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CONTENT OF ELEMENTS AND STRUCTURAL CHANGES IN NATURAL PYROPHYLLITE BY THE INFLUENCE OF GAMMA IRRADIATION

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Changes in the structure of natural pyrophyllite by long-term irradiation of gamma rays with a low dose rate have been studied. A comparative analysis of the sequence and nature of structural changes in pyrophyllite by long-term irradiation of gamma rays and accelerated irradiation with electrons up to a dose of $3.6 \cdot 10^7$ Gy was carried out. It has been established that irradiation by gamma quanta for 12 years, in contrast to an accelerated experiment on irradiation by high-energy electrons to the same dose within 48 h, does not lead to dehydroxylation or hydration of pyrophyllite and the impurity phases and elements contained in it, due to which the structure of pyrophyllite remains close to the original state.

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INTRODUCTION

The natural pyrophyllite studied in this article has some valuable technological properties, which include a high melting point (1700 ºC), chemical resistance, low thermal expansion, and good dielectric properties [1–3].

Due to this, pyrophyllite is used in nuclear energy as a refractory material, as well as a component of insulating electrical ceramics and cement for various purposes. In addition, natural minerals and rocks of the Ukrainian crystalline shield, on the territory of which one of the largest pyrophyllite deposits is located, are considered promising matrices and protective barriers or components of building materials for protective structures for the immobilization and disposal of radioactive waste. This is related to the relevance of research into the influence of radiation on the structure and physicochemical properties of minerals.

Our previous publications presented the results of studies of the phase composition of natural pink pyrophyllite shale of the Ovruch deposit in the Northwestern region of the Ukrainian Crystal Shield and structural and phase transformations by irradiated with accelerated high-energy electrons and gamma-quanta up to a maximum absorbed dose of 10^7 Gy. In these experiments, due to the fairly high dose rate, the duration of irradiation ranged from 48 h (in the case of electron irradiation) to seven years (in the case of gamma-quanta irradiation) [4].

The purpose of this work was to study pyrophyllites to long-term irradiation with converted gamma-quanta up to a maximum dose of $3.6 \cdot 10^7$ Gy for 12 years under conditions as close as possible to the natural conditions of irradiation of rock in the case when the radioactive waste is in it, as well as the analyze of the influence of irradiation dose on the character and sequence of radiation-stimulated structural transformations in natural minerals using the example of a silicate mineral with a complex layered structure.

1. MATERIALS AND RESEARCH METHODS

The object of study in this work was natural pink pyrophyllite from the Ovruch deposit in the northwestern region of the Ukrainian crystalline shield (UKSh).

Irradiation with gamma rays was carried out at the linear accelerator "KUT-1" NSC KIPT. The bremsstrahlung gamma radiation for irradiation, which was formed during the interaction of an electron beam with a thick aluminum absorber was used. The boundary electron energy was 12 MeV, the beam current was 450 μA, the pulse frequency was 200 Hz, the pulse duration was 3.8 μs, the photon energy was 4 MeV, and the absorbed dose $D = 10^6 \ldots 3.6 \cdot 10^7$ Gy.

The diffractometric study was carried out on a DRON-UM1 gamma-ray diffractometer in copper Cu-Kα radiation using a nickel selectively absorbing β-filter. The diffracted radiation was recorded by a scintillation detector. Pyrophyllite has perfect cleavage along the {001} crystallographic planes, so the samples are characterized by the presence of a strong {001} texture. For texturing, the experimental samples were ground into powder to obtain more peaks in the diffraction patterns. Qualitative phase analysis was performed using the COD crystallographic compound database; quantitative phase analysis was carried out using the Rietveld method (MAUD software).

IR absorption spectra were recorded on an IRS-29 spectrophotometer in the frequency range 400...4000 cm^{-1} with a measurement error of ±5…7 cm^{-1}. The samples were prepared in the form of transparent compressed tablets from a mixture of KBr and the test substance in an amount of 1%.

Crystal optical studies were carried out on a polarizing microscope POLAM-211L using immersion liquids.

The samples of natural pink pyrophyllite and standards in the aluminum container were irradiated by the bremsstrahlung on the electron accelerators with the energy 23 MeV and current 500 A [10]. Activation of

samples was carried out on air, the temperature of samples in the course of the activation did not exceed 40 °C. The determination of element content in samples was performed by a Ge(Li)-detector with a volume of 50 cm^3 and resolution of 3.2 at the 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 analyses was 10^{-4} wt.%.

2. RESULTS AND DISCUSSION

The initial pyrophyllite is a dense rock of light pink color. This color of the mineral is caused by the presence of an impurity of iron hydroxides.

Microscopic studies of immersion preparations of the initial pyrophyllite showed that the sample consists of fine-crystalline aggregates 10…15 μm in size, among which needle-shaped crystals measuring 5 μm (Fig. 1). The aggregates have a yellowish-grayish color. The measured optical constants correspond to pyrophyllite: Np = 1.551 ± 0.003; Ng = 1.605 ± 0.003; Nm = = 1.588 ± 0.003; Δ = 0.050.

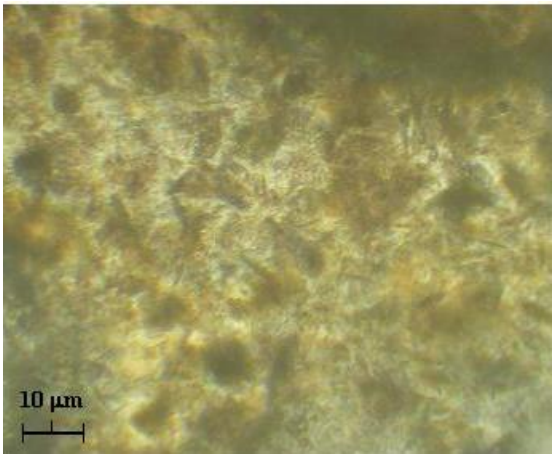


Fig. 1. Microphotograph of the initial pyrophyllite in an immersion preparation. Without analyzer. Fine-crystalline aggregate massa

Three phases were revealed in the sample of pyrophyllite at the initial state (Fig. 2, Table 1): pyrophyllite $Al_2Si_4O_{10}(OH)_2$, dykite $Al_2Si_2O_5(OH)_4$ and a trace (insignificant amount) of quartz α-SiO_2. The basis of the composition is profile-1Tc (triclinic modification of profile [5] with a mass fraction of 67.1 wt.%. The lattice parameters of pyrofilite-1Tc are: a = 5.164 Å; b = 8.967 Å; c = 9.359 Å; α = 91.09°; β = 100.39°; γ = 89.82°; volume of the elementary component V = 426.19 Å. Literature data for pyrophilite-1Tc: a = 5.160 Å; b = 8.966 Å; c = 9.347 Å; α = 91.18°; β = 100.46°; γ = 89.64°. The mass fraction of dickite (monoclinic polymorph modification of kaolin) in the sample is 31.9 wt.%, lattice parameters: a = 5.149 Å; b = 8.973 Å; c = 14.737 Å; β = 103.48°, unit cell volume V = 662.12 Å. The quartz with a mass fraction of 1.0 wt.% and lattice parameters: a = 4.923 Å; c = 5.405 Å also identified in the sample.

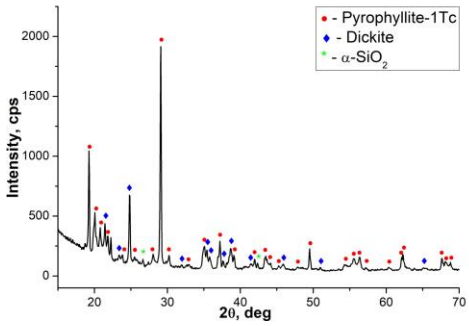


Fig. 2. Diffraction pattern of pyrophyllite in the initial state

Table 1

Phase composition of experimental samples of pyrophylite

Sample	Radiation dose, Gy	Phase	Content,wt.%	Lattice parameters, Å
1	0	Pyrophyllite	67.1	a = 5.164; b = 8.967; c = 9.359; α = 91.09°; β = 100.39°; γ = 89.82°
		Dickite	31.9	a = 5.149; b = 8.973; c = 14.737; β = 103.48°
		Quartz	1.0	a = 4.923; c = 5.405
2	$1 \cdot 10^6$	Pyrophyllite	60.9	a = 5.163; b = 8.969; c = 9.361; α = 91.10°; β = 100.35°; γ = 89.82°
		Dickite	38.2	a = 5.149; b = 8.973; c = 14.737; β = 103.48°
		Quartz	0.9	a = 4.924; c = 5.405
3	$1 \cdot 10^7$	Pyrophyllite	62.0	a = 5.163; b = 8.968; c = 9.360; α = 91.10°; β = 100.40°; γ = 89.82°
		Dickite	36.7	a = 5.150; b = 8.973; c = 14.739; β = 103.48°
		Quartz	1.3	a = 4.924; c = 5.405
4	$3{,}6 \cdot 10^7$	Pyrophyllite	64.4	a = 5.163; b = 8.970; c = 9.360; α = 91.09°; β = 100.34°; γ = 89.81°
		Dickite	34.4	a = 5.151; b = 8.970; c = 14.741; β = 103.49°
		Quartz	1.2	a = 4.923; c = 5.405

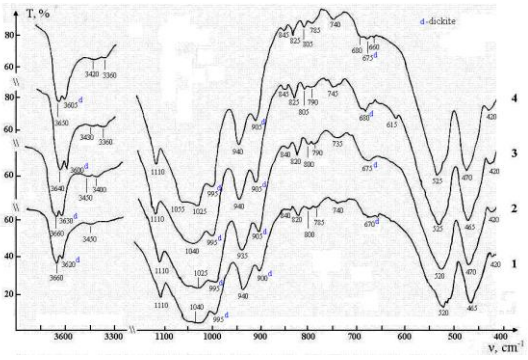


Fig. 3. IR absorption spectra of pyrophyllite before and after irradiation with gamma-quanta: 1 – initial pyrophyllite; 2 – D = 10^6 Gy; 3 – D = 10^7 Gy; 4 – D = 3.6 10^7 Gy

Table 2

Identification of IR absorption bands in the spectra of pink pyrophyllite

Spectral region, ν, cm^{-1}	Link assignment [6, 7]	
3660	stretching vibrations of hydroxyl groups O-H in the structure of pyrophyllite	O-H
3620	stretching vibrations of hydroxyl groups O-H in the dickite structure	
3450	molecular water H_2O	H–O–H
1110	ν_{as}	Si–O
1040	Si–O	Si–O–Si, Si–O
1000,,,900	(Si–O) – $(Al, Fe)_{VI}$	Si–Al_{IV}, Al–O–H
940, 900	stretching vibrations hydroxyls in the presence of Al ion	O–Al–(OH), Si–O–Al, Al–OH
840,,,780	E_2 ν_5	Si–O–Si, (Al_{IV} -O)–Al_{VI}
740	–	Si–O–Si, Si–O–Al
400,,,500	–	Si–O, Si–O–Si, Si–O–Mg
420	–	Si–O

The IR spectrum of the initial pyrophyllite (Fig. 3, curve 1) contains absorption bands characterized by a complex structure, and consisting of several components. The identification of pyrophyllite absorption bands is given in Table 2. Several bands in the spectrum correspond to vibrations in the structure of the dickite impurity phase ($Al_2Si_2O_5(OH)_4$): 670, 900, 995, and 3620 cm^{-1}, and a doublet band in the region of 790…800 cm^{-1} confirms the presence of a small amount of silica (SiO_2).

Microscopic studies have shown that as a result of irradiation, intense development of orange-brown color tones and the formation of coagulates and point inclusions of the oxide composition: Fe_2O_3 and $Fe(OH)_3$ occur (Fig. 5). The content of such neoplasms ranges from 3 to 5 vol.%.

Irradiation with gamma-quanta. The structure of pyrophyllite (Fig. 4) is characterized by a layer-by-layer arrangement of two networks composed of $[SiO_4]$-tetrahedra with free vertices facing each other. Between the Si tetrahedra, there is a network of Al(Mg) octahedra connecting them (see Fig. 4). Hydroxyl ions OH^- are present in the interlayer space. In initial pyrophyllite, there is a slight replacement of silicon by aluminum and aluminum by Mg, Fe^{2+}, Fe^{3+}, etc. [8].

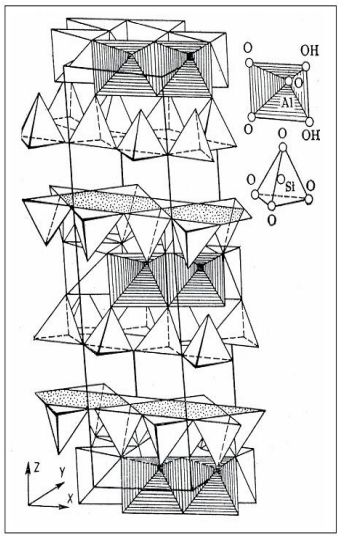
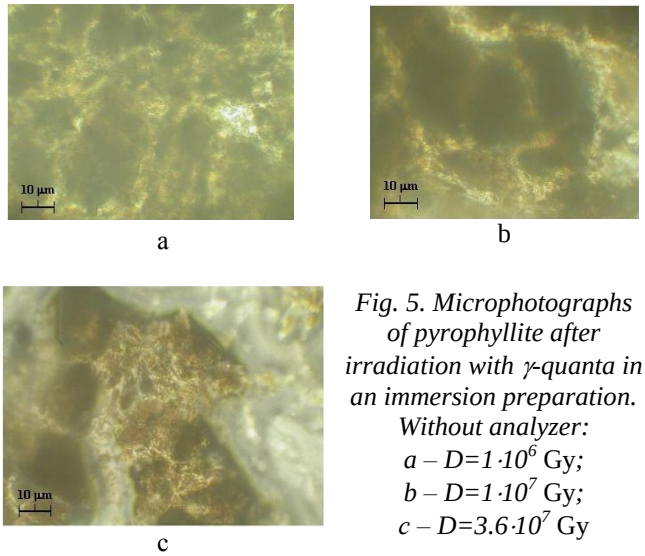


Fig. 4. Structure of pyrophyllite $Al_2[Si_4O_{10}](OH)_2$ [8]



a b c

Fig. 5. Microphotographs of pyrophyllite after irradiation with γ-quanta in an immersion preparation. Without analyzer: a – D=1·10^6 Gy; b – D=1·10^7 Gy; c – D=3.6·10^7 Gy

According to X-ray diffraction analysis, the samples after gamma-irradiation in phase composition and structural parameters (Fig. 6) are almost identical to non-irradiated pyrophyllite (see Table 1). No additional phases were detected, and differences in lattice parameters and half-widths of diffraction peaks were within the measurement error.

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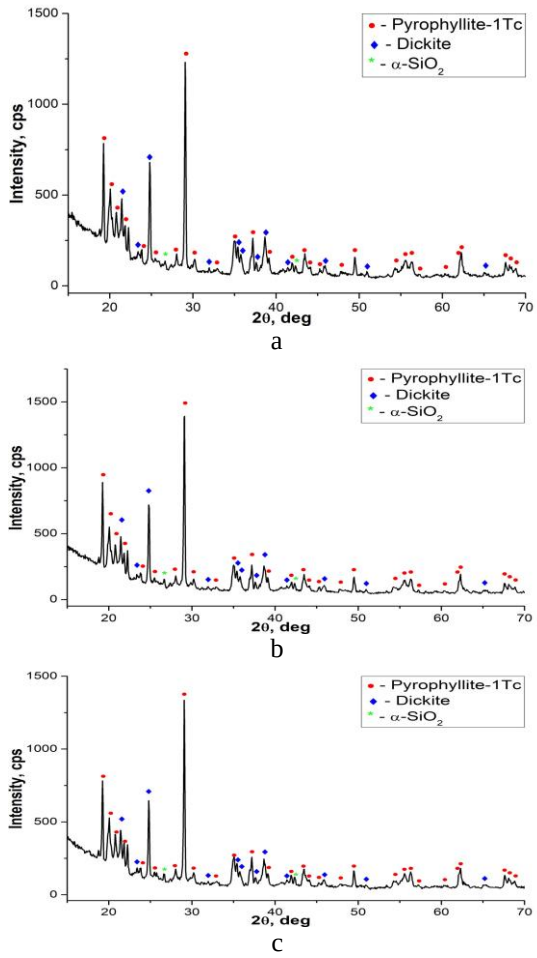

Fig. 6. Diffraction patterns of pyrophyllite after irradiation with γ-quanta: a – D=1·10⁶ Gy; b – D=1·10⁷ Gy; c – D=3.6·10⁷ Gy

For pyrophyllite, as for other layered silicates, by radiation, processes of oxidation, dehydroxylation, and associated phase transformations are characteristic [9]. In this regard, to study radiation-stimulated structural-phase transformations of pyrophyllite by gamma-quanta, the IR spectroscopy method was used, which is the most sensitive to such structural changes.

In our previous work [4], it was established that by irradiation with high-energy accelerated electrons up to a dose of 10^7 Gy changes in the structure of pyrophyllite occur, associated with the decomposition of the impurity clay phase (dickite). Hydroxyl groups released during the decomposition of dickite partially replace oxygen ions in Al octahedra, which leads to the hydration of the pyrophyllite structure. These transformations did not lead to disruption of the structure within the tetrahedral layers.

A comparison of the IR spectra of the initial and irradiated pyrophyllite showed that in contrast to irradiation with high-energy electrons with a high dose rate, long-term irradiation with gamma-quanta, the decomposition of the clay phase of dickite begins only at a maximum dose of $3.6\cdot10^7$ Gy and is not accompanied by its dehydroxylation, since dickite bands in the spectrum associated with Al-O-H vibrations – 900 and 3620 cm^{-1}, remain unchanged in intensity and shape. In this case, a splitting and decrease in the intensity of the absorption bands corresponding to the Si-O-Al vibrations – 670 and 995 cm^{-1} – are observed. This indicates the weakening and disruption of Si-O-Al bonds in the dickite structure. The structure of the main phase of pyrophyllite remains close to the initial state until the maximum radiation dose.

Gamma radiation recorded by the Ge(Li)-detector in the spectra of pyrophyllite samples is given in Table 3.

Table 3

Radioactive isotopes after activation of pyrophyllite samples by bremsstrahlung gamma radiation

E_γ, keV	Nuclear.-$K_{\alpha,\beta}$	Reactions	n_i ,%
5.90	Mn - $\alpha_{1,2}$	$^{56}Fe(91.68\%)(\gamma,n)^{55}Fe(T_{1/2}=2.73Y) -> {}^{55}Mn$	25.0
13.38	Rb - $\alpha_{1,2}$	$^{86}Sr(9.86\%)(\gamma,n)^{85}Sr(T_{1/2}=64.84D) -> {}^{85}Rb$	50.1
14.14	Sr - $\alpha_{1,2}$	$^{89}Y(100.0\%)(\gamma,n)^{88}Y(T_{1/2}=106.64D) -> {}^{88}Sr$	33.6
14.93	Y - $\alpha_{1,2}$	$^{90}Zr(51.46\%)(\gamma,n)^{89}Zr(T_{1/2}=78.43H) -> {}^{89}Y$	40.9
15.78	Zr - $\alpha_{1,2}$	$^{93}Nb(100.0\%)(\gamma,n)^{92}Nb(T_{1/2}=10.15D) -> {}^{92}Zr$	27.8

CONCLUSIONS

1. The natural pink pyrophyllite of the Ovruch deposit consists of a mixture of the triclinic modification of pyrophyllite 1Tc (~ 60…65 wt.%) $Al_2Si_4O_{10}(OH)_2$, of the clay phase - dickite (~ 35 wt.%) $Al_2Si_2O_5(OH)_4$, and of impurities quartz (~ 1…3%) α-SiO_2.

2. As a result of long-term irradiation of pink pyrophyllite by gamma-quanta up to a dose of $3.6\cdot10^7$ Gy, no disturbances in the structure of pyrophyllite occur. With increasing radiation dose, a consistent formation of clots and point inclusions of the oxide composition: Fe_2O_3 and $Fe(OH)_3$, caused by oxidative processes, is observed. At the maximum irradiation dose, the structure of the dickite impurity phase begins to decompose.

3. The results obtained conclude that irradiation by gamma-quanta up to a dose of $3.6\cdot10^7$ Gy with a low dose rate, which was accumulated over 12 years, in contrast to the accelerated experiment by irradiation with high-energy electrons up to the same dose over 48 h, does not lead to dehydroxylation or hydration of pyrophyllite and the impurity phases contained in it. Due to this, the structure of pyrophyllite remains close to its initial state.

4. Gamma spectra were measured in activated pyrophyllite samples. The following radioactive isotopes are registered: ^{55}Mn, ^{56}Fe, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{92}Zr.

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ВМІСТ ЕЛЕМЕНТІВ ТА СТРУКТУРНІ ЗМІНИ У ПРИРОДНОМУ ПІРОФІЛІТІ ПІД ДІЄЮ ГАММА-ОПРОМІНЕННЯ

О.П. Березняк, М.П. Дикий, І.В. Колодій, О.П. Медведєва, Д.В. Медведєв

Вивчено зміни структури природного пірофіліту під дією довготривалого опромінення гамма-квантами з низькою потужністю дози. Проведено порівняльний аналіз послідовності та характеру структурних змін пірофіліту під дією довготривалого опромінення гамма-квантами та прискореного опромінення електронами до дози $3{,}6 \cdot 10^7$ Гр. Встановлено, що опромінення гамма-квантами впродовж 12 років на відміну від прискореного експерименту по опроміненню високоенергетичними електронами до такої ж дози впродовж 48 год не призводить до дегідроксилації або гідратації пірофіліту, а також до змін вмісту домішкових фаз та елементів внаслідок чого структура пірофіліту залишається близькою до вихідного стану.