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THE INFLUENCE OF THERMODYNAMIC PROCESSES OF EXPLOSIVE IMPACT ON THE CRYSTAL STRUCTURE OF QUARTZ GRANITES OF THE STAROKODATSKYI QUARRY ^{1,2}Ishkov V., ³Baskevych O., ^{1,4}Kozii Ye., ²Pashchenko P.

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Abstract. The study was conducted on granite samples collected from one area of the Starokodatskyi quarry. They were selected before (core from an exploration well) and after (outsize rock torn off by an explosion near the southern side of the quarry) drilling and blasting operations. To obtain optically monomineralic phases, the samples were subjected to magnetic separation on a three-roller separator, which allowed to isolate four fractions with different magnetic properties. After that, all samples were sent for X-ray structural analysis using DRON-3 X-ray diffractometer with monochromatized Co-K- α radiation (I = 1.7902Å). Identification of individual minerals was performed manually by comparing the interplanar distances (d, Å) and relative intensities of the experimental curve with the data of the PCPDFWIN electronic file. All X-ray phase studies were carried out within angles of 10–90° with a step of 0.1° and an exposure time of 5 seconds.

The analysis of the obtained results indicates a significant impact of drilling and blasting operations at the Starokodatskyi granite quarry on the size of quartz crystallites, one of the most important elements of its fine crystalline structure. The phenomenon of a decrease in both the total size of crystallites and their dispersion along individual crystallographic planes under the influence of drilling and blasting operations has been established. It has been proven that an increase in the content of different sizes "impurities" significantly affects the reduction in the size of crystallites of optically monomineral quartz granitoids of the Starokodatskyi quarry, which leads to changes in its physical properties, in particular magnetic.

The scientific novelty of the results consists in establishing the phenomenon of a decrease in the size of the coherent scattering regions of X-rays (crystallites) of optically monomineral quartz of granitoids of the Starokodatskyi quarry under the thermodynamic influence of drilling and blasting operations. This is one of the main characteristics of changes in the substructure of the crystal lattice of quartz - one of the main rock-forming minerals of granites of this deposit under the thermodynamic influence of blasting operations.

The practical significance of the results of the work consists in the identification of significant qualitative changes in the crystallochemical structure of quartz granitoids of the Starokodatskyi quarry, which can be used to predict their properties in the production of concrete products, the manufacture of decorative materials and the construction industry in general.

Keywords: quartz crystallites, crystal structure, crystallographic planes, granitoids, Starokodatskyi quarry, drilling and blasting operations, magnetic separation.

1. Introduction

The Starokodatskyi granite quarry (Fig. 1) is located on the right bank of the Dnipro River, near the southeastern outskirts of the Dnipro city. Currently, the industrial development of the quarry is suspended, and it is partially flooded. In tectonic terms, the territory of the quarry belongs to the Dnipropetrovsk block of the Prydniprovsk subzone of the Middle Prydniprovsk megablock of the Ukrainian crystalline shield. The rocks that were mined in the quarry belong to the granitoids of the Dnipropetrovsk complex (Ar₁dn) of Paleoarchean age.

It is known that the mechanical and generally physicochemical properties of crystalline phases directly depend on the symmetry of their structure, composition, nature of the bonds of structural elements and defects of their real crystal structure, topography on the surface and their distribution within the analyzed phase [1]. Increasingly, when studying the strength and other physical and mechanical properties of solids, turn to the study of structural imperfections, such as © Publisher M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine, 2024

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microdistortions of crystal lattices and the dispersion of coherent X-ray scattering regions (crystallites), which belong to the fine crystal structure (or substructure of minerals).



Figure 1 – Starokodatskyi granite quarry. View of the lower northern side

Analysis of previous studies. The work [2] is devoted to the study of the substructure parameters of some minerals of the Maikainskyi gold deposit. Recently, a wide range of research has been conducted in some countries on the use of non-traditional (non-mechanical) physical and physico-chemical methods of influencing minerals and mineral suspensions to increase the contrast of physico-chemical and technological properties of minerals, and therefore the efficiency of separation of mineral components during enrichment of ores of complex substance composition [3].

According to infrared Fourier spectroscopy, as a result of an impulse effect, slight changes in the structure of diamond crystals were observed, which were appeared in an increase in the concentration of microshear defects represented by interstitial carbon atoms - platelets or B2 [4-5]. The following changes in the structure of diamond crystals were established:

- a systematic increase in the absorption coefficient of the IR spectral line at about 1365 cm⁻¹, caused by B2-defects, with an increase in the duration of processing with short (nanosecond duration ~1-10 ns) electromagnetic pulses;

- formation of new B2-defects in samples with an increased relative content of nitrogen B-defects, which is 35-65% of the total nitrogen impurity content in crystals.

In works [1, 3-8], B-defects are represented by nitrogen atoms tetrahedrally grouped around a vacancy, which replace carbon in diamond lattices.

Previously, the authors studied the distribution of trace element composition of coal in Donbas [9-13]. A methodology for classifying coal deposits and oil fields of the Dnipro-Donetsk Basin by the content of various trace elements was also developed [14-15]. Other studies focused on the analysis of the distribution of germanium in individual coal seams of the Pavlohrad-Petropavlivskyi geological and industrial area of Donbas. However, the specifics of the impact of drilling and blasting operations on the size of quartz crystallites from granitoids of the Starokodatskyi quarry have not yet been considered.

The aim of the study is to determine the characteristics of changes in the size of quartz crystallites of granites of the Starokodatskyi quarry under the influence of drilling and blasting operations. It is worth noting that such studies have not been conducted before.

2. Methods

In the framework of the study, granite samples collected from one area of the Starokodatskyi quarry were used.

The samples were taken before (core from an exploration well) and after (oversize rock torn off by an explosion near the southern side of the quarry) drilling and blasting operations. To obtain optically monomineralic phases, the samples were subjected to magnetic separation using a three-roller separator, which allowed to separate four fractions with different magnetic properties. The sequence of separation of fractions in increasing magnetic properties is as follows:

- 1) non-magnetic fraction;
- 2) fraction from the upper roller;
- 3) fraction from the lower roller;
- 4) fraction from the drum of the magnetic separator.

After that, all samples were consistently subjected to X-ray diffraction analysis using a DRON-3 X-ray diffractometer with monochromatized Co-K- α radiation (I = 1.7902Å). Identification of mineral compounds was performed manually by comparing the interplanar distances (d, Å) and relative intensities (I otn-I/I 0) of the experimental curve with the data of the PCPDFWIN electronic file. All X-ray phase studies were carried out within the angles of 10-90° with a step of 0.1° and an exposure time of 5 seconds.

3. Results and discussion

As a result of the research, X-ray diffractograms of general granite samples before and after the explosion, as well as granite samples after magnetic separation for all four of its products both before and after the explosion, were created. X-ray structural studies were carried out within the angles of 10-90°, but with a smaller step - 0.01° and an exposure time of 15 seconds to clarify the structure. As a result, X-ray diffractograms of quartz were created along two crystallographic planes: 101 and 221.

The sizes of quartz crystallites along crystallographic planes 101 and 211 (L101 and L211) were determined using the Seliakov-Sherrer formula:

$$L_{HKL} = \frac{0.94\lambda}{\beta Cos\theta_{HKL}}$$

The general crystallite sizes (L) of quartz were calculated from two lines corresponding to X-ray prints from the main crystallographic planes of this mineral (101 and 211, respectively) by solving the system of equations:

$$L = \frac{0.94\lambda}{\beta Cos\theta_{HKL}};$$
$$\frac{\Delta d}{d} = \frac{\Delta a}{a} = \frac{\beta}{4tg\theta_{HKL}} = M.$$

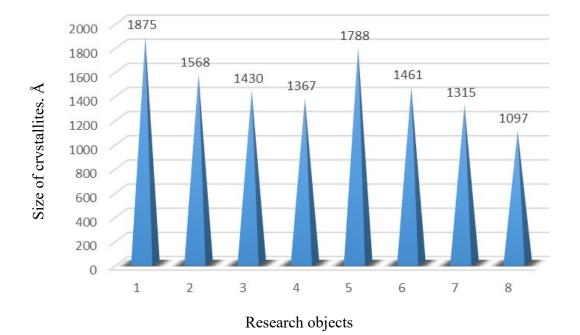
Analysis of the results of X-ray phase studies of general granite samples before and after blasting confirms their belonging to the granites of the Starokodatskyi quarry. Some variations in their composition, given modern ideas about the conditions for the formation of the main rock-forming mineral phases, are most likely a manifestation of local anisotropy of the mineral composition in the selected samples.

Figure 2 shows changes in the total size of quartz crystallites in various products of magnetic separation of granites from the Starokodatskyi quarry before and after blasting. Analysis of the presented data of X-ray structural studies demonstrates a gradual and regular decrease in the total size of crystallites, which has an almost linear character, both in the products of magnetic separation in the series: "drum MS" \rightarrow "lower roller" \rightarrow "upper roller" \rightarrow "non-magnetic product", and between the same products from granite samples before drilling and blasting to granite samples after their conduct.

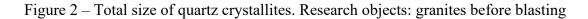
The maximum gradient of quartz crystallite size reduction is observed in both cases between the "non-magnetic" and "upper roller" products. Before drilling and blasting, the crystallite size reduction occurs by 307 Å (16.37%), and after the blasting, the crystallite size reduction is 327 Å (18.29%).

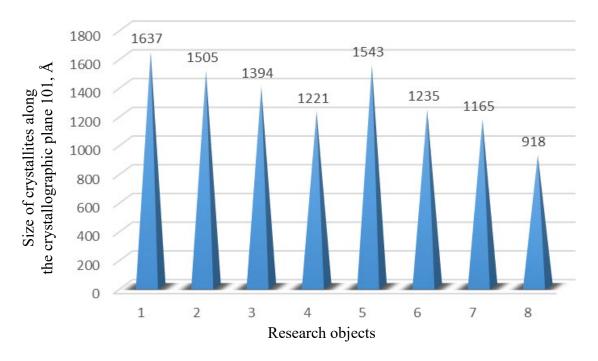
Taking into account the percentage output of each magnetic separation products, the weighted average value of the total size of quartz crystallites in granite samples before blasting is 1660.15 Å, and in granite samples after blasting is 1545.84 Å. Therefore, the weighted average value of the total size of quartz crystallites as a result of the thermodynamic effect of drilling and blasting is reduced by 6.89%.

The results of studies of the quartz crystallites size along crystallographic planes 101 and 211 in all products of magnetic separation of granite samples before and after blasting are presented in Figures 3 and 4. These data provide additional information about spatial changes in crystallite sizes under the man-made influence of mining operations, which affects the overall mechanical stability and properties of the material.



1 - product "non-magnetic", 2 - product "upper roller", 3 - product "lower roller",
4 - product "drum MC"; granites after blasting: 5 - product "non-magnetic",
6 - product "upper roller", 7 - product "lower roller", 8 - product "drum MC"





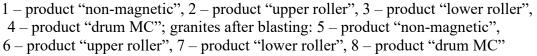


Figure 3 – The size of quartz crystallites along the crystallographic plane 101. Research objects: granites before blasting

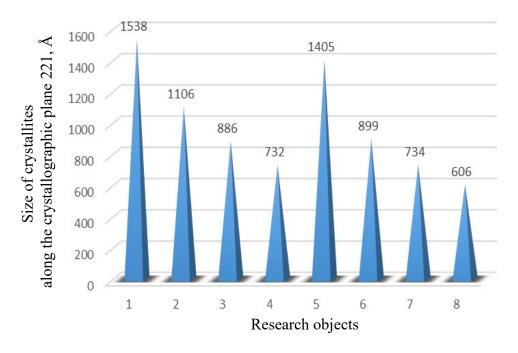


Figure 4 – Size of crystallites along the crystallographic plane 221, Å.
Research objects: granites before blasting:
1 – product "non-magnetic", 2 – product "upper roller", 3 – product "lower roller",
4 – product "drum MC"; granites after blasting: 5 – product "non-magnetic",
6 – product "upper roller", 7 – product "lower roller", 8 – product "drum MC"

In both cases, there is a significant decrease in the size of quartz crystallites of granites, both before and after blasting, in the series: "MC drum" \rightarrow "lower roller" \rightarrow "upper roller" \rightarrow "non-magnetic product", their dynamics are very similar.

In the first case, the maximum gradient of crystallite size reduction is observed between quartz from granite samples before the explosion in the products "MC drum" – "lower roller" (reduction of crystallite size by 173 Å), and after the explosion between the products "non-magnetic" – "upper roller" (here a reduction of crystallite size by 308 Å is observed).

Taking into account the percentage output of each magnetic separation products, the weighted average value of the size of quartz crystallites in granite samples before blasting is 1517.54 Å, and in granite samples after blasting is 1329.39 Å. Thus, the weighted average value of the size of quartz crystallites along the crystallographic plane 101 as a result of the technogenic impact of blasting is reduced by 12.4%.

In the second case, the maximum gradient of crystallite size reduction is observed between quartz from granite samples both before and after drilling and blasting in the products "non-magnetic" – "upper roller". Before blasting, the reduction is 432 Å, and after – 506 Å).

Taking into account the percentage output of each magnetic separation products, the weighted average value of the size of quartz crystallites along the crystallographic plane 211 in granite samples before blasting is 1222.82 Å, and in granite samples after blasting is 1065.57 Å. Thus, the weighted average value of the size of quartz

crystallites along the crystallographic plane 211 as a result of the thermodynamic effect of blasting is reduced by 12.86%.

Special interest is the presence of optically monomineral quartz grains in weakly (the "upper roller" product), moderately (the "lower roller" product) and especially strongly magnetic (the "MC drum" product) separation products. It is well known that the polymorphic modification of low-temperature quartz (α -quartz) of the trigonal syngony (trigonal-trapezoidal class) belongs to non-magnetic minerals. At the same time, natural monomineral quartz grains on an optical scale can contain and very often contain numerous prisoner minerals visible only with an electron microscope, gas-liquid inclusions and impurity elements: Li, Al, Na, K, H, Mn, Fe, Ti, Rb, Ca, Cs, Ba, Pb, Ag, Sn, Cu, Zn, V, Ge, Cr, U, etc. The authors believe that in this context it is appropriate to generalize all of them with the term impurities. In our opinion, it is reasonable to assume that the content of certain "impurities" significantly affects the magnetic properties of optically monomineral quartz grains.

Therefore, an increase in the content of such "impurities" can lead to the appearance and concentration of optically monomineral quartz grains in weakly, moderately and strongly magnetic separation products.

Thus, the presence of optically monomineral quartz grains in various degrees of magnetic separation products, a unidirectional increase in their "magnetism" with an increase in both the total size of crystallites and their sizes along crystallographic planes 101 and 221 in the line: product "non-magnetic" \rightarrow product "upper roller" \rightarrow product "lower roller" \rightarrow product "drum MC" receive a logical explanation.

4. Conclusions

Analysis of the results of the conducted research indicates a significant impact of drilling and blasting operations at the Starokodatskyi granite quarry on one of the most important elements of the fine crystalline structure of quartz - the size of its crystallites. The phenomenon of a decrease in both the overall size of crystallites and their dispersion along individual crystallographic planes has been established. It has been proven that an increase in the content of various-scale "impurities" significantly affects the reduction in the size of crystallites of optically monomineral quartz granitoids of the Starokodatskyi quarry and, therefore, leads to a change in its physical properties, in particular, magnetic ones.

The main scientific novelty of the obtained results consists in the established phenomenon of a decrease in the size of the regions of coherent scattering of X-rays (one of the main characteristics of the substructure of the crystal lattice) of optically monomineral quartz (one of the main rock-forming minerals of granites) of granitoids of the Starokodatskyi quarry under the thermodynamic influence of drilling and blasting operations.

The main practical value of the conducted research consists in establishing significant qualitative changes in the crystallochemical structure of quartz granitoids of the Starokodatskyi quarry, which can be used to predict their properties in the construction industry, production of concrete products, and the manufacture of decorative materials.

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ВПЛИВ ТЕРМОДИНАМІЧНИХ ПРОЦЕСІВ ВИБУХОВОГО ВПЛИВУ НА КРИСТАЛІЧНУ СТРУКТУРУ КВАРЦУ ГРАНІТІВ СТАРОКАЙДАЦЬКОГО КАР'ЄРУ

Ішков В., Баскевич О., Козій Є., Пащенко П.

Анотація. Дослідження проводилося на зразках гранітів, зібраних з однієї ділянки Старокайдацького кар'єру. Вони були відібрані до (керн з розвідувальної свердловини) і після (відірваний вибухом негабарит біля південного борту кар'єру) проведення буровибухових робіт. Для отримання оптично мономінеральних фаз, зразки піддавалися магнітній сепарації на трьохроликовому сепараторі, що дозволило виділити чотири фракції з різними магнітними властивостями. Після цього всі зразки проходили рентгеноструктурний аналіз за допомогою рентгенівського дифрактометра ДРОН-3 з монохроматизованим Со-К-α випромінюванням (I = 1.7902Å). Ідентифікацію окремих мінералів виконували вручну, порівнюючи міжплощинні відстані (d, Å) та відносні інтенсивності (I otn-I/I 0) експериментальної кривої з даними електронної картотеки PCPDFWIN. Усі рентгенофазові дослідження проводилися в межах кутів 10–90° з кроком 0,1° та витримкою 5 секунд.

Аналіз отриманих результатів свідчить про значний вплив буровибухових робіт на Старокайдацькому гранітному кар'єрі на розміри кристалітів кварцу, одного з найважливіших елементів його тонкої кристалічної структури. Встановлено явище зменшення як загальних розмірів кристалітів, так і їх дисперсності по окремих кристалографічних площинах під впливом буровибухових робіт. Доведено, що збільшення вмісту різнорозмірних "домішок" суттєво впливає на зниження розмірів кристалітів оптично мономінерального кварцу гранітоїдів Старокайдацького кар'єру, що призводить до змін його фізичних властивостей, зокрема магнітних.

Наукова новизна результатів полягає у встановленні явища зменшення розміру областей когерентного розсіювання рентгенівських променів (кристалітів) оптично мономінерального кварцу гранітоїдів Старокайдацького кар'єру під термодинамічним впливом буровибухових робіт. Це одна з основних характеристик змін субструктури кристалічної ґратки кварцу – одного з головних породоутворюючих мінералів гранітів цього родовища під термодинамічним впливом вибухових робіт.

Практична значимість результатів роботи полягає у виявленні суттєвих якісних змін кристалохімічної структури кварцу гранітоїдів Старокайдацького кар'єру, що може бути використано для прогнозування їх властивостей у виробництві бетонних виробів, виготовленні декоративних матеріалів та будівельній індустрії загалом.

Ключові слова: кристаліти кварцу, кристалічна структура, кристалографічні площині, гранітоїди, Старокайдацький кар'єр, буровибухові роботи, магнітна сепарація.