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The radionuclide distribution onto different mineral phases of the rocks of the exocontact zone of Nizhnekansky granitoid massif☆

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Abstract The sorption experiments with the five rock samples drilled in the deep-well in the exocontact zone of Nizhnekansky granitoid massif (EZNGM) in the range of depth 166—476 m were carried out. The distribution of radium was studied. The radiograms of radionuclide sorption were obtained by digital autoradiography. Heterogeneous sorption of radium was demonstrated by digital radiography and phases with higher sorption ability were revealed. The technique for the treatment of radiograms with the help of ImageJ program for obtaining quantitative parameters of radionuclides distribution in the granite-gneiss rock samples was developed. Relative sorption efficiency of different mineral phases of the rock samples of Eniseysky area (EZNGM) toward radium is presented in the paper.

Introduction

The development of nuclear energy is impossible without solving problems associated with the disposal of radioactive waste. In our days there are no repositories for the final isolation of conditioned high level wastes (HLW). Nevertheless,

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all countries that use nuclear energy have recognized the necessity of arranging of safe radioactive waste repositories; research works in this direction are successfully carried out in Switzerland, France, Belgium, Finland, Canada, Sweden, and the United States. The most preferred and safe method to isolate conditioned HLW is disposal in the deep, weakly permeable geological formations that have sufficient retention toward radionuclides into the biosphere (Anderson et al., 2011; Revenko et. al., 2011). Different types of geological formations are suitable for safe disposal of HLW. For example, in Finland and Sweden, crystalline rocks (granites, gneisses) were chosen as the geological environments suitable for disposal of HLW, in France sedimentary (claystones) rocks were considered. Evaporite rocks (salts) and claystones are suggested as geological formations for underground isolation of HLW in Germany, but for the final decision it is necessary to carry out detailed experiments (STUK-B 138, 2011; Sailer, 2008; NDA, 2010).

At the moment, in Russia the HLW storage repository project is realized in the EZNGM in the ''Eniseysky'' area (Krasnoyarsk region). The repository depth will be about 400—500 m. One of the key tasks is to evaluate the evolution of the multi-barrier storage protection system, where the last barrier according to the IAEA concept are the host rocks, which are represented by different mineralogical compositions and are characterized by different parameters of the porous medium (IAEA, 2011). One of the problems of simulation of the radionuclides is the determination of sorption properties of minerals and rocks in relation to long-lived radionuclides. Earlier sorption of plutonium, neptunium, radium, cesium on plates of the samples of the EZNGM has already been studied and a qualitatively estimate of the distribution of radionuclides in mineral phases has been given (Vlasova et al., 2016).

Conditions of sorption experiments

To analyze the distribution of the sorbed radionuclide ^{226}Ra (II) five rock samples of the EZNGM drilled in the deep-well R12 were used from different depths: 166 m — layered biotite-sillimanite plagiogneiss; 417 m — layered sillimanite-biotite plagiogneiss, plagiogranite-gneiss with garnet and muscovite; 443 m — fine-grained gabbro-diabase with muscovite; 459 m — migmatized quartz-feldspar granite-gneiss with xenoliths of chloritized amphibolite; 476 m — banded-spotted garnet-biotite plagiogneiss, with granitized sections of quartz-feldspar-biotite composition. To carry out the sorption experiments, the drill samples of the EZNGM were cut into polished sections of 8 mm × 12 mm × 30 mm. The plates of the samples were polished on two long faces for the carrying radiography. Sorption experiments were carried out at room temperature in plastic pots using model water: model groundwater with hydrocarbonate-calcium mineralization 200 mg/L and water filtrate pre-equilibrated with bentonite in the ratio 1 g/L (bentonite from the ''Khakasskoe'' deposit, Russia). The concentration of radionuclides was 10^{-9} mol/L, the pH of the system was 7—8. In order to avoid co-precipitation of radionuclides on the surface of the rock samples, the polished plates of the samples were installed vertically. Microdistribution of radionuclides on the surface of polished samples was investigated using the digital autoradiography method after the sorption equilibrium was achieved and rinsing and the drying of samples were done. The determination of the mineral phases in the samples was carried out using a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX).

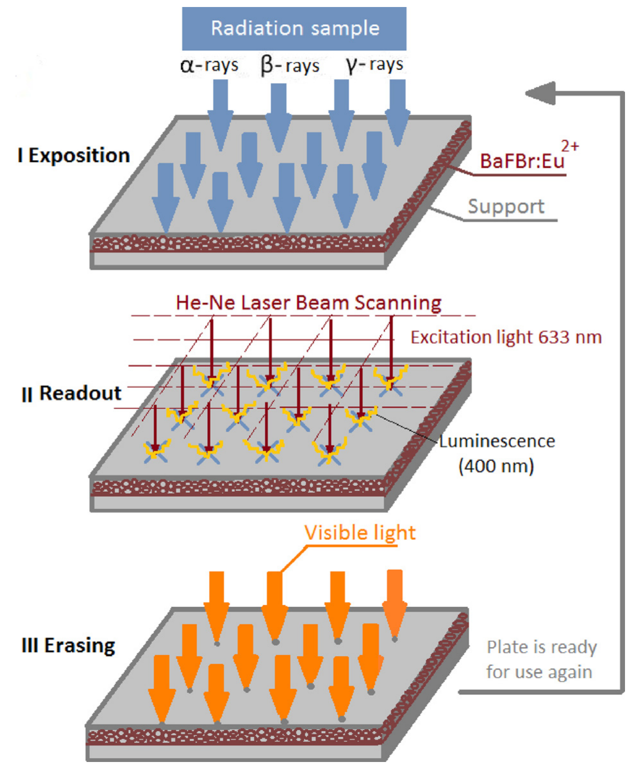

Figure 1 The basic digital autoradiography (DAR) cycle.

Digital autoradiography method

Distribution of sorbed radionuclides onto polished rock surfaces was investigated by digital autoradiography (DAR) with Cyclone Storage System (Perkin Elmer).

DAR technique is based on the storage-phosphor screen (''Imaging Plate'') (Takahashi, 2002). DAR is a powerful method to determine quantitatively the ''small-scale'' distribution of a radiotracer in different solid samples and tissue sections. The method has a high specification in terms of sensitivity and linear dynamic range of five orders of magnitude for signal/exposure (Zhang et al., 2008).

This technique uses a storage photostimulable detector Imaging Plate (IP) which consists of a plastic support and a detective layer. The detective layer consists of a BaFBr:Eu $^{2+}$photostimulable crystals. A typical IP can store a latent image some time, not more than 24 h. The basic DAR imaging cycle is not conversion process and it has three steps: (1) exposure, (2) readout, and (3) erasure (Fig. 1).

The first step is exposing of radiation source (X-Ray, γ, β or α-emitting) to IP, which contacts closely with radiation source. During this process the energy of radiation is deposited in the phosphor crystals, and Eu^{2+} cation is oxidized to Eu^{3+}. Photoelectrons exited into the conduction band of the crystal and trapped by the ''F centers''. Such

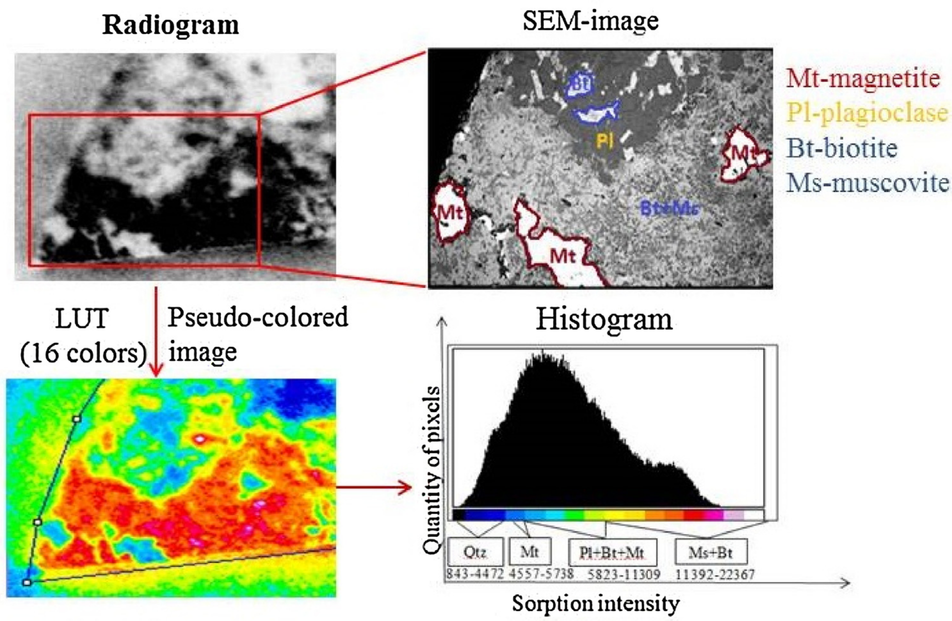

Figure 2 Steps of the technique of relative sorption efficiency definition. Combined analyses of radiogram of Ra sorption on the 166 sample and the corresponding SEM image of the same fragment of 166 sample.

Table 1 Sorption of radium on the different minerals of EZNGM rock samples.

Mineral phases	Number of sample	Portion of radionuclide sorption	Portion of area	Relative sorption efficiency
Quartz	166	4	11	0.36
Quartz	417	17	37	0.46
Quartz	476	1	2	0.5
Magnetite	166	8	12	0.67
Plagioclase	476	65	73	0.89
Hornblende	443	79	85	0.93
Plagioclase + Biotite + Magnetite	166	50	52	0.96
Chlorite + Magnetite + Quartz	459	28	28	1
Plagioclase + Biotite	417	89	83	1.07
Zeolite in hornblende	443	19	14	1.36
Biotite + Garnet	476	34	25	1.36
Muscovite + Biotite	166	38	25	1.52
Muscovite + Plagioclase	459	55	35	1.57
Muscovite	417	2	1	2
Zeolite with clays	443	2	1	2

electrons are in metastable states and collectively constitute the acquired image named ''latent image''.

The readout of ''latent image'' by an image reader (scanner) is the second step. Image reader scans the IP by red laser beam (excitation light 633 nm). The photostimulated light (400 nm) from the Imaging Plate is collected by a photostimulated tube and is then converted to a digital image. The DAR image intensity in each pixel ($42\,\mu m \times 42\,\mu m$) is measured in digital luminescence units (DLU) value, which is proportional to the stored radioactivity.

Finally the third step of the basic DAR imaging cycle is the residual signal erasure. IP is erased by using of a high-intensity white light source that flushes the traps without reintroducing electrons from the ground energy level. So the IP can be reused till thousand times (Lanca and Silva, 2013).

Development of the technique of relative sorption efficiency definition

Using the method of digital autoradiography with storage Imaging Plates, radiograms of EZNGM samples were obtained in the form of black and white images. For the treatment of radiograms, a technique was developed as follows (Fig. 2).

This technique is based on the application of ImageJ, which allows converting a black and white radiogram image into a pseudo-colored image, which consists of 16 colors.

Conversion takes place using Lookup table (LUT). This procedure simplified the analysis of radiograms and made it possible to compare the mineral phases of the samples with the intensities of photostimulated luminescence (FSL) at various areas of the rock sample. Further the resulting pseudo-colored images and radiograms were compared with the SEM image to distinguish the mineral phases with different luminescence intensities.

So the intensity of FSL in each pixel of the radiogram is directly proportional to the activity of the radionuclide under study, the intensity of distribution of the FSL at the radiogram made it possible to determine the portion of the sorbed radionuclide in different parts of the samples. Portion of sorbed radionuclide as well as portion of area with certain intensity was found with the help of histograms. The results are shown in Table 1.

The relative sorption efficiency was determined, based on the following relationship:

$$\text{Relative sorption efficiency} = \frac{\text{Portion of radionuclide sorption on the mineral phase}}{\text{Portion of area which is occupied by mineral phase}} \quad (1)$$

Conclusion

Study of sorption behavior of radium toward rock samples drilled in the deep-well R12 in the exocontact zone of Nizhnekansky granitoid massif was carried out with the help of autoradiography method. The technique of quantitative analysis of relative sorption efficiency was developed with applying of SEM-EDX and radiograms.

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