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# Groundwater From Abandoned Mines of the Partizansk Coal Basin, Primorye: Isotope-Geochemical Features of Composition and Regularities of Formation

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**Abstract.** The underground waters from the abandoned mines of the Partizansk coal basin were subjected to isotope-geochemical study to investigate their compositional features and regularities of their formation. The study has shown that flooding of the mines caused origin in the natural and industrial structures of a succession of water solutions with changeable composition:  $\text{HCO}_3\text{-Ca} \rightarrow \text{HCO}_3\text{-Mg} \rightarrow \text{HCO}_3\text{-Na} \rightarrow \text{HCO}_3\text{-SO}_4\text{-Na} \rightarrow \text{SO}_4\text{-Na}$ . The sulfur variability here is conditioned by the amount and level of oxidation of pyrite inherent in coals, bacterial component is important as well. The natural and industrial structures under consideration demonstrate zonality of geochemical conditions. Deeper horizons are the place where aerobic systems transit into anaerobic ones, and predominantly deoxidizing environment stimulates generation of biochemical natural gases, such as  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{H}_2$ . It has been established also that transformation of groundwater composition influences the rare-earths behavior; distribution of the dissolved REE depends on the water type and is controlled by the water-rock interaction processes and equilibrium – non-equilibrium state. Mineralization of the waters under study correlates with  $\delta^{18}\text{O}$  and  $\delta\text{D}$  parameters, and variation of their values can be used for estimation of the water-rock interaction degree.

## 1. Introduction

The relevance of this research is defined by a broad development of processes caused by flooding of abandoned coal mines. The flooding is a little-known factor of technogenic impact on the subsoil which provokes change of a hydrochemical background with following formation of new geochemical types of waters uncharacteristic of the upper underground hydrosphere prior to. The underground water composition transformation in natural and industrial structures has been under study for more than 10 years. The observations showed that in time the flooding waters acquired geochemical specific in situ, with further transformation in the direction of filtration flow. This geochemical specific is governed by the geological structure of sedimentary basins and is correlated with the presence in coal seams and above layers of marine, salt- or freshwater-bearing geological formations [1–4].

This paper presents the results of research into the isotope-geochemical features of groundwater composition, the REE concentration level and fractionation in waters of natural and industrial hydrogeological structures within the Partizansk coal basin.



## 2. Objects and methods of investigation

The work is based on the continuous, standardized by methodology and technique, process of observations and measurements of the indicators characterizing the hydrodynamic features of the coal mine flood, as well as the fluctuations of compositions of the underground and surface waters.

The underground waters of Glubokaya, Nagornaya, Avangard, Uglekamenskaya, and Severnaya mines within the Partizansk coal basin have been analyzed. These are waters that are flowing through the Quaternary deposits, exogenous fractures of the Cretaceous deposits, faults and intrusive contacts, as well as from a technogenic water-bearing complex.

The hydrogeochemical samples for analysis of cations and sulfates were filtered through the cellulose filter (0.45 mm) at the place of sampling to remove the suspension. To determine the ions, the samples were also filtered and gathered into the polyethylene vessels without acidifying. The unstable parameters were determined at the place of water sampling. The analytical investigations were carried out at the Analytical Center of Far East Geological Institute FEB RAS (accreditation certificate N ROSS RU.0001.518986). The element contents in waters were determined with the methods of mass-spectrometry at the inductively coupled plasma spectrometer Agilent 7700 (Agilent Technologies, USA) and atomic-emission spectrometry at the inductively coupled plasma spectrometer iCAP 6500Duo (Thermo Scientific Corporation, USA).

Sample preparation for sulfur isotope analysis was carried out using the elemental analyzer FlashEA-1112 (Thermo Scientific, Germany) in S configuration and according to a standard protocol for converting of sulfur into SO<sub>2</sub>. Measurement of <sup>34</sup>S/<sup>32</sup>S isotope relations was executed relative to regular laboratory gas SO<sub>2</sub> calibrated according to the international standards: IAEA-S-1, IAEA-S-2, IAEA-S-3 and NBS-127, on MAT-253 mass spectrometer (Thermo Scientific, Germany) in continuous helium flow. Measuring results are presented in the standard form:  $\delta^{34}\text{S} = (\text{R}_{\text{sample}}/\text{R}_{\text{standart}} - 1)$  and expressed in (‰), where  $\text{R}_{\text{sample}}$  and  $\text{R}_{\text{standart}}$  is <sup>34</sup>S/<sup>32</sup>S relation in the sample and in the standard, respectively. The reproducibility of  $\delta^{34}\text{S}$  results constituted 0.1 ‰ (1σ) both for the standards (n=10) and the samples. The  $\delta^{34}\text{S}$  measuring results are given in relation to VCDT international standard.

Sample preparation for oxygen and hydrogen isotope analysis followed the standard procedure of high-temperature pyrolysis of water with carbon. For receiving of CO and H<sub>2</sub> as a result of water-carbon reaction at 1450° C in reducing conditions and subsequent chromatographic fractionation of the thermal decomposition products, the ThermoQuest (Bremen, Germany) TC/EA high temperature conversion elemental analyzer connected to the ThermoQuest MAT 253 isotope mass spectrometer was used. The water samples (0.5 μl) were introduced in the pyrolyzer's reactor automatically, by Combi PAL autosampler. For calibration of the analytical system during the process the following isotopic standards distributed by the International Atomic Energy Agency (Vienna) were utilized: VSMOW (Vienna Standard Mean Ocean Water)  $\delta^{18}\text{O} = (0.0) \text{‰}$ ;  $\delta\text{D} = (0.0) \text{‰}$ ; SLAP (Standard Light Antarctic Precipitation)  $\delta^{18}\text{O} = (-55.50) \text{‰}$ ;  $\delta\text{D} = (-427.5) \text{‰}$ ; GISP (Greenland Ice Sheet Precipitation)  $\delta^{18}\text{O} = (-24.76) \text{‰}$ ;  $\delta\text{D} = (-189.5) \text{‰}$ . The reproducibility of results was controlled by the repeated measurements by the laboratory standard and averaged  $\pm 0.1 \text{‰}$  and  $\pm 0.3 \text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively.

## 3. Results of investigations and discussion

It has been established that in the natural and industrial hydrogeological structures of the Partizansk coal basin there took place a significant change in groundwater circulation conditions resulted in formation of a technogenic water-bearing complex characterized by considerable deviations in filtration speed and water head level as compared to the natural one. The recharge of the aquifers currently occurs at the expense of the waters percolating through the fissured rock massif and the mine goafs which are often filled with disintegrated rocks characterized by maximum water transmissibility.

The underground waters have subacid-to-neutral pH (6.8–7.6) and a mineralization in the range of 200–6290 mg/l. As they circulate through the natural and industrial structures of mines, they obtain higher concentrations of sodium ions, hydrocarbonates and sulfates; mineralization growths as well.

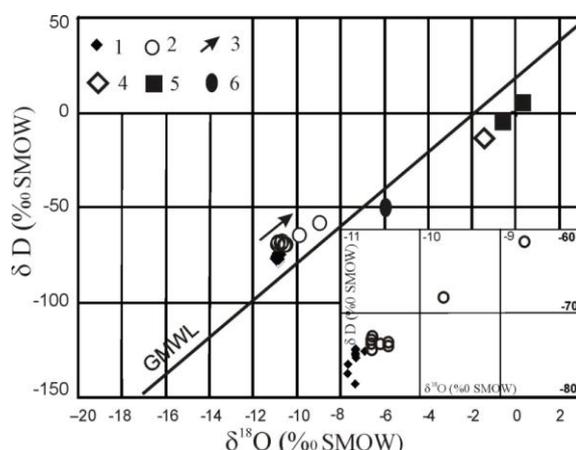
The natural hydrocarbonate waters, combined by the cations, gain sulfate-hydrocarbonate and hydrocarbonate sulfate sodium composition.

All the defined water-bearing complexes are hydraulically bound owing to the fracturing structure of rocks, multiple tectonic dislocations and lack of continuous watertight stratum. Therefore, for correct conclusions about the features of the groundwater composition transformations in the natural and industrial structures, the available hydrochemical samples were divided by means of the cluster analysis into two groups: 1 – underground waters of natural complex; and 2 – waters of technogenic water-bearing complex. The waters of each complex are subdivided into types:  $\text{HCO}_3\text{-Ca}$ ,  $\text{HCO}_3\text{-Mg}$  and  $\text{HCO}_3\text{-Na}$  for the first group, and  $\text{HCO}_3\text{-SO}_4\text{-Na}$  and  $\text{SO}_4\text{-Na}$  for the second one. Selektor-S software package was utilized to create a model of physical-chemical conditions in natural and industrial structures of the Partizansk coal basin. The technique of modeling of hydrogeochemical processes involved a series of calculations of the water-rock system equilibrium state. The specified parameters reflected external conditions under which the system exists (temperature, common pressure and chemical potentials of each quite mobile component). High reliability of computation was conditioned by the actual ion concentrations taken into account. The natural chemical composition of the aquifers recalculated to the amount of moles for each component was also put. Combination of phases and existing forms of chemical elements in the modeling system was described based on the chemical elements migration forms calculated by the AquaChem V. 5.1 software and with regard to components of the secondary mineralization. The modeling imitated incongruent solution of rock minerals under the following conditions: 1) closed carbonate and atmospheric gas system ( $\text{CO}_2$  – 0.01 kg per one kilo of  $\text{H}_2\text{O}$ , atmospheric gas – 0.3 kg per one kilo of  $\text{H}_2\text{O}$ ); 2) open carbonate system ( $\text{CO}_2$  grew from 0.01 to 1.28 kg per one kilo of  $\text{H}_2\text{O}$ ). Initially (the first step of computing) the partial pressure of carbonic acid was accepted as  $10^{-2.0}$  bars that on the average correspond to that of the underground waters from a zone of regional jointing.

The results showed that the water-rock system closed for  $\text{CO}_2$  (0.01 kg per one kilo of  $\text{H}_2\text{O}$ ) and atmospheric gas (0.3 kg per one kilo of  $\text{H}_2\text{O}$ ) sequentially produces the aqueous solutions corresponding to the following row of compositional changes:  $\text{HCO}_3\text{-Ca} \rightarrow \text{HCO}_3\text{-Mg} \rightarrow \text{HCO}_3\text{-Na} \rightarrow \text{HCO}_3\text{-SO}_4\text{-Na} \rightarrow \text{SO}_4\text{-Na}$ . The carbonate closeness of a system always means the protection of an aqueous phase from higher concentrations of  $\text{HCO}_3^- + \text{CO}_3^{2-}$  and favour of  $\text{SO}_4^{2-}$  growth (with a source).

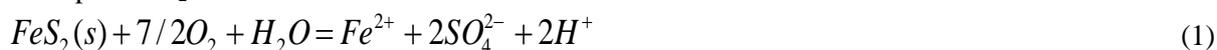
The results of  $\delta^{32}\text{S}$  and  $\delta^{34}\text{S}$  study showed that the waters of technogenic complex of the abandoned coal mines are enriched with  $\delta^{34}\text{S}$  which values fluctuate between 10.0 ‰ and 15.6 ‰. The arrangement of points of sulfate isotope composition balanced with the underground waters of a technogenic complex of the flooded coal mines testifies that the observed distribution of  $\delta^{34}\text{S}$ -sulfate and  $\delta^{18}\text{O}$ -sulfate in mine waters and sulfur variability is not bound to a marine source that might be expected from the stratigraphic and structural position of coal basins of Primorsky Region. In  $\delta\text{D}$  and  $\delta^{18}\text{O}$  isotopic compositions, the waters under consideration also are lighter than the seawater and are not subject to the influence of oceanic waters. The figurative points of their compositions are located along the Global Meteoric Water Line (GMWL) that points to their infiltration nature (fig. 1).

The natural and technogenic complexes demonstrate pronounced isotopic compositions. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of their waters were calculated as (-10.6 up to -8.7 ‰) and (-74.4 up to -61.3 ‰) for the industrial complex, and (-10.9 up to -10.7 ‰) and (-78.5 up to -74.4 ‰) for the natural one. The composition of the water types is conditioned by the time of water-rock interaction that influences on mineralization and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values growth. It has been established that there is a correlation between mineralization and such parameters as  $\delta^{18}\text{O}$  and  $\delta\text{D}$ .



**Figure 1.** The  $\delta D$  vs.  $\delta^{18}O$  values diagram for underground waters from the abandoned coal mines of Primorsky Region: 1–2 – natural (1) and technogenic (2) waters; 3 – trend in isotopic compositions. Oceanic water standard [Ref. 5] – 4; sea water of the Amur Bay [Ref. 6] – 5; atmospheric precipitation of the Primorye south [Ref. 6] – 6; GMWL – the Global Meteoric Water Line (Craig's equation). The insert is the scaled-up fragment with figurative points of isotopic composition of the studied waters.

As is known [7], the  $\delta^{18}O$ -sulfate content characterizes conditions of pyrite oxidation in the natural and industrial structures. The pyrite oxidation at almost neutral pH assumes a direct oxidation by the atmospheric  $O_2$ :



There is a high probability that oxygen atoms of the atmospheric  $O_2$  can be added to the sulfate molecule. At the same time the atmospheric  $O_2$  is isotopically heavy, with  $\delta^{18}O \sim 23.5$  ‰ [Ref. 8] and  $\delta^{18}O$ -sulfate  $\sim 24.2$  ‰. If pH is rather low and  $Fe^{3+}$  is soluble, the pyrite oxidation reaction will run as follows:



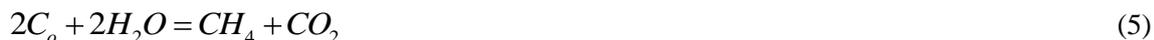
In this case, 100% of oxygen atoms come to  $SO_4^{2-}$  from water and the  $\delta^{18}O$ -sulfate content is strongly depleted.

It was found out that oxidation of pyrite inherit in coals was the major source of sulfate supply in the waters under consideration. The sulfur content of coals of the Partizansk basin is low (0.2–0.3 %) and conditioned by various syngenetic and epigenetic processes, including action of the sulfate-reducing bacterium [9] and assimilation of biogenic  $H_2S$  into organic material.

The conclusion is drawn that both reactions, (1) and (2), run in the oxidation of pyrite from the coals, and the enrichment of waters with  $^{34}S$  testifies an important role of bacterium in formation of increased sulfur contents.

The natural and industrial structures under consideration were demonstrated to have a zonality of geochemical conditions. In deeper horizons there occur a transition from aerobic systems ( $PN_2 = 7.7267e-01 - 8.2929e-01$  bar;  $PO_2 = 3.6951e-02 - 1.4457e-01$  bar) to anaerobic ones in the environment of almost full oxygen disappearing and emerging of biochemical natural gases. The simulation of gradual atmospheric gas reduction from 0.3 to 0.003 kg per one kilo of  $H_2O$  and at a constant rock -to- water ratio  $R/W = 0.032$  has clearly shown that the decrease of an equilibrium concentration of  $O_2$  in an aqueous solution leads to negative values of Eh and the emergence of reduced forms of sulfur (3, 4), methane (5), or free hydrogen (6):





The process is followed by the formation of carbonic acid and hydrocarbonate ion that broadens the area of existence of the HCO<sub>3</sub>-Na water type.

Noteworthy are the extremely low concentrations of rare earths – only hundredths and thousandths mg/l. SumREE varies within 0.01–1.53 mg/l. It is clearly seen on plots with curves normalized to the North American slate (NASC) [Ref. 10] that by level of REE content natural HCO<sub>3</sub>-Ca water (Fig. 2 A) as well as HCO<sub>3</sub>-Na and HCO<sub>3</sub>-Mg water types (Fig. 2 B, C) occupy lower position as compared to the waters of the technogenic complex (HCO<sub>3</sub>-SO<sub>4</sub>-Na, SO<sub>4</sub>-Na) (Fig. 2 D, E). The contribution of REE to a composition of salt in solutions however is insignificant. Nevertheless, a relation between the  $\sum$ REE, total dissolved solids and selected water types is observed (Fig. 3). In spite of the fact that the HCO<sub>3</sub>-SO<sub>4</sub>-Na water types of the technogenic complex are notable for lower mineralization than it is for the SO<sub>4</sub>-Na waters, in most cases the REE content in them is higher (Fig. 3, field II). This can testify that a process of water transformation, from the HCO<sub>3</sub>-SO<sub>4</sub>-Na type to the SO<sub>4</sub>-Na one, occurred with formation of complex REE compounds and their deposition in the form of mineral phases. A share of LREE and HREE in waters of the natural complex varies from 71 to 83 % and from 17 to 29 %, respectively. As for the technogenic water-bearing complex, it looks like: from 43 to 87 % and from 13 to 57 %, respectively. When analyzing the succession HCO<sub>3</sub>-Ca→HCO<sub>3</sub>-Mg→HCO<sub>3</sub>-Na→HCO<sub>3</sub>-SO<sub>4</sub>-Na→SO<sub>4</sub>-Na (fig. 2), there observed a gradual increase of HREE portion in the distinguished types of underground waters that is most likely determined by the time of water interaction with surrounding rocks.

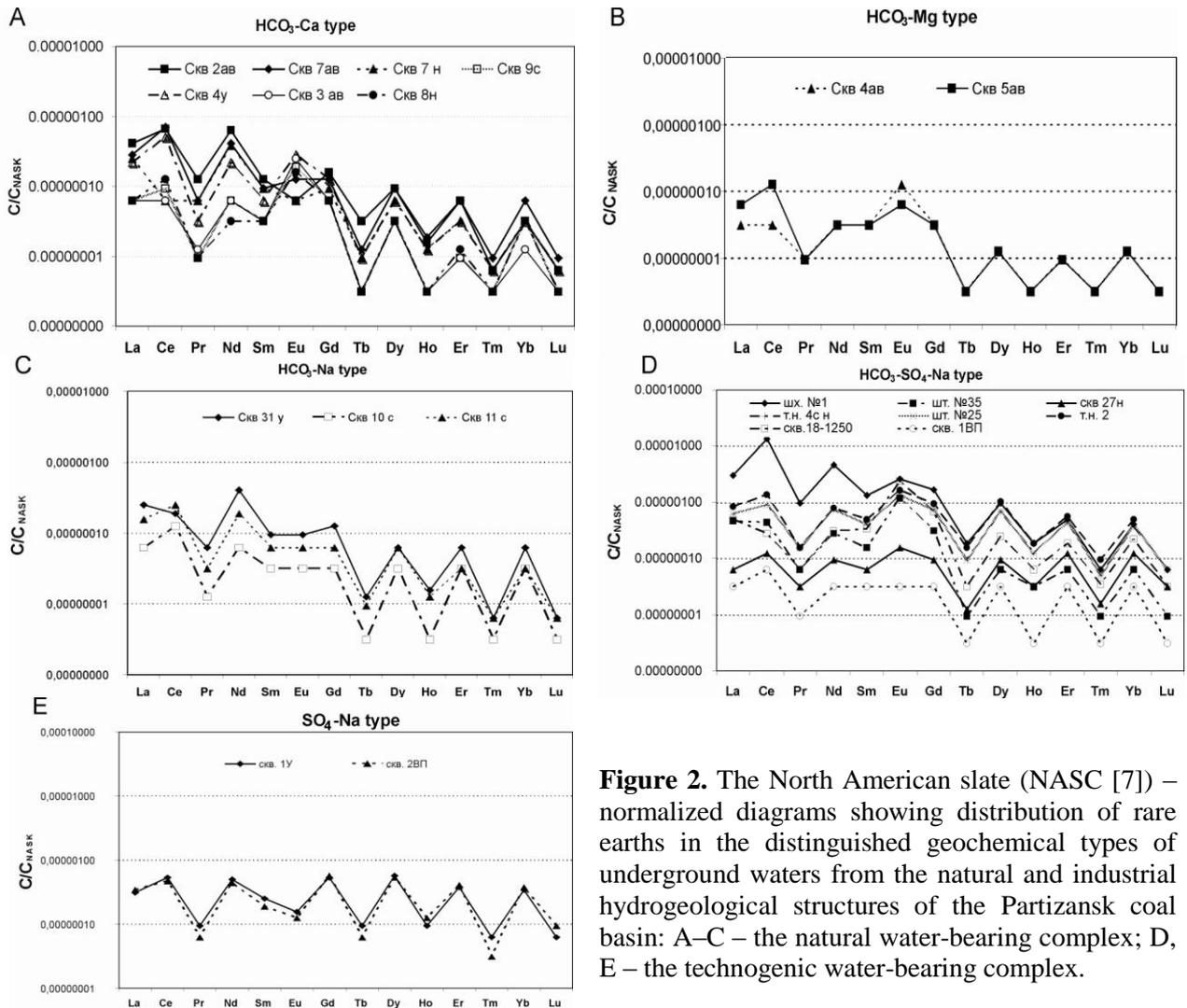
Almost all water types under consideration possess positive cerium anomaly, with Ce/Ce<sup>a</sup> values varying from 1.0 to 6.92. The exception is the HCO<sub>3</sub>-Ca water type from the water well 7H, where Ce/Ce<sup>a</sup> = 0.4 (Fig. 2). This anomaly is traced as gradually growing in the succession of water composition transformation that is testimony to the predominance of Ce<sup>3+</sup> in the waters.

The Europium anomaly is more changeable and differs according to a water type, keeping within the interval of 0.44–5.33. The ratios of measured - to - expected values in case of normal Eu/Eu<sup>a</sup> distribution indicate the enrichment in Eu relative to comparatively adjacent Sm and Gd in the natural waters of HCO<sub>3</sub>-Ca, HCO<sub>3</sub>-Mg and HCO<sub>3</sub>-Na types and the technogenic waters of HCO<sub>3</sub>-SO<sub>4</sub>-Na type. The exceptions are the waters from wells 2aB (0.44) and 7H (0.67). However, the SO<sub>4</sub>-Na waters and the HCO<sub>3</sub>-SO<sub>4</sub>-Na waters from well 1BII (0.35) demonstrate depletion in Eu relative to neighboring REE. Such depletion may be due to formation of complex compounds of these elements and their subsequent removal from the water in forms of neogenic mineral phases.

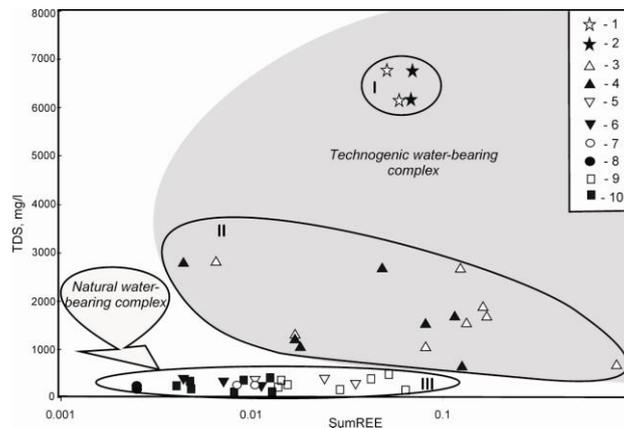
The N coefficient in La/Yb ratio is also different depending on water types, with gradual decreasing from 0.57 for the HCO<sub>3</sub>-Ca waters to 0.09 for the SO<sub>4</sub>-Na waters.

The analysis of patterns of REE distribution in coal ashes of the Partizansk basin and in the precipitations deposited at sites of the technogenic complex water outcropping shows similar picture of distribution. The curve of the chondrite-normalized contents [11] has the negative inclination that allows speaking about enrichment of rock with light lanthanoids (LREEs) relative to heavy ones (HREEs).

The sumREE in rock samples is in the range of 26–396 mg/kg. All the rock samples, including the substance from the sites of the groundwaters' outcropping on the surface, exhibit similar picture of REE distribution with the observed negative europium anomaly. The Eu/Eu<sup>a</sup> ratio (0.06–0.09) points to relative depletion in Eu in the considered rocks regarding to adjacent REE (Sm and Gd). The Ce anomaly values are similar in all the rocks samples varying from 0.93 to 0.95. The calculated ratios (La/Yb)<sub>N</sub> and (Pr/Yb)<sub>N</sub> range from 3.07 to 8.86 and from 2.02 to 5.75, respectively, almost no matter what is the type of rocks. This can be indicative of the coal source of REE for waters.



**Figure 2.** The North American slate (NASC [7]) – normalized diagrams showing distribution of rare earths in the distinguished geochemical types of underground waters from the natural and industrial hydrogeological structures of the Partizansk coal basin: A–C – the natural water-bearing complex; D, E – the technogenic water-bearing complex.



**Figure 3.** Plot of SumREE against TDS, mg/l, where 1, 3, 5, 7, 9 – LREE; 2, 4, 6, 8, 10 – HREE; 1–4 –technogenic water-bearing complex (1, 2 – SO<sub>4</sub>-Na; 3, 4 – HCO<sub>3</sub>-SO<sub>4</sub>-Na); 5–10 – natural water-bearing complex (5, 6 – HCO<sub>3</sub>-Na; 7, 8 – HCO<sub>3</sub>-Mg; 9, 10 – HCO<sub>3</sub>-Ca); I-III – fields with points.

To summarize, interaction processes and equilibrium-nonequilibrium state of the water–rock system are major factors that had influence on changes in water compositions and behavior of REE in the distinguished water types of natural and industrial structures of the abandoned mines of the Partizansk coal basin.

#### 4. Conclusion

The research into isotope-geochemical features and regularity in composition formation of underground waters in the abandoned coal mines of the Partizansk basin have brought to the following conclusions:

1. The flooding of mines causes formation of natural and industrial structures where waters underwent changes in composition according to the following succession:  $\text{HCO}_3\text{-Ca} \rightarrow \text{HCO}_3\text{-Mg} \rightarrow \text{HCO}_3\text{-Na} \rightarrow \text{HCO}_3\text{-SO}_4\text{-Na} \rightarrow \text{SO}_4\text{-Na}$ .
2. The variability of sulfur in the waters under study is not connected to a marine source, but is a result of oxidation of pyrite which is contained in coal.
3. Bacteria play a significant role in formation of rather high contents of sulfur that is evidenced by the water enrichment in  $^{34}\text{S}$ .
4. The analysis of the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data for the underground waters has shown that the waters are rather light in comparison with the sea waters and do not experience the influence of oceanic water.
5. The content of stable isotopes in the considered waters changes in the range inherent to the meteoric waters testifying that the underground waters have infiltration nature.
6. The studied water salt content is correlated with such parameters as  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . Variation value of these parameters can be used for assessment of a degree of water-rock interaction.
7. The natural and industrial structures are characterized by the zonality of geochemical conditions. At the depth, aerobic systems are changed to anaerobic ones in the predominantly reducing environment and with formation of biochemical natural gases ( $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{H}_2$ ).
8. The REE content is in dependence to mineralization and the distinguished water type. HREEs content gradually increases from type to type in the succession:  $\text{HCO}_3\text{-Ca} \rightarrow \text{HCO}_3\text{-Mg} \rightarrow \text{HCO}_3\text{-Na} \rightarrow \text{HCO}_3\text{-SO}_4\text{-Na} \rightarrow \text{SO}_4\text{-Na}$ . The assumption was made that at the  $\text{HCO}_3\text{-SO}_4\text{-Na} \rightarrow \text{SO}_4\text{-Na}$  transformation stage the REE form complex compounds and leave the water as neogenic mineral phases.
9. Coal ashes of the Partizansk basin and precipitates from places where the underground waters of industrial complex exit on the surface are enriched with light lanthanoids (LREEs) relative to heavy (HREEs) ones. The calculated ratios  $(\text{La}/\text{Yb})_{\text{N}}$  and  $(\text{Pr}/\text{Yb})_{\text{N}}$  for the considered rocks have approximate values that may be indicative of a coal source of REE in the waters.

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