

THE EFFECT OF THE EXTERNAL MEDIUM ON THE STRUCTURAL-PHASE TRANSFORMATIONS OF QUARTZITE UPON HIGH-ENERGY ELECTRON IRRADIATION

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The structural transformations of the natural quartzite under the electron irradiation in doses range of $10^7 \dots 10^8$ Gy in various medium were studied using IR-spectroscopy, X-ray diffraction, and crystal-optical analyzes. It was established that under the irradiation, both in air and in a water stream, intense crystallization of the amorphous component occurs, which is siliceous cement. The initial crystal structure of quartzite is also improved as a result of radiation annealing of defects and impurities present in the initial quartz. It was found that the water medium significantly accelerates these processes, however, in the studied doses range for both types of irradiation, degradation of the quartzite crystal structure is not observed.

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INTRODUCTION

The object of the study in this work is the natural gray quartzite of the Ovruch deposit in the north-eastern part of the Zhytomyr region belonging to the Chernobyl region [1–6]. The thickness of quartzite in this region can be considered as one of the most promising geological formations for the construction of a radioactive waste storage facility. Since the rock will be exposed to ionizing radiation from the radioactive waste during deep burial, it is necessary to study the resistance of its structure to radiation, including possible contact with groundwater.

Structural transformations of natural quartzite as a result of electron irradiation in the air medium were studied in previous researches [7, 8]. It was found that quartzite is highly radiation resistant and retains its crystalline structure after electrons irradiation to a dose of 10^8 Gy. In this work, in order to assess the prospects of using quartzite rocks as a natural barrier for the safe isolation of radioactive waste for a long time, as well as to study the impact of the irradiation medium on the radiation-stimulated structural-phase transformations of quartzite, the experiments were carried out on by irradiation with accelerated electrons in two mediums: in the air and in the water stream. A comparative analysis of the quartzite structural transformations under irradiation in various medium was carried out on the basis of the obtained experimental data.

EXPERIMENTAL TECHNIQUE

The samples were irradiated at the linear electron accelerator KUT-1 with the following parameters: electron energy $E \approx 7$ MeV, average beam current $I = 500$ μ A, temperature of the irradiated samples $T_{\text{irr}} \approx 40$ °C, absorbed dose $D_{\text{abs}} = 10^6 \dots 10^8$ Gy, electron flux density $\Phi = 3 \cdot 10^{16} \dots 3 \cdot 10^{17}$ cm^{-2} . The indicated dose range was chosen because it is known that the maximum dose of external radiation from the radioactive waste, which can be accumulated by the

geological medium for 1000 years, is $\sim 3 \cdot 10^7$ Gy [9]. Irradiation in the air was carried out in a cooling water medium in airtight copper containers (copper foil thickness 0.5 mm). To simulate possible contact with groundwater during the irradiation process samples irradiation experiments were carried out without container directly in the cooling water stream.

The structure and phase composition of quartzite were studied by infrared spectroscopy, petrographic analysis and X-ray diffraction. Infrared absorption spectra were recorded using UR-20 (Zeiss, Jena) and IRS-29 (LOMO) spectrophotometers in the frequency range of $400 \dots 4000$ cm^{-1} with a measurement error of $\pm (2 \dots 7)$ cm^{-1} . Petrographic studies were carried out on polarizing microscopes MIN-8, POLAM-211L using immersion liquids. X-ray diffraction analysis was performed using DRON-4-07 diffractometer in Cu-K α -radiation equipped with Ni selective absorbing filter and scintillation detector.

RESULTS AND ITS DISCUSSION

Microstructure study of the initial quartzite using petrographic analysis of transparent thin sections in transmitted light showed that it consists of large grains of α -quartz (SiO_2) (≈ 90 vol.%), tightly adjacent to each other and interconnected by semi-amorphous siliceous cement (≈ 10 vol.%) (Fig.1.1, a, b). The width of the binder layer of siliceous cement is $8 \dots 15$ μm . Grains of quartz have sizes from 60 to 120 μm . Some grains contain gas-liquid inclusions and opaque impurities of ore minerals. Such a structure of quartzite is explained by the processes of metamorphism happening during its formation under conditions of intense influence of temperature and pressure [10]. The chemical composition of the studied gray quartzite from the Ovruch deposit is represented by the following oxides: $\text{SiO}_2 - 97.52\%$; $\text{Al}_2\text{O}_3 - 1.54\%$; $\text{Fe}_2\text{O}_3 - 0.34\%$; $\text{CaO} - 0.12\%$; $\text{MgO} - 0.09\%$; $\text{TiO}_2 - 0.09\%$; $\text{Na}_2\text{O} - 0.05\%$ [8].

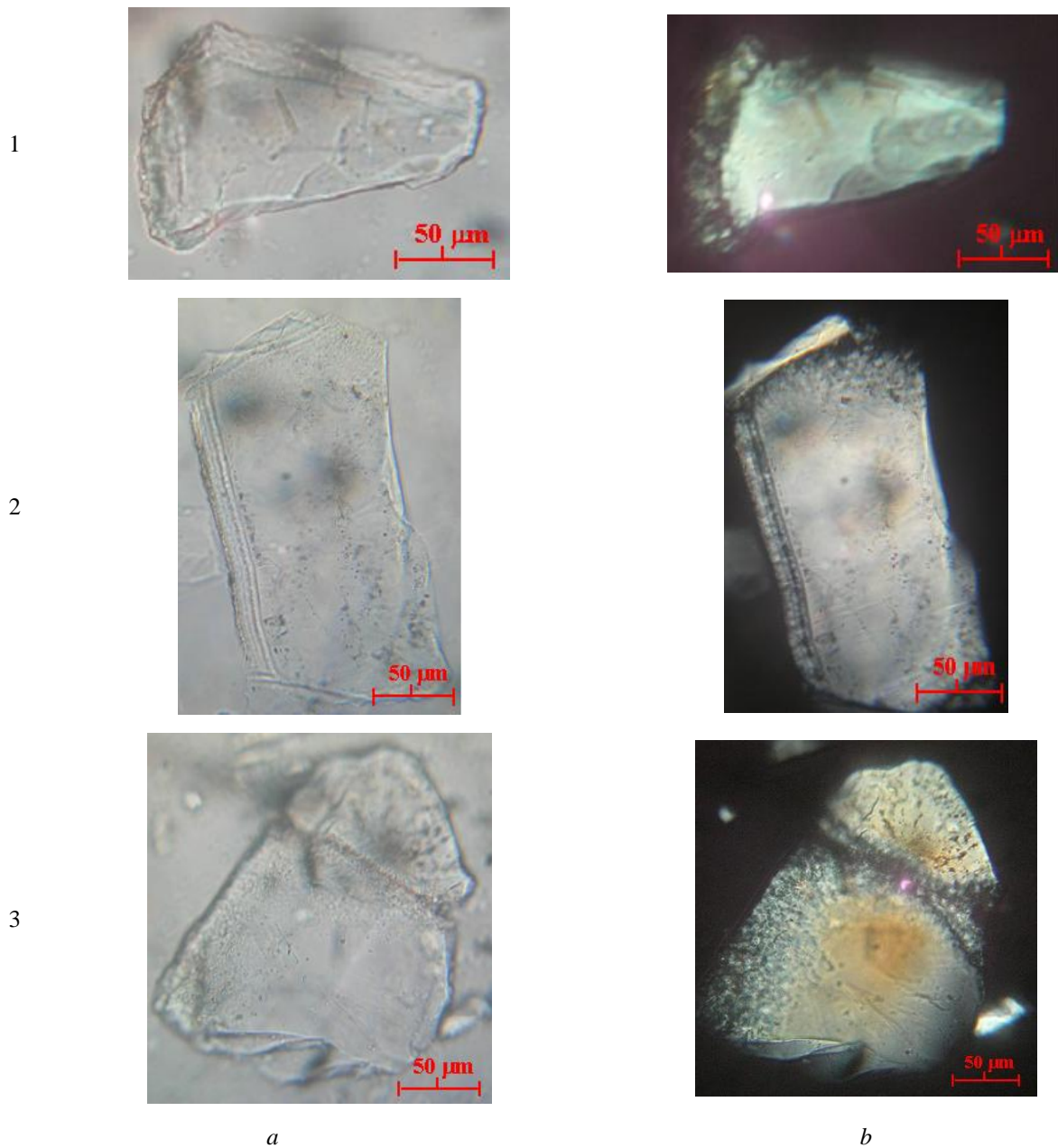


Fig. 1. Microphotographs of quartzite grains in an immersion preparation: a – without analyzer, b – with analyzer; 1 – initial quartzite – pure crystalline quartz grain with an isotropic rim of a semi-amorphous cementing substance; 2 – after electron irradiation in the air ($D = 10^8$ Gy) – quartz grain with point inclusions and an anisotropic polycrystalline rim consisting of secondary quartz grains; 3 – after electron irradiation in a water stream ($D = 10^8$ Gy) – a quartz grain containing clusters of point defects surrounded by an anisotropic polycrystalline quartz mass. In the transmitted light

Diffraction pattern of the initial sample is shown in Fig. 2, curve 1. Position of the diffraction peaks and their integrated intensity fully correspond to polycrystalline quartz. Lattice parameters of the initial quartz, which is part of quartzite, are: $a = 4.9140$ Å, $c = 5.4075$ Å. These values are close to the literature data for α -quartz: $a = 4.914$ Å and $c = 5.405$ Å (ICDD PDF-2 database, #85-0798) [11]. A slight increase in the lattice parameter c (compared with the published data) indicates the presence of defects and impurities in the initial structure of α -quartz (Table).

The IR-spectrum of the initial quartzite contains the main absorption bands of α -quartz: 470, 700, 810, 1100 cm^{-1} , which are typical for Si-O [12] vibrations. However, the bands are somewhat blurred and in the region of 830...750 cm^{-1} there is no doublet caused to ν_s Si-O-Si vibrations, which indicates the presence of an amorphous component (probably semi-amorphous siliceous cement), as well as defects and impurities in the initial structure of quartz. There are no bands in the spectra characterizing the presence of other minerals or high-temperature quartz modifications. The presence of absorption bands in the spectrum in the frequency range 1600 and 3400 cm^{-1} indicates the presence of OH^- groups in the initial sample (Figs. 3, 4, curve 1).

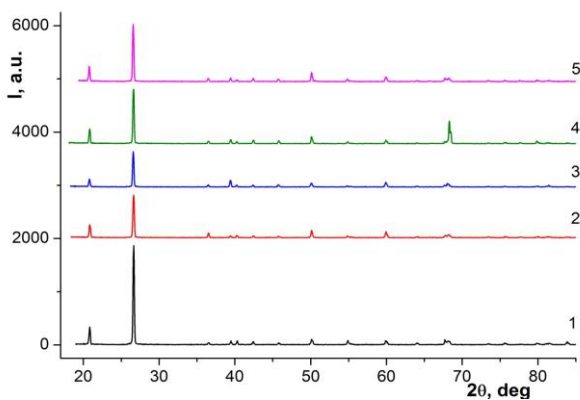


Fig. 2. Diffraction patterns of the studied quartzite samples: 1 – initial quartzite; 2 – irradiation in water stream $D = 10^7$ Gy; 3 – irradiation in water stream $D = 5 \cdot 10^7$ Gy; 4 – irradiation in water stream $D = 10^8$ Gy; 5 – irradiation in air $D = 10^8$ Gy

Lattice parameters of the initial and irradiated (in the water stream and in the air) quartzite samples

Dose D , Gy	Lattice parameters	
	a , Å	c , Å
α -quartz [11]	4.914	5.405
initial	4.9140	5.4075
10^7 (irradiation in a stream of water)	4.9156	5.4073
$5 \cdot 10^7$ (irradiation in a stream of water)	4.9172	5.4074
10^8 (irradiation in a stream of water)	4.9154	5.4066
10^8 (irradiation in a stream of water)	4.9144	5.4045

Crystal-optical studies of quartzite irradiated with electrons up to $D_{\text{sup}} = 10^7 \dots 10^8$ Gy have shown that the grains of α -quartz retain their shape and size up to a maximum dose of 10^8 Gy both under irradiation in the air and in the water stream. The refractive index did not change. Under both types of irradiation a large number of smoky-colored grains appear (up to volume 40%) and the formation of accumulations of gas-liquid inclusions in quartz grains is observed (see Fig. 1.2,a,b). This is due to the formation of color centers and radiation-induced diffusion of impurities in the initial quartz [13].

In contrast to irradiation in the air, in which a noticeable crystallization of siliceous cement is observed only at the maximum dose of 10^8 Gy, intensive irradiation of the cementitious substance occurs during irradiation in the water stream already at the first dose of radiation (10^7 Gy) (see Fig.1.2,b). It is known that the solubility of amorphous silica and quartz glass is almost 10 times greater than in crystalline quartz [14]. Therefore, under irradiation in water stream due to the formation of water radiolysis products: $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \rightarrow \text{H}^+ + \text{OH}^-$, $\text{H}^+ + \text{H}^+ \rightarrow \text{H}_2$, $\text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O}_2$, $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, crystallization acceleration process of semi-amorphous silica occur. When crystals of stable modification of α -quartz are formed in

siliceous cement, this process stops and there is no increase in their number with further radiation dose increasing.

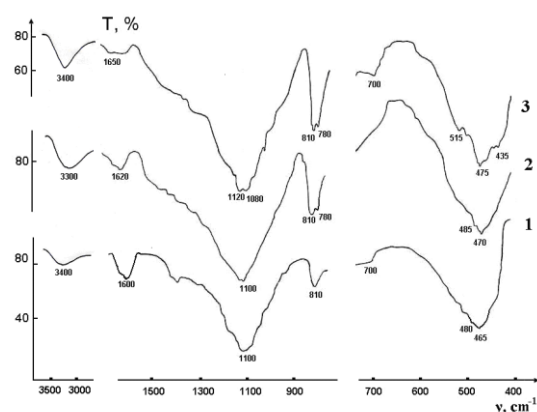


Fig. 3. IR-spectra of quartzite absorption: 1 – initial quartzite; 2 – after irradiation with electrons in the air up to $D = 10^7$ Gy; 3 – the same up to $D = 10^8$ Gy

In contrast to irradiation in the air, in which a noticeable crystallization of siliceous cement is observed only at the maximum dose of 10^8 Gy, intensive irradiation of the cementitious substance occurs during irradiation in the water stream already at the first dose of radiation (10^7 Gy) (see Fig.1.2,b). It is known that the solubility of amorphous silica and quartz glass is almost 10 times greater than in crystalline quartz [14]. Therefore, under irradiation in water stream due to the formation of water radiolysis products: $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \rightarrow \text{H}^+ + \text{OH}^-$, $\text{H}^+ + \text{H}^+ \rightarrow \text{H}_2$, $\text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O}_2$, $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, crystallization acceleration process of semi-amorphous silica occur. When crystals of stable modification of α -quartz are formed in siliceous cement, this process stops and there is no increase in their number with further radiation dose increasing.

The lattice parameters of α -quartz after irradiation in the air up to a dose of 10^8 Gy are: $a = 4.9144$ Å ($\Delta a = 0.0005$ Å), $c = 5.4045$ Å ($\Delta c = -0.003$ Å) (see Table). In comparison with the initial ones ($a = 4.9140$ Å, $c = 5.4075$ Å) these values are closer to the literature data for α -quartz ($a = 4.914$ Å and $c = 5.405$ Å). In addition, there is a decrease in the FWHM of the quartz lines, as well as an increase in the number of diffraction peaks, which can be explained by the formation of a large number of small α -quartz crystals during crystallization of amorphous cement under irradiation (see Fig. 2, curve 5). At lower doses these changes are weakly expressed. Therefore, we can say that under irradiation in the air up to a dose of 10^8 Gy radiation annealing of defects occurs in the α -quartz.

Diffraction pattern of quartzite, irradiated in the water stream already at a dose of 10^7 Gy, shows a redistribution of the intensities and an increase in the FWHM of individual diffraction peaks caused by the mass formation of gas-liquid inclusions in quartz grains (see Fig. 2, curve 2). The lattice parameters of α -quartz are: $a = 4.9156$ Å, $c = 5.4073$ Å (see Table). Lattice

parameter a increased (compared with the initial value $a = 4.9140 \text{ \AA}$) by 0.0016 \AA (approximately 0.03%), the change in the parameter c is within the measurement error. The accumulation of impurity ions in the structural channels of α -quartz leads to increase in the parameter a , it is caused by the fact that as a result of irradiation the mobility of structural elements-impurities in quartz (Al, Ti, Na, etc.) increases, which, being released from the nodes of the crystal lattice, occupying free structural channels [14]. In addition, the presence of water dissociation products accelerates the accumulation of impurities and defects in the structural channels and voids of the α -quartz crystal lattice.

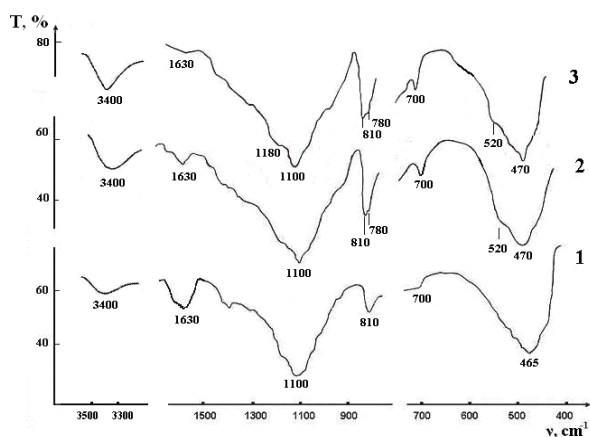


Fig. 4. IR-spectra of quartzite absorption:
1 – initial quartzite; 2 – after electrons irradiation
in a water stream up to $D = 10^7 \text{ Gy}$;
3 – the same up to $D = 10^8 \text{ Gy}$

Upon subsequent irradiation in water to $D = 5 \cdot 10^7 \text{ Gy}$ the intensity and FWHM of the diffraction peaks do not change (see Fig. 2, curve 3). The measured lattice parameters of α -quartz at $D = 5 \cdot 10^7 \text{ Gy}$ are: $a = 4.9172 \text{ \AA}$ ($\Delta a = 0.0032 \text{ \AA}$, approximately 0.07%), $c = 5.4074 \text{ \AA}$. Parameter a continues to increase due to the accumulation of radiation defects.

A number of significant changes occur in quartzite under irradiation in the water up to a maximum dose of 10^8 Gy . There is a normalization of the peaks intensities, a decrease in FWHM (see Fig. 2, curve 4), as well as a decrease in the lattice parameters a and c : $a = 4.9154 \text{ \AA}$, $c = 5.4066 \text{ \AA}$ (compared with a dose of $5 \cdot 10^7 \text{ Gy}$, where $a = 4.9172 \text{ \AA}$, $c = 5.4074 \text{ \AA}$) (see Table). This indicates that radiation-induced diffusion of impurities and defects contained in the sample leads to their drain to the surface of quartz grains.

As a result of quartzite irradiation, both in the air and in the water stream, infrared spectra change significantly. These changes are accompanied by an increase in the intensity of the main absorption bands, a narrowing of their maxima and the appearance of doublets typical for α -quartz, which is caused by radiation annealing of structural defects of the initial quartz, as well as the gradual crystallization of semi-amorphous siliceous cement around grains of quartz. However, under irradiation in the water stream changes in the spectrum appear already at the first irradiation dose of 10^7 Gy (see Fig. 4, curve 2). The main

absorption bands in the spectrum become sharper, and a number of characteristic peaks of α -quartz are also appears, which are most dependent on the level of crystallinity: $520, 700 \text{ cm}^{-1}$, as well as the doublet $780 \dots 810 \text{ cm}^{-1}$. The reasons for this are both intensive crystallization of the bulk of silica cement, accelerated by the presence of an water medium, and radiation annealing of defects and impurities presented in the initial quartz, which is part of quartzite.

A change of the shape and a redistribution of the intensities of the absorption bands in the vibration area of the hydroxyl groups 1630 and 3400 cm^{-1} is similar to that described in work [8] under irradiation in the air. With an increase in the radiation dose to 10^8 Gy , a noticeable increase in the intensity of the band is observed, which is typical for molecular water in the region of 3400 cm^{-1} , which is contained in gas-liquid inclusions and intergranular space. The main maxima of α -quartz in the spectrum ($470, 700, 810 \text{ cm}^{-1}$) become narrower, and a characteristic shoulder of 1180 cm^{-1} appears, which is associated with stretching vibrations of Si-O in the quartz structure (see Fig. 4, curve 3). Thus, after irradiation to a maximum dose of 10^8 Gy the crystal structure of α -quartz, which is part of quartzite, becomes even more ordered, which may indicate its high radiation resistance.

CONCLUSION

It was established that as a result of irradiation of natural quartzite with electrons in the dose range of $10^7 \dots 10^8 \text{ Gy}$, both under irradiation in the air and in the water stream, intensive crystallization of the amorphous component occurs, which is a siliceous cement, as well as improvement of the initial crystal structure of quartzite due to the radiation annealing of defects and impurities, presented in the initial quartz.

It was found that the irradiation medium has a significant effect on the rate of these processes. Hence, under the irradiation in the water medium, intensive crystallization of the bulk of silica cement and radiation annealing of defects in the initial structure begin at lower doses (10^7 Gy), which is due to the presence of water radiolysis products – H^+ - and OH^- -ions. However, in the studied dose range for both types of irradiation, no degradation of the crystal structure of quartzite is observed. This indicates the high stability of the studied rock to the effects of ionizing radiation from radioactive waste, including possible contact with groundwater.

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ВЛИЯНИЕ ВНЕШНЕЙ СРЕДЫ НА СТРУКТУРНО-ФАЗОВЫЕ ПРЕОБРАЗОВАНИЯ КВАРЦИТА ПРИ ОБЛУЧЕНИИ ВЫСОКОЭНЕРГЕТИЧНЫМИ ЭЛЕКТРОНАМИ

Е.П. Березняк, И.В. Колодий, Ю.С. Ходырева

Методами ИК-спектроскопии, рентгеноструктурного и кристаллооптического анализов изучены преобразования структуры природных кварцитов при облучении электронами в интервале доз $10^7 \dots 10^8$ Гр в различных средах. Установлено, что в результате облучения как на воздухе, так и в потоке воды происходят интенсивная кристаллизация аморфной составляющей, которая представляет собой кремнеземистый цемент, а также совершенствование исходной кристаллической структуры кварцита в результате радиационного отжига дефектов и примесей, присутствующих в исходном кварце. Обнаружено, что водная среда существенно ускоряет эти процессы, однако в исследуемом диапазоне доз при обоих видах облучения не наблюдается какой-либо деградации кристаллической структуры кварцита.

ВПЛИВ ЗОВНІШНЬОГО СЕРЕДОВИЩА НА СТРУКТУРНО-ФАЗОВІ ПЕРЕТВОРЕННЯ КВАРЦИТУ ПРИ ОПРОМІНЕННІ ВИСОКОЕНЕРГЕТИЧНИМИ ЕЛЕКТРОНАМИ

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Методами ІЧ-спектроскопії, рентгеноструктурного і кристаллооптичного аналізів вивчені перетворення структури природних кварцитів при опроміненні електронами в інтервалі доз $10^7 \dots 10^8$ Гр у різних середовищах. Встановлено, що в результаті опромінення як на повітрі, так і в потоці води відбуваються інтенсивна кристалізація аморфної складової, яка представляє собою кремнеземистий цемент, а також вдосконалення вихідної кристалічної структури кварциту в результаті радіаційного відпаду дефектів і домішок, присутніх у вихідному кварці. Виявлено, що водне середовище істотно прискорює ці процеси, однак у досліджуваному діапазоні доз при обох видах опромінення не спостерігається будь-якої деградації кристалічної структури кварциту.