Studies of water treatment influence on the structure of vein quartz from shungite rocks

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Abstract. The article presents the results of the research of the structure and composition of one of the morphological varieties of quartz – vein quartz of shungite rocks from Zazhogino deposit of Karelia and a reference quartz sample. The values of the crystal lattice parameters were determined by full-profile analysis (Rietveld method). Coherent scattering region (CSR) for vein quartz samples are determined using the Debye-Scherrer formula after applying the background subtraction function. The influence of water treatment on the content of impurity elements in samples of vein quartz was also studied. The most common impurity elements in natural vein quartz samples, such as Al, Na, Li and Ge, are identified. It is shown that water treatment is effective for reducing the content of impurity elements and obtaining the minimum size of vein quartz crystallites.

1. Introduction

Recently, more and more attention is being paid to the possibilities of obtaining and applying nanoparticles in various production areas. Nano- and biomedicine occupy a special place here. It is these areas that are interested in the possibilities of developing and expanding the possibility of various applications of nanoparticles and nanomaterials [1, 2].

Quartz is a popular material in many industrial areas, such as machine and aircraft construction, production of new-generation composite materials, biomedicine, etc. Each application area requires used material to comply with strict parameters, such as dispersion and purity [3]. The size of a nanoparticle is a critical parameter that largely determines its properties. Depending on the size, the properties of nanoparticles, such as toxicity, adsorption properties, and many others, may change [4]. Therefore, the preparation of nanoparticles is a challenging task.

Quartz content is one of the main criteria for distinguishing of the most valuable industrial types of shungite rocks from the currently developed Zazhogino field. Quartz is represented by two genetic varieties that differ in the morphology of manifestation and time of formation. The first is terrigenous-chemogenic microsized and nanosized quartz of massive shungite rocks. The second is hydrothermal quartz presented as consisting of in veins and veinlets [3, 5, 6].

Regardless of the rock composition, quartz of all varieties is well crystallized and is characterized by nanosized crystallites [7].

The aim of this work is to study the structure of vein quartz of shungite rocks from Zazhogino deposit of Karelia and search for ways to clean it.
2. Materials and Methods

Quartz grains were selected manually for the study (figure 1 a). Then, the obtained grain sample was ground to powder (figure 1 b) with the particle size less than 40 microns (sample 1) and was subjected to purification. To remove soluble impurities, initial quartz powder was repeatedly washed with water to obtain an aqueous suspension of quartz particles (figure 1 c) and then filtered.

![Figure 1](image)

**Figure 1.** Scheme of obtaining the samples of vein quartz:

a) quartz grains from veins of shungite rocks; b) powder after water treatment (sample 2); c) suspension passed through the filter, sample 3 was obtained after drying (sample 3).

X-ray diffraction measurements of sample performed with the laboratory diffractometer DRON-6 with a monochromated CuKα radiation source (λ = 1.54178 Å), 2θ range 19°-145.

Qualitative phase analysis and Rietveld full-profile analysis were performed using PDWin software [8].

The quartz coherent scattering region (CSR) was determined based on the maximum intensity peak of diffraction reflection (101) in the angular region 2θ from 26.54° to 26.66° according to the Debye-Sherrer formula after the application of background subtraction function:

\[
D_{hkl} = \frac{0.9 \lambda}{b \cos \theta},
\]

where \( \lambda \) is the monochromatic wave length CuKα = 1.540562 Å, \( b \) is the peak width at half the height of the line, \( \theta \) is the diffraction angle. The commonly accepted error in calculating the ACL with dimensions up to 200 nm is about 20% [9].

Using the reflection (101) which characterizes the sample as belonging to quartz, the quartz coherent scattering region was defined using the Debye-Sherrer formula (equation 1) that is assumed
to be the average crystallite size in the studied sample.

The X-ray phase analysis showed that the X-ray patterns of all studied samples are qualitatively similar and have the distinctive appearance of crystalline α-quartz.

The Rietveld method was used to specify structural and profile characteristics of X-ray patterns of the studied samples. Initial data on crystallographic characteristics, coordinates, atomic vibration parameters and thermal parameters were taken from the ICSD database.

The Rietveld method includes the refinement of structural and profile parameters. At the first stage, profile parameters are refined, such as background polynomial coefficients, profile function parameters, periods and unit cell angles. At the second stage, structural parameters, such as atomic coordinates and atomic thermal vibration coefficients, are specified. Only after obtaining satisfactory results of the refinement of the structural and profile characteristics we may then proceed to introducing impure atoms in the samples into the refinement process.

Precision study of the content of impurity elements in vein quartz of shungite rocks of Zazhogino deposit of Karelia was performed using a Thermo scientific XSeries-2 ICP-MS quadrupole mass-spectrometer with the new Wave research UPP266 Macro laser ablation attachment (Nd:YAG laser, radiation wavelength 266 nm, pulse energy 0.133 MJ, scanning speed 70 microns/s, pulse repetition frequency 10 Hz, ablation spot diameter 515 microns). The measurement error on the mass spectrometer was taken as the value of the standard deviation $S$ when determining the concentration of each element in the sample under study. The absolute measurement error, expressed in mg/kg, is equal to the value of the standard deviation, and the relative error (as a percentage) is equal to the relative standard deviation [12].

3. Results

The parameters of unit cell refined by the full-profile analysis as well as calculation reliability were estimated with the help of R-factors (Table 1). Profile (Rp) and weight-profile (Rwp) factors characterize the accuracy of agreement of the profile of the experimental and theoretical X-ray diffraction patterns in the entire range of dispersion angles (Rp) and mainly in the region of high intensity lines (Rwp), respectively. Bragg factors (Re and GoF) give an assessment of the crystal structure model.

The parameters of the quartz crystal lattice refined by the full-profile analysis method (Table 1) show that the removal of impurities from the studied samples affected the parameters of the unit cell.

| Sample | $a = b$ [Å] | $c$ [Å] | $\alpha = \beta$ | $\gamma$ [°] | Rwp [%] | Rp [%] | Re [%] | GoF |
|--------|-------------|---------|-----------------|-------------|--------|-------|-------|-----|
| Starting ICSD_174 | 4.9134(0) | 5.4052(0) | 90.0 | 120.0 | - | - | - | - |
| 1 | 4.9128(1) | 5.4038(7) | 90.0 | 120.0 | 17.16 | 12.23 | 12.89 | 1.33 |
| 2 | 4.9135(8) | 5.4046(8) | 90.0 | 120.0 | 12.02 | 9.23 | 13.01 | 0.92 |
| 3 | 4.9138(6) | 5.4048(8) | 90.0 | 120.0 | 9.14 | 7.10 | 6.40 | 1.43 |

All studied samples contain well-crystallized α-quartz as the obtained structural parameters indicate. The samples of vein quartz belong to low-temperature α-quartz since the vein quartz is characterized by trigonal lattice (they are related to P 3 2 1 2 space group) [13-15].

It is known that structural distortion can be influenced by impurity elements, adsorptive water, occurrence of OH-group instead of oxygen [16, 17]. ICP-MS is one of the basic methods of analysis of impurity content. Studies of the content of impurities in the vein quartz were carried out in Institute of Geology Karelian Research Center RAS.
Table 2. Content of impurity elements in quartz samples.

| Sample | Li, ppb | Na, ppb | Mg, ppb | Al, ppb | Ti, ppb | Ge, ppb |
|--------|---------|---------|---------|---------|---------|---------|
| 1      | 0.381   | 218.4   | 58.63   | 6.851   | 88.43   | 0.027   |
| 2      | 0.321   | 18.63   | 0.73    | -       | 0.182   | 0.015   |

The amount of structural impurities mainly depends on the genesis and thermodynamic conditions of rock formation [18]. The results presented in Table 2 show that the most common impurities are Al, Li, Na and Ge, the content of which varies depending on different treatments of the initial quartz sample and can be reduced with water treatment.

The coherent scattering region characterizes the average size of crystallites. The studied vein quartz of shungite rocks is hydrothermal quartz, so the main factor affecting the change in the parameters of the crystal lattice [17, 19] and CSR is the crystallization temperature. The CSR value is the most characterizing for determining the size of pure quartz crystallites [15-17].

In this paper, the calculation was performed using the Debye-Scherrer formula (equation (1)). Results are presented in Table 3.

Table 3. Apparent coherent length of vein quartz samples.

| Sample | ACL, nm |
|--------|---------|
| 1      | 114.69  |
| 2      | 104.28  |
| 3      | 118.67  |

The results presented above (see Table 3) show that the CSR values in the direction (101) for all samples have a size close to 100 nm. However, sample 2 is highlighted by the lowest CSR value. According to the results of studies (see Table 2, Table 3), it can be said that water treatment of the sample leads to a decrease in the content of impurity elements, and, consequently, a decrease in the size of the crystallites and stabilization of the structure. Thus, quartz of the shungite rock from Zazhogino field of Karelia has a nanometric size.

4. Conclusion

The values of crystal lattice parameters of vein α-quartz sample of shungite rocks were determined by X-ray diffraction analysis using the Rietveld method.

The coherent scattering regions of vein α-quartz sample of shungite rocks were calculated using the Debye-Scherrer formula. Quartz sample 2, treated with water, is characterized by a minimum content of impurity elements. This type of processing provides a minimum size of crystallites of vein quartz of shungite rocks.

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