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# Advantages and Limitations of Laser-Assisted Mass Spectrometry for the Local Determination of the Trace Element Composition of Fluid Inclusions in Quarzites in the Bural-Sardyk Deposit (Vostochny Sayan, Buryatia)

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**Abstract**—The effect of laser radiation on the surface and volume of natural quartz of the Bural-Sardyk deposit (East Sayan, Buryatia) is studied. The influence of the main parameters of laser radiation with a wavelength of 213 nm (prefix NWR-213) and the properties of the sample on the results of elemental mass spectrometric analysis with inductively coupled plasma are established. The features of laser ablation of various microinclusions in quartz are considered. The main problems arising from the laser evaporation of fluid inclusions in quartzites for the quantitative determination of their chemical composition are indicated.

**Keywords:** quartz, superquartzite, fluid inclusions, inductively coupled plasma mass spectrometry, laser ablation, LA-ICP-MS

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## INTRODUCTION

Today, providing the industry with high-quality quartz concentrates (highly pure quartz (HPQ)) is one of the main tasks of the federal programs for the development of the microelectronics, lighting, fiber-optic, and semiconductor industries [1]. The stricter requirements for the quality of products made from special quartz glasses have led to the rapid reassessment of the resources and reserves of natural quartz raw materials suitable for obtaining HPQ. The most stringent requirements are imposed on quartz concentrates used for melting transparent quartz glass [2, 3], tubes, and rods made of quartz glass [4, 5]. The content of impurity elements, the transmittance rate, the amount of high-temperature form of water, and the content of mineral impurities in them is limited. The composition of the residual fluid phase, which affects the quality of the glass, is not taken into account.

Quartzites of the Bural-Sardyk deposit are a promising source of highly pure quartz raw materials for a number of industries [6, 7]. The total content of ten permissible impurities in the concentrates after the first stage of enrichment is 10.1 ppm; and after the second stage, 7.2 ppm. These values are comparable with the data for ultra high purity quartz concentrates at the IOTA-4 level [8]. In [9], absorption spectra of transparently polished plane-parallel quartz glass plates with a thickness of 1.5 to 3.5 mm were measured in the spectral range from 190 to 2500 nm, and in the IR range 2500–3500 nm. The resulting glass is characterized by a high light transmission rate in a wide spectral region and this corresponds to the parameters of KI glass according to *GOST* (State Standard) *15130-86*. Glass obtained based on quartz concentrates from superquartzites had the maximum transparency.

A distinctive feature of quartzites of the Bural-Sardyk deposit, in comparison with natural quartz of other deposits [11], is the insignificant amount of structural and mineral impurities [12], as well as fluid inclusions (FI).

The residual fluid phase in quartz may contain the following impurity elements: $Na^+$, $K^+$, $Ca^{2+}$, $H_2O$ $CO_2$, CO, and hydrocarbons [13]. Raw materials with a high content of these impurities do not guarantee the production of glass that meets the technical conditions [6].

The composition of the fluid phases in quartzites can be estimated using inductively coupled plasma mass spectrometry in combination with laser evaporation (LA-ICP-MS). The method allows the analysis of small solid-phase natural objects (minerals, glass, etc.) of up to 5 μm with the simultaneous determination of a large number of elements with low and ultra low concentrations. Despite the advantages of the method, it is necessary to take into account the characteristics of the sample: size, distribution, and amount of FI. The optical transparency and fracture of quartz affect the

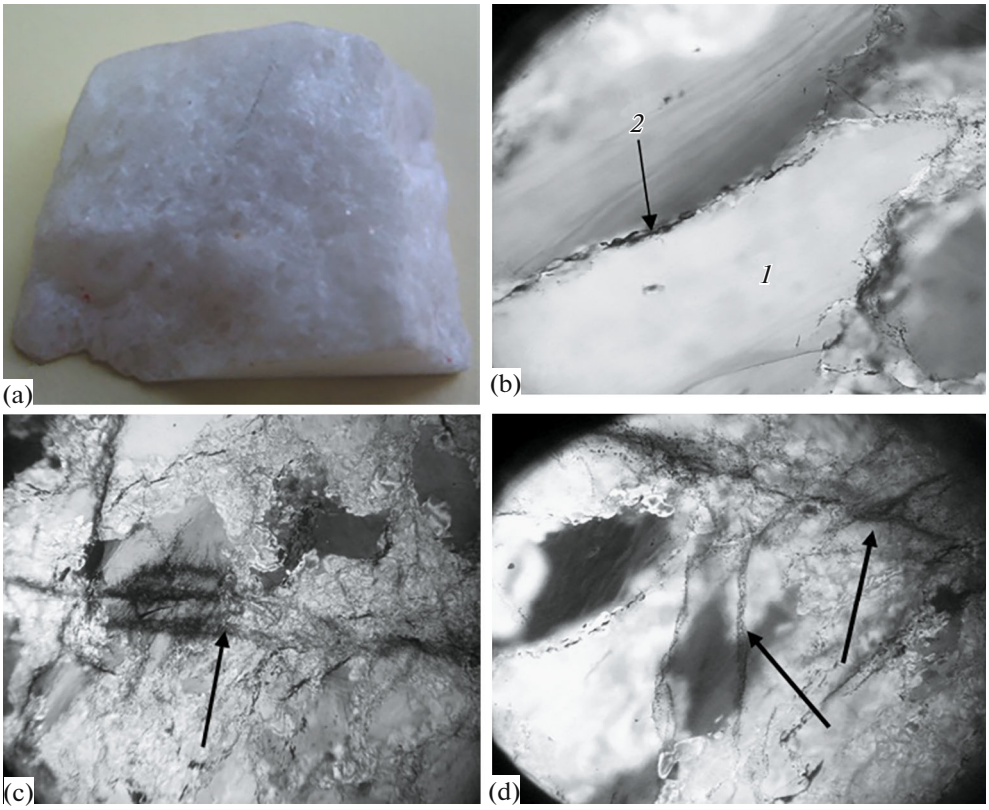


**Fig. 1.** Superquartzite. Appearance of the sample (a), quartz grains (b): large porphyry inclusions of quartz (*1*), the development of carbonaceous matter along grain boundaries in the form of: individual point inclusions (*2*); crack systems (c); crack running along the entire specimen (cracks are indicated by arrows) (d).

laser sampling process, the stability of the analytical signal, and the final results of the mass spectrometric analysis.

The purpose of the work is to study the features of the effect of laser radiation on the surface and volume of natural quartz to determine the composition of the FI, and to evaluate the interaction of the texture and structural features of quartz raw materials with laser radiation during the evaporation of natural quartz.

## EXPERIMENTAL

Two varieties of quartzites of the Bural-Sardyk deposit were investigated: superquartzite (rocks of uneven-grain structure) and fine-grained quartzite (quartz grains of slightly elongated shape and more even boundaries).

The presence of carbonaceous matter and its accumulation over weakened zones (grain boundaries and cracks) are typical of quartzites of this deposit (Fig. 1).

In the finely grained white quartzite of the Bural-Sardyk deposit (Fig. 2a), large (1.0 × 0.5 mm) quartz crystals are found among the predominantly finely grained mass; they are distributed evenly in the thin section without a clear orientation. In some areas, some grains are located subparallelly.

Roughness, cracks, and chips are visible on the polished quartzite surface; the presence of mineral phases is noted both in grain boundaries and in individual quartz grains. Large cracks were noted in the sample and the small sizes of the cracks extending from them significantly differ from the cracks in other types of quartzites under study. Cracks are found both as single cracks and in the form of systems. Large quartz grains intersect with small randomly located cracks (Figs. 2a, 2b).

Microscopic studies of transparently polished quartzite plates were performed in transmitted and reflected light using an Olympus BX 51 microscope equipped with a PixeLink 1394 camera and QImaging MicroPublisher 5.0 RTV software.

The effect of laser radiation on the surface of natural quartz using the example of determining the component composition of fluid inclusions in quartzite was studied using a laser ablation complex (LA) based on a NexION 300D quadrupole mass spectrometer (PerkinElmer, United States) and a laser platform based on a solid-state Nd:YAG laser with an operating wavelength of 213 nm NWR-213 (New Wave Research, United States). The pulse energy was 9.3 J/cm$^2$, the pulse repetition rate was 5 Hz, the number of pulses was 400, the laser beam diameter was 50 μm, the pulse

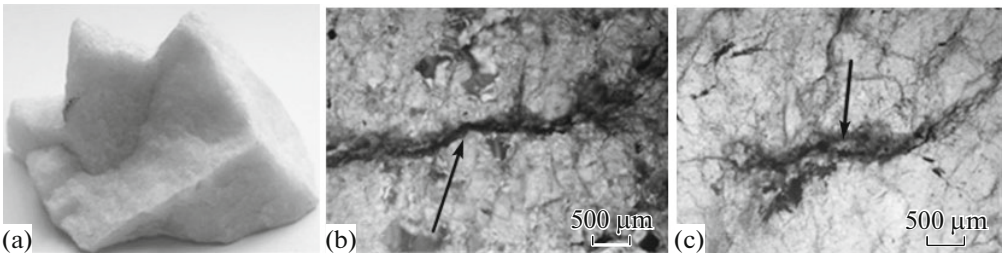


**Fig. 2.** Fine-grained quartzite of the Bural-Sardyk deposit (East Sayan). External view (a), large crack (b), smaller cracks extending from large crack (c).

duration was 4 ns, the carrier gas flow rate was 0.6 l/min He, and the carrier gas flow rate was 0.8 l/min Ar; the other gases were Plasma/Cool and Auxiliary Gas 18 L/min and 2 L/min Ar, respectively; plasma power, 1400 W; and signal accumulation time, 2 ms/cell. The use of LA for sampling in combination with a quadrupole mass spectrometer makes it possible to analyze small PVs and to reveal the presence of mineral and structural impurities in the deep layers of the material.

## RESULTS AND DISCUSSION

As a result of the experiments, a database and a file of craters [8, 14] arising from laser evaporation were formed. The main importance in laser evaporation is the crystal structure, mineral transparency, chemical composition, surface properties, and laser operating conditions (power, repetition rate, diameter of the laser beam).

The studied superquartzites for a wavelength of 213 nm are practically transparent media, characterized by a high light transmission rate: the transmittance rate is 1 $cm^{-1}$ at a depth of 20 μm [3, 10, 14]. The interaction with the laser beam occurs mainly in optically inhomogeneous regions.

When analyzing optically pure regions, the laser freely passes through these regions and interacts with impurity inclusions outside such a grain. As a result, explosive expansion occurs in areas adjacent to the grain, followed by the ejection of material from areas outside the scope of the analysis. The evaporation zone is blurred and the excess sample is captured from the adjacent area.

In [14], a local analysis of FI accumulations in superquartzite was performed, where after selecting the optimal parameters of the NWR-213 laser platform with an Nd:YAG laser, it was possible to achieve the effective evaporation of the material.

In order to determine the component composition of impurities in samples of superquartzite (Fig. 3), laser evaporation was performed on optically clean regions (Fig. 3, crater *1*) and zones with FI (Fig. 3, crater *2*). Laser evaporation of the studied material was carried out in series, each of which began with processing an optically clean region by a laser, followed by analysis of the FI accumulations.

Quartzite regions in which there are no mineral or fluid components are optically pure regions. When calculating the contents of the main elements for FI in samples of superquartzite and fine-grained quartzite, NIST SRM 612 synthetic glass was used as the standard (Table 1).

The content of potassium, lithium, boron, and aluminum in the optically clean regions and areas of FI accumulations differ insignificantly. The sodium content in areas with FI is significantly higher compared with the content of this element in areas without FI (Table 1) in the studied area. Apparently, the main alkaline element in the composition of the aqueous FI solution is sodium. This is confirmed in other works [8].

The choice of this method for determining the component composition of the FI by laser evaporation is associated with the absence of sufficiently large FI

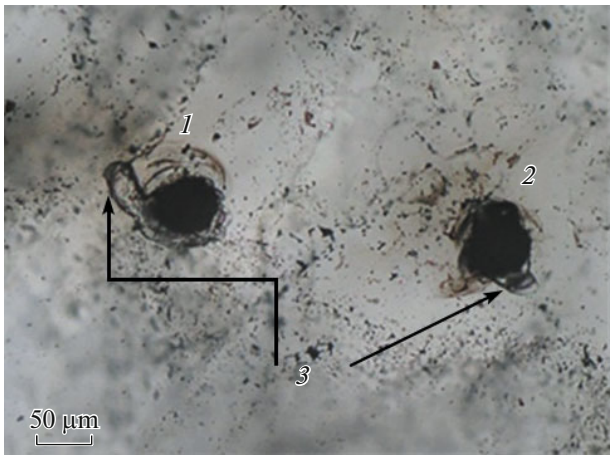


**Fig. 3.** Image of craters obtained by laser ablation of gas-liquid inclusions in superquartzite in the analyzed regions: optically clean region (the boundary of inclusions does not fall into the crater) (crater *1*), accumulations of gas-liquid inclusions (obtained from a concentrated FI cloud) (crater *2*), chips and cracks in the craters (depending on the purity of the area) (*3*).

**Table 1.** The contents of the main elements in the samples of superquartzite according to the LA-ICP-MS method (ppm)

| Area type | Mass fraction of element, ppm | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Li | B | Na | Mg | Al | P | K | Fe |
| Optically clean area | 0.20 | 0.17 | 1.04 | 3.64 | 1.48 | 2.67 | 0.43 | 3.28 |
| Area off FI accumulations | 0.74 | 0.22 | 4.29 | 5.23 | 1.70 | 3.25 | 0.67 | 3.92 |

(the size of the inclusions in the samples was not more than 12 μm). The analysis was carried out by burning areas with clusters of inclusions located as close as possible to each other (Figs. 4, 5).

A slight blurring of the ablation zone and the unwanted capture of the excess amount of the sample from the adjacent area (Fig. 3) imposes significant restrictions on the values of the determined element

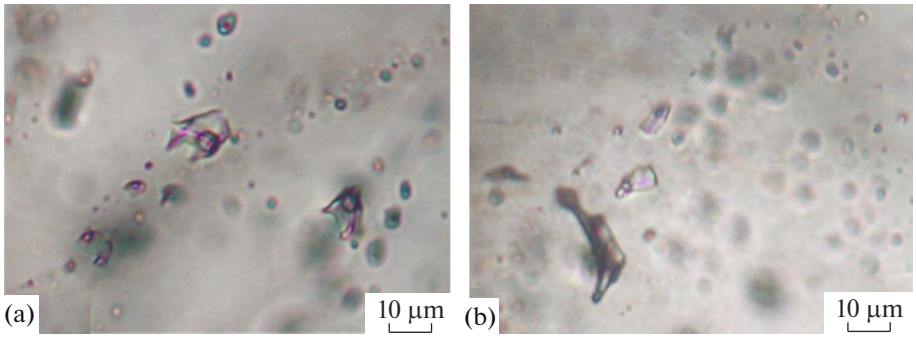


**Fig. 4.** Images of fluid inclusions in superquartzite.

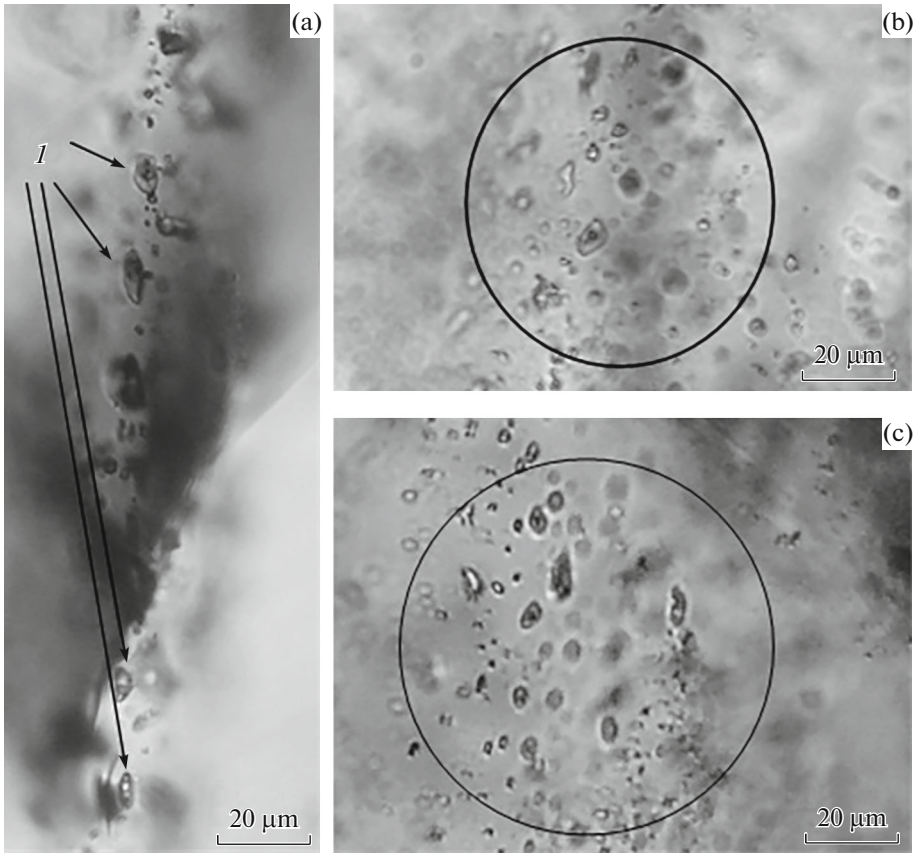


**Fig. 5.** Images of fluid inclusions in fine-grained quartzite. *1*, FI are arranged in the form of a chain (a), clusters of small inclusions located close to each other (b, c).

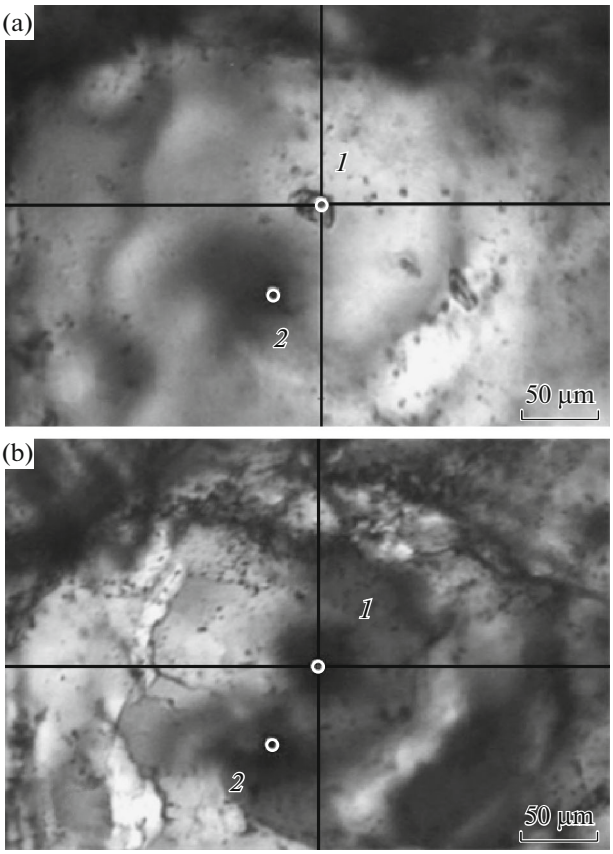


**Fig. 6.** Fluid inclusions in fine quartzite up to (a) and after laser exposure (b). *1*, *2*, fluid inclusions.

concentration (deterioration of the sensitivity and reproducibility of the method). The transparency of pure quartz for this wavelength leads to an uneven effect of radiation on the selected region, which distorts the localization of this effect.

Given these circumstances, extensive areas were selected in the sample, the work on which eliminates the influence of localization, and also allows working with large diameters of the laser beam to increase sensitivity.

For finely grained quartzite, single fluid inclusions larger than 20 μm were detected. Large inclusions in quartzites are rare. The nature of the laser evaporation of this type of quartzite was similar to the processes of laser burning in superquartzites (Fig. 6).

The amount of aerosol obtained by the laser action is proportionally related to the radiation power. There is a minimum power value at which the sensitivity of the device is not sufficient to register the selected elements.

It was found that for samples of less transparent quartz (gray and dark gray quartzites), more thorough mapping of the sample using additional methods is required, since the choice of the laser exposure zones is very difficult.

## CONCLUSIONS

A preliminary microscopic assessment revealed structural and textural features of each type of the quartz raw material under study (the presence of cracks and their orientation, carbonaceous matter, mineral and fluid inclusions). The process of laser evaporation in the grain of the mineral is individual. The quality of craters depends on the parameters of laser radiation correlated with the structural features and chemical composition of the grain of the mineral, surface properties, intrinsic structural defects, and the basic physical characteristics of the analyzed solid samples (absorption and reflection coefficients of radiation, crystal structure, etc.). The proposed method for determining the composition of elemental fluid inclusions by comparing the signals of a clean region and a region with clusters of small PVs makes it possible to estimate the elemental composition of small PVs, improve the positional accuracy of the analysis (localization of the evaporation zone), and to a large extent eliminate the deterioration of the stability of the analytical signal by the material from the chips of the sample.

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