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INFLUENCE OF IONIZING RADIATION ON THE ELEMENTAL CONTENT AND STRUCTURE OF NATURAL MINERALS

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The granites of the Ukrainian crystalline shield and the Donetsk-Dnieper hollow of the Pre-Cambrian basement, discovered at a depth of 840…900 to 3420 m were irradiated on a KUT-1 linear electron accelerator with the following parameters: electron energy E ≈ 7 MeV, average beam current I = 500 μA, temperature of the irradiated samples T~ 40°C, absorbed dose $D_{abs} = 10^7$ Gy. Gamma-activation analysis was used to determine the content of elements in the samples. The samples were irradiated by bremsstrahlung from the linear accelerator electron NSC KIPT with energy 23 MeV and current 500 μA. The structure and phase composition of samples were investigation by infrared spectroscopy in the frequency 400…4000 cm^{-1}. Crystal optical studies were carried out on polarizing microscope using immersion liquides. It is shown that high-energy electron irradiation of granites causes radiation-stimulated transformations in the structure and phase homogeneity of mineral. The most pronounced changes in biotites after high-energy electron irradiation of granites are manifested in a change in the color of biotite, apparently due to oxide phases Fe_2O_3 and Fe_3O_4. Considering the state of granites under radiation conditions it can be used for the immobilization and disposal of radioactive waste.

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INTRODUCTION

In countries where nuclear power is being developed, the geological disposal of radioactive waste (RW) using natural minerals is considered as one of the most promising ways to reliably isolate these sources from the human environment [1–4]. Most countries, when developing systems for the geological isolation of waste, adhere to a multi-barrier system of protection for RW disposal. It is the barriers that guarantee isolation from the environment for the time required for the decay of the most dangerous radionuclides [5–14].

As a rule, small doses of radiation act on natural minerals in the environment for a long geological time (from 10 to 100 thousand years). Structural defects that form in minerals are similar to radiation defects: a displacement of atoms in the crystal lattice and the formation of point defects. In this case, atoms can move to new sites of the crystal lattice due to the exchange with lattice atoms. As a result, such processes can lead to deformation, expansion of the lattice of minerals and, as a result, to disruption of their structure [15–19].

Basically, rock-forming minerals belong to the class of silicates. A large number of publications on the effect of various types of irradiation on natural minerals are available. But there are very few works on the effect of irradiation on promising minerals that are necessary for the disposal of radioactive waste in Ukraine. There are practically no data on changes in the elemental content, structure, and phase composition of natural minerals under the action of ionizing radiation. To predict the behavior of natural minerals (granites, tuffs, etc.) under the conditions of radioactive waste disposal, data on the study of radiation-stimulated defect formation in some inorganic materials were used. When irradiated at accelerators, in nuclear reactors, with isotopes of sources of quanta, for example, ^{60}Co, data were obtained that made it possible to use some minerals that have optimal resistance to radiation exposure. The beginning of qualitative changes in natural minerals under the influence of irradiation, as a rule, should be formed at the early stages of irradiation. Therefore, it is important to know the dynamics of these changes in order to assess the consequences of radiation exposure [20].

To elucidate the nature of changes in the elemental content, structure and phase state of complex radiation transformations in mineral phases, it makes sense to use nuclear physics methods: γ-activation analysis, IR-spectroscopy method, combined with crystal optical analysis.

As a rule, any rearrangement of the basic structure is accompanied by amorphization of the mineral. At the initial stages, this occurs in local areas [21], and then, with increasing dose, a complete transition to the amorphous state is observed throughout the entire volume of the irradiated object.

The purpose of this work is to establish the changes in the elemental content, structure and phase composition of granites and its constituent fraction - biotite under the influence of high-energy electrons.

1. EXPERIMENTAL TECHNIQUE

The samples of study were the granites of the Ukrainian crystalline shield and the Donetsk-Dnieper hollow of the Pre-Cambrian basement, discovered at a depth of 840…900 to 3420 m.

The samples were irradiated on linear electron accelerator with the following parameters: electron energy E ≈ 7 MeV, average beam current I = 500 μA, temperature of the irradiated samples T ~ 40°C, absorbed dose $D_{abs} = 10^7$ Gy at electron fluence $\Phi = 3 \cdot 10^{16} \ldots 3 \cdot 10^{17}$ cm^{-2}. The indicated dose range was chosen because it is known that the maximum dose of external radiation from RAW, which can be collected by the geological enviroment for 1000 years, is $\sim 3.5 \cdot 10^7$ Gy. Irradiation of the samples was carried out in sealed copper containers (copper foil thickness 0.5 mm) with water cooling.

Gamma-activation analysis was used to determine the element content in the samples. The samples were irradiated by bremsstrahlung from the linear accelerator electron NSC KIPT with energy 23 MeV and current

500 μA. Activation of samples was carried out on air, the temperature of samples in the course of activation did not exceed 40°C. Gamma activation analyses is no destroying for native samples.

The determination of elements content in samples performed by gamma spectrometer method in Ge(Li)-detector with the volume of 50 cm^3 and resolution of 3.2 at 1332 keV line. To reduce the influence of background, the detector is equipped with a three-layer Pb-Cu-Al protection. The errors of measurements were from 7 to 25% .The limit of detection elements for photo activation analysis was $10^{-4}…10^{-7}$ wt.%.

The structure and phase composition of samples were investigation by infrared (IR) spectroscopy (IRS-29, LOMO) in the frequency 400…4000 cm^{-1} with a measurement error of ± 2…7 cm^{-1}. For IR spectroscopy anlysis the samples were prepared in the form of transparently compressed tablets from a mixture of KBr and the test substance in an amount of 1% (100 mg sample). The pressing pressure was 9200 kg/cm^2. To eliminate matrix absorptio bands, a tablet of pure potassium bromide preliminarily dried at 180°C for 10 hours was placed in the comparison channel of the device. The powders were ground in agate mortars to a size of ~ 1…10 μm and mixed in a special closed box; pressing was carried out immediately before the spectra were recorded. Graduation in the range of 4000...700 cm^{-1} was carried out according to the spectrum of polystyrene with known frequencies of absorption maxima, and in the range of 700…400 cm^{-1} according to the bands of atmospheric water and CO_2. The correction averaged 15…5 cm^{-1}.

Crystal optical studies were carried out on polarizing microscope POLAM-L211 using immersion liquides.

2. RESULTS

Fig. 1 shows the spectrum of granite.

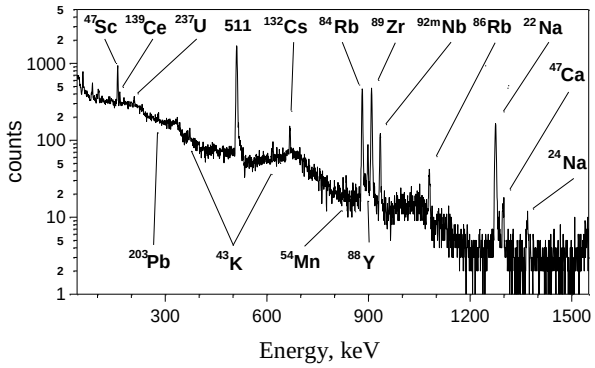

Fig. 1. Gamma-spectrum of granite

The sample of granite includes such elements as Si, Ti, Al, Fe, Ca, Mg, K, Na, Rb, Mn, Pb, Nb, and others.

The naturale granite was a crystalline rock with a uniform distribution of small scales of biotite (1…1.2 mm) against the background of quartz feldspar.

Fig. 2 shows micrographs (in reflected light) of the granite surface before and after electron irradiation.

The photographs show that as a result of irradiation to a dose of 10^7 Gy, no significant damage occurred in the structure of granite. The appearance of the surface has not practically changed, however, the appearance of a system of small and medium cracks (no more than 3…7 μm thick) at the grain boundaries is noted.

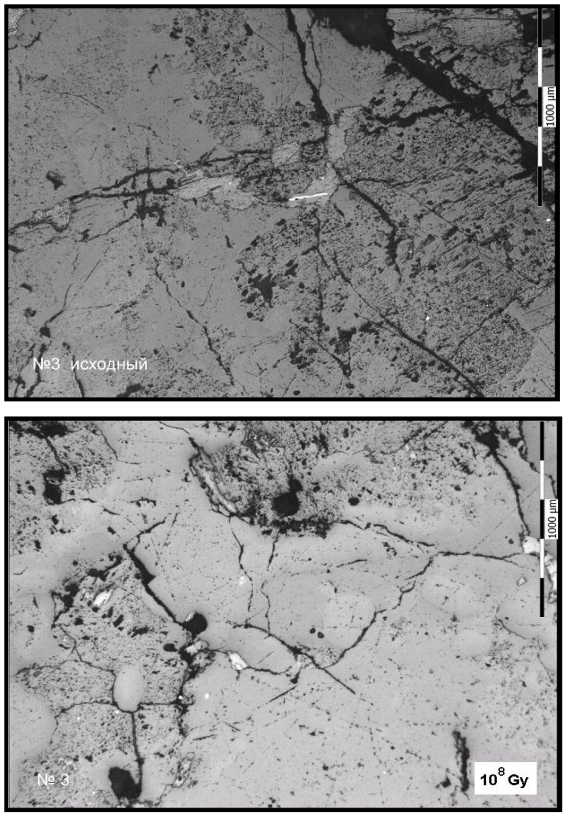

Fig. 2. Granite surface microstructure in reflected light before and after electron irradiation ($D_{abs}=10^7$ Gy)

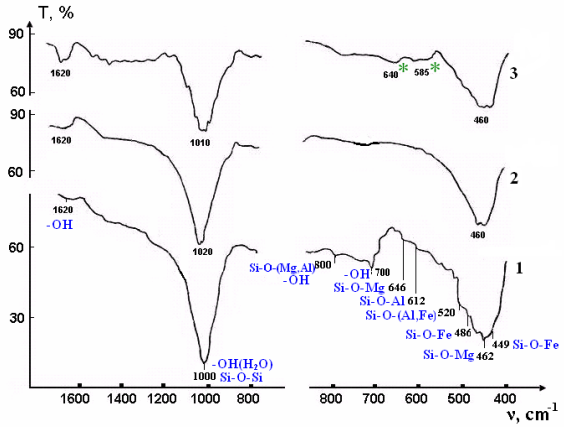

Fig. 3. IR-spectra of granite: 1 – initial; 2 – after irradiation up to D = 107 Gy; 3 – new formations of Fe oxides

IR spectra of granite in the initial state and after electron irradiation are presented. The main absorption bands of strong intensity in the IR spectrum of the original granite appear at 460 and 1010 cm^{-1}. These regions are characterized by vibrations Si-O, Si-O-Si, Si-O-Mg(Fe). The Si-O bond is the strongest in the structure of layered silicates. In the region of 600…800 cm^{-1}, more moderate and weaker absorption bands are found, which are characteristic of Si-O-Mg, Si-O-Al, Al-OH vibrations [22]. In addition, the spectrum contains a number of absorption bands in the

region of 1620, 1000, 800, 700 cm^{-1}, which are characteristic of vibrations of the OH-group in biotite.

The IR spectrum clearly shows maxima in the region of 585 and 640 cm^{-1}, which are caused by an increase in the percentage of Fe^{3+} ions due to radiation oxidation of iron ions (Fig. 3, curve 3). In addition, the maximum of 1620 cm^{-1} noticeably increases, which is associated with an increase in OH-groups and a gradual transition to the hydrobiotite structure.

Both the initial and irradiated granite samples were separated under a binocular microscope into monomineral fractions in order to establish the mechanisms of radiation changes, for example, in such fractions as biotite.

Structural changes in granite that occur after irradiation were studied using biotite ($K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$), a mineral that is a part of granites. This mineral has the ability to form parallel-oriented interlayers in granitoid rock. When they break, cracks can form. In addition, since structural or uncombined water is present in the composition of the studied minerals, it can be assumed that they are the most sensitive to radiation exposure [23, 24].

The investigated biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$), the grain size was 2…3 mm. According to γ-activation analysis, the elemental content of biotites includes the following elements: Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, F, etc.

The most pronounced changes after high-energy electron irradiation of biotite are manifested in a change in its color from completely transparent to brown. Apparently, these changes occur due to the Fe_2O_3 oxide phases.

On Fig. 4 shows micrographs of an immersion preparation of biotite.

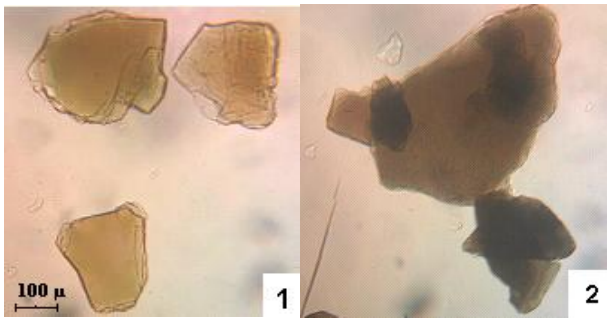

Fig. 4. Microphotographs of an immersion preparation of biotite, in transmitted light, view without an analyzer: 1 – initial biotite; 2 – after irradiation to D=10^7 Gy

It has been established that after electron irradiation up to doses of 10^7 Gy, the refractive indices of ordinary biotite ($N_g = N_m = 1.630$) increase sequentially to 1.650 due to the oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ ions during the transition of hematite to magnetite. The processes of iron oxidation are accompanied by a change in the color of biotite with the manifestation of intense brown tones.

The identification of absorption bands in the spectra of biotite is given in Table.

A comparison of the IR spectra of the original and irradiated granite showed that, after irradiation, it retains its crystal structure with its partial disordering. When irradiated to a dose of 10^7 Gy, a number of small peaks disappear in the spectral range of 600...800 cm^{-1}, characteristic of Si-O-Me bonds (see Fig. 3, curve 2) due to the replacement of Mg by Fe^{+2}, Mn^{+2}, Al^{+3}, Fe^{+3} as a result of heterovalent isomorphism.

Identification of IR absorption bands in spectra biotite $K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$

Assigment of band, ν, cm^{-1}	Chemical connection
3660	(Mg,Fe^{2+})–O–H
3590	$(Fe^{2+}$, Al)–O−H
3548	(Fe^{2+},Fe^{3+})–O–H
1000	Si–O–Si, –OH(H_2O)
1049…1075	Si–O, Si–O–Si
980…1055	(Si–O)–$(Al, Fe)_{VI}$, $Si–Al_{IV}$
830…1000	$Si–Al_{IV}$, Al–O–H
948…955	O–Al–(OH), Si–O–Al, Al–OH
915	Al–O–H
980…940	Si–O–Mg
840…820	Si–O–Si
600…800	$(Al_{IV}–O)–Al_{VI}$
750…752	Si–O–Si, Si–O–Al
540	δ Si–O (Al–O), $Si–O–Al^{VI}$
482…485	Si–O
400…500	δ(O–Si–O), Si–O–Si
450…500	O-Si(Al)–O, Si–O–Mg(Fe)
420	Si–O

Thus, based on the analysis of the obtained experimental data on high-energy electron irradiation of granite, the elemental content was established, as well as the characteric of changes in the structure and phase composition of granite and the silicate mineral – biotite which is of component of granite rock.

CONCLUSIONS

It is shown that high-energy electron irradiation of a natural mineral (granite) causes radiation-stimulated transformations in the structure and phase homogeneity of mineral.

The investigated mineral, which has an ordered structure, with a minimum number of defects and impurities, as a result of irradiation to a dose of 10^7 Gy, retains its crystalline structure.

The most pronounced changes in biotite after high-energy electron irradiation of granite are manifested in a change in the color of biotite, apparently due to oxide phases Fe_2O_3 and Fe_3O_4. The processes of iron oxidation are accompanied by a change in the color of biotite with the manifestation of intense brown tones.

The results obtained can serve as recommendations for modeling the behavior of natural minerals under radiation conditions for the immobilization and disposal of radioactive waste.

REFERENCES

1. Concepts for the Conditioning of Spent Nuclear Fuel for Final Waste Disposal // *IAEA Technical Reports.* Vienna. 1992, ser. N 345, 123 p.
2. S. Masuda, H. Umeki, M. Naito. Reliability of High Specific Activity Waste Disposal in Deep

Underground Storage Facilities in Japan // *Nuclear Engineering Abroad.* 2001, N 2, p. 21-30.
3. *IAEA Safety Series: Safety assessment for Underground Disposal of Radioactive Waste.* 1981, N 56, 16 p.
4. O.I. Kedrovskiy, C.G. Chuhin RW: principles and criteria for safe disposal // *Energy*. 1993, N 2, p. 2-5.
5. A.G. Tsukynov. Long-term storage and disposal of radioactive waste // *Nuclear Engineering Abroad*. 2002, N 10, p. 16-19.
6. Concepts for the Conditioning of Spent Nuclear Fuel for Final Waste Disposal // *IAEA Technical Reports.* Vienna, 1992, ser. N 345, 123 p.
7. M. Ginniff. Disposal of radioactive waste // *Nuclear Engineering Abroad*. 1984, N 7, p. 42-45.
8. G.M. Deconik. E.V. Sabotovich, V.M. Shestopalov, et al. Investigation of the possibility of burying radioactive waste in deep geological formations // *"Cassiopeia" project Bulletin of the ecological state of the state of alienation and the zone of unconditional (compulsory) resettlement*. 1999, N 13, p. 64-66.
9. S. Masuda. H. Umeki, M. Naito. Reliability of disposal of high specific activity waste in deep underground storage facilities in Japan // *Nuclear Technology Abroad.* 2001, N 2, p. 21-30.
10. Safety in handling radioactive // *Nuclear Engineering Abroad.* 2002, N 10, p. 3-6.
11. O.I. Kedrovskiy, I.U. Shushuts, T.A. Gupalo. Justification of the localization conditions of high-level waste and spent nuclear fuel in geological formations // *Nuclear Technology Abroad.* 1991, v. 70, iss. 5, p. 294-297.
12. I.U. Shushuts. *Complex forecasting of safety assessments during the disposal of radioactive waste:* Study guide. Publishing House of the Moscow State Mining University. 2006, 263 p.
13. N.P. Laverov, A.V. Chancellor, A.K Lysytsyn, et al. Basic tasks of radiogeoecology in connection with disposal of radioactive waste // *Atomic energy*. 1991, v. 71, iss. 6, p. 523-534.
14. *Radioactive waste disposal and geology. Top. Earth Sci* / Ed. Krauskopf K.B.L.: N.Y.: Chapman and Hall. 1988, XII, v. 1.
15. M.B Ahmanova, L.L. Leonova. Investigation of metamict decomposition of silicates using IR spectroscopy // *Proceedings of the Mineralogical Museum named after A.E. Fersman*. 1963, iss. 14, p. 3-31.
16. Yu.M. Polezhaev. Isotherms and polytherms of recrystallization of metamict zircons // *Geochemistry*. 1974, N 11, p. 1648-1652.
17. Y.V. Pertov. Natural nuclear reactor Oklo // *UFN*. 1977, v. 123, iss. 3, p. 473-486.
18. I.M. Lipova. *Nature of metamict zircons*. M.: "Atomizdat", 1972, 160 p.
19. I.M. Lipova, G.A. Kuznetsova, E.S. Makarov. Study of the metamict state of zircons and cirtholites // *Geochemistry.* 1965, N 6, p. 681-682.
20. A.A. Botaki, A.A. Vorob'ev, V.L. Ul'yanov. *Radiation physics of ionic crystals.* M.: "Atomizdat", 1980, 208 p.
21. G.S. Gdanov, V.G. Zubov, E.V. Kolontsova, et al. Radiation effects in d-quartz // *Crystallography*. 1963, v. 8, p. 207-212.
22. A.I. Boldirev. *Infrared spectra of minerals.* Publishing house "Nedra", Moscow, 1976, p. 198.
23. L. Pauling The structure of micas and related minerals // *Proc. Nat. Acad. Sci. USA*. 1930, v. 16, N 123, p. 123-129.
24. W.L. Bragg, C. West. The structure of certain silicates // *Proc. Roy. Soc.* 1937, v. 114A, p. 371-377.

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ВПЛИВ ІОНІЗУЮЧОГО ВИПРОМІНЮВАННЯ НА ЕЛЕМЕНТНИЙ СКЛАД І СТРУКТУРУ ПРИРОДНИХ МІНЕРАЛІВ

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Граніти Українського кристалічного щита та Донецько-Дніпровської впадини докембрійського фундаменту, виявлені на глибині від 840…900 до 3420 м, були опромінені на лінійному прискорювачі електронів КУТ-1 з такими параметрами: енергія електронів E ≈ 7 МеВ, струмом 500 мкА. Температура опромінюваних зразків T~40°C, поглинена доза $D_{пог} = 10^7$ Гр. Для визначення вмісту елементів у пробах використовували гамма-активаційний аналіз. Зразки опромінювали гальмівним випромінюванням лінійного прискорювача електронів ННЦ ХФТІ з енергією 23 МеВ та струмом 500 мкА. Структуру та фазовий склад зразків досліджували методом інфрачервоної спектроскопії на частоті 400…4000 $см^{-1}$. Кристалооптичні дослідження проводилися на поляризаційному мікроскопі з використанням імерсійних рідин. Показано, що опромінення граніту високоенергетичними електронами викликає радіаційно-стимульовані перетворення у структурі та фазової однорідності мінералів. Найбільш виражені зміни біотиту після опромінення граніту високоенергетичними електронами проявляються у зміні забарвлення біотиту, мабуть, за рахунок оксидних фаз Fe_2O_3 та Fe_3O_4. Враховуючи стан гранітів у радіаційних умовах, його можна використовувати для іммобілізації та захоронення радіоактивних відходів.