for REEs determination, hydrogeochemical monitoring was also conducted. It was shown that the concentration of Na, Mg, and hydrocarbonate ions is higher in the more active gryphons [5]. The concentration of Cl ions is approximately the same for all gryphons, i.e., it does not depend on their activity, and varies only with dilution by rainwaters. We can see that the content of REEs in the mud volcanic waters also depends on the level of activity of gryphons. Spearman's rank correlation coefficient between the sum of REEs and the concentration of Mg ions is 0.88. This is more than a critical value, which is 0.74 for our number of samples and a significance level of 0.05. Statistically significant correlations between the sum of REEs and the concentration of Cl ions are absent. Therefore, with other conditions being equal, the sum of REEs in the active gryphons will be higher than in the passive ones. The $(La/Yb)_N$ coefficient increases with the growth of the concentration of Mg ions, the Spearman's rank correlation coefficient is 0.86. We did not observe statistically significant relations between the concentration of Mg ions and the Ce/Ce* coefficient.

Our studies allowed us to determinate the levels of REEs accumulations in mud volcanic waters. We established that the REE spectra in the waters of mud volcanoes from different regions of the world have similar profiles, which allowed us to use REEs for identification of mud volcanic waters. We also demonstrated the possibility to use REEs as indicators of mud volcanic activity.

References

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