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Using Laser Ablation to Study Gas–Liquid Inclusions in Natural Quartz via Mass Spectrometry with Inductively Coupled Plasma

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Abstract—Gas–liquid inclusions of superquartzites from the the Bural-Sarjdag mines are studied using a laser ablation complex based on a NexION 300D quadrupole mass spectrometer. It is found that the results from mass spectrometric elemental analysis with inductively coupled plasma are influenced by the main parameters of laser radiation with a wavelength of 213 nm (using an NWR-213 platform) and by a sample's properties.

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INTRODUCTION

The problem of obtaining superpure quartz materials has grown recently, due to the development of high technology. World markets for high purity quartz concentrates with production volumes of more than 60 thousand tonnes per year for the melting of quartz glasses include the following main areas of production: semiconductor (crucibles used in the production of monocrystalline quartz, diffusive reactors, and holders and containers for silicon plates); photometric (tubes for tungsten halogen and mercury-discharge lamps used in street lighting and spotlighting); fiber (waveguide lines, holders); optical (mirrors, prisms, lenses); special-purpose glasses (reactors, liquid-crystal glass, fiberglass, and glass fiber cloths); and research instrument (epoxy fillers, tubes, chambers, chemical glassware).

One of the most important factors of such raw material for monocrystal synthesis and glass melting is the content of impurity elements (e.g., sodium, potassium, aluminum, and titanium). Quartz contains these impurities in the form of mineral gas–liquid inclusions (GLIs), and they are localized in the quartz crystalline structure.

Gas–liquid inclusions are hermetically isolated spaces inside a mineral and are filled at room temperature with either liquid, gas, or liquid–gas mixtures in different volume ratios, and often with solid phases in the form of minerals of different compositions. Gas–liquid inclusions form during the growth of minerals (primary and imaginary secondary inclusions), or after their final crystallization. When this happens, some of the GLIs are localized in very thin healed cracks (secondary inclusions). In both cases, mineral-forming solutions are encapsulated in the inclusions, but only in the first case does the mineral consume microportions of the solutions from which it is crystallized as it grows. In the second case, the inclusions store solutions that are unrelated to the growth of the mineral in which they are contained but are later characteristic of the conditions of mineral formation. The content of inclusions in a mineral is enormous. Transparent minerals are often turbid, milky, or grey, depending on the gas–liquid inclusions they contain [1].

Gas–liquid impurities play a key role in superpure quartz concentrates. Since these impurities are found in the crystalline quartz structure both in the form of inclusions (in vacuoles) and in molecular-dispersion dissolved form, they are quantitatively most important and thus determine the transparency or vesicular structure of the resulting quartz glass, along with many more of their important properties [2]. Gas–liquid inclusions cannot be completely removed via enrichment processes, but they can served as a criterion for the enrichment limits of different natural quartz materials. It was noted in [3] that inclusions can act as modified impurities and determine the structure and properties of manufactured cristobalite. It was also noted that in a number of cases, gas–liquid inclusions play the role of the mineralizers, while a cristobalite phase is born and develops in regions of increased GLI concentration (i.e., in cracks). During cristobalite formation, however, these regions are saturated with the centers of nuclei of the new phase (cristobalite) and are characterized by weakened mechanical strength and excess surface energy, affecting the properties of the final product.

The main ways of studying impurities in quartz are usually divided into two groups: nondestructive and destructive. The first group involves studying the composition of liquid, solid, and gas phases without the opening of inclusions; infrared (IR) and ultraviolet

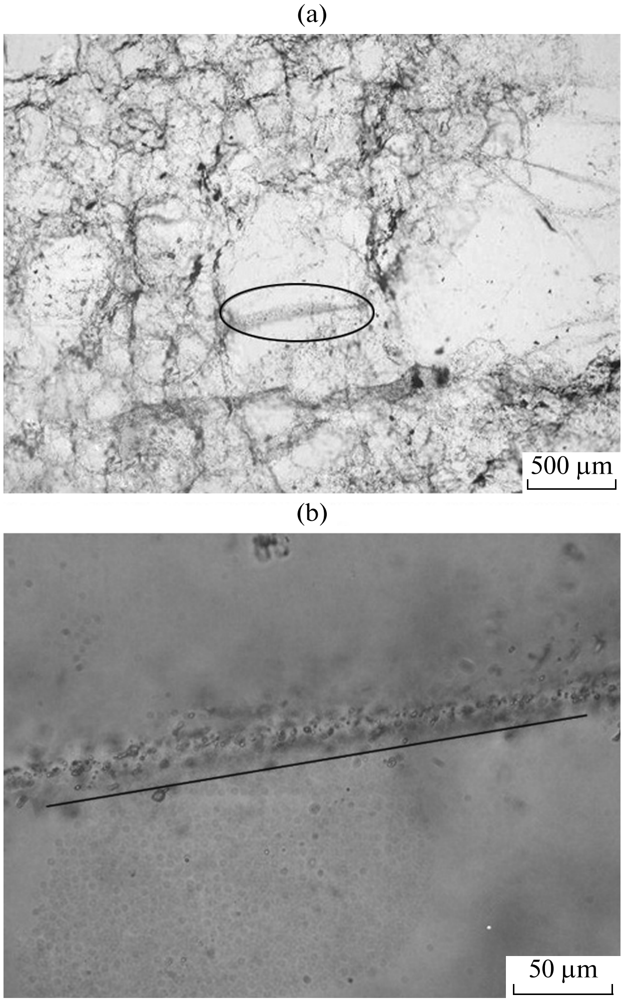

Fig. 1. Images of secondary GLIs in superquartzite, concentrated along a crack at different microscope magnifications (a, b). The photo was taken with a PixeLink 1394 camera mounted on an Olympus C-4000 microscope.

(UVP absorption, traditional microscopy, and Raman spectroscopy all belong to this group [1]. Destructive methods enable us to open up, extract, and analyze gases and liquid inclusions by means of mass spectrometry and gas chromatography, along with microanalysis based using different kinds of radiation (i.e., laser and electron microanalyzers or scanning electron microscopes).

Current geochemical studies are largely based on mass spectrometry data, and the devices used most widely are ones that excite the mass spectra of investigated samples in inductively-coupled plasma (ICP). ICP mass spectrometry (MS) is a state-of-the-art method of high-sensitivity analysis that allows us to determine simultaneously a large number of elements within low and ultra-low detection limits (μg/t). ICP-MS is one way of analyzing multielement and isotopic solutions. The invention of high-power lasers solved the problem of directly analyzing the microelement contents of such solid-phase objects as natural minerals, metals, and glasses [4].

The most informative and sensitive way of studying GLIs is currently mass spectrometry using inductively coupled plasma and laser evaporation (i.e., laser ablation, or LA). Using laser evaporation in combination with ICP-MS for sampling allows us both to exclude the problems associated with converting investigated samples into solutions and the introduction of unwanted contaminants into samples, since there is no decomposition (dilution) stage. It allows enables us to perform local studies of quite small (up to 5 μm) defects on sample surfaces and different inclusions in a material's deep layers.

When laser radiation interacts with opaque solid bodies (minerals), three stages of the process can be distinguished: (1) heating without changing the phase state; (2) melting and evaporation; and (3) material ionization and plasma initiation. This method has been used routinely in many analytical laboratories around the world, but it requires detailed workup of the initial analysis stage: evaporating the sample and creating necessary particle aerosol for a plasma burner while minimizing the effects of sample element fractionation [4].

The aim of this work was to study the possibility of using the laser evaporation (ablation) of gas–liquid inclusions in natural quartz for subsequent analysis of the obtained aerosol via mass spectrometry with inductively coupled plasma and establishing the parameters of the NWR-213 laser platform using a Nd:YAG laser for effective and constant evaporation of a material.

EXPERIMENTAL

In this work, we studied superpurity quartzites from the Eastern Sayan Mountains (Buryat Republic, Russia). These quartzites are referred to as superquartzites to distinguish their distinctive properties from those of other quartzites. Superquartzites are thus characterized by their high chemical purity and almost complete monomineralization [5].

Transparent polished superquartzite plates from the Bural-Sarjdag mines were microscopically studied using an Olympus C-4000 microscope. A great number of secondary gas–liquid inclusions were found in examining the plates (Fig. 1). Their sizes varied from 4 to 8–10 μm in diameter, making it difficult to study the inclusions and considerably reducing the number of ways to determine their compositions.

The same samples with their areas of GLIs identified and noted were then studied using a laser ablation setup based on a NexION 300D quadrupole mass spectrometer (PerkinElmer, United States) and an NWR-213 laser platform (New Wave Research, United States) containing a Nd:YAG solid-state laser with a working wavelength of 213 nm. The energy in each pulse was 0.07 J/cm^2; the pulse repetition frequencies were 1, 3, 5, 10, and 20 Hz; the number of

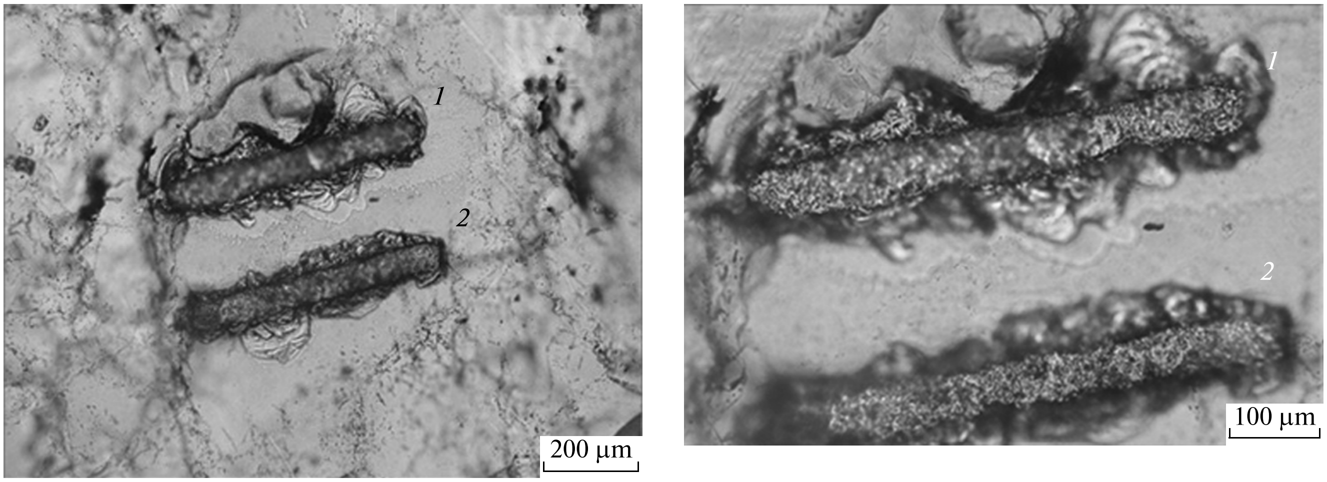

Fig. 2. Typical images of the pits resulting from the laser ablation of GLIs in superquartzite at a laser pulse frequency of 5 Hz, a pulse energy of 0.07 J/cm^2, and a beam diameter of 65 μm. The number of pulses was 400. The photos were taken with a PixeLink 1394 camera mounted on an Olympus C-4000 microscope. (*1*) optically pure area, (*2*) GLI agglomerates in a line.

pulses was 400; the ablation spot diameter was 65 μm; and pulse duration was up to 4 ns. The combination of an LA platform and a NexION 300D quadrupole-type ICP mass spectrometer allowed us to analyze the rapidly changing composition of a sample's aerosol efficiently.

RESULTS AND DISCUSSION

Laser melting and evaporation depend on the radiation parameters (wavelength, power, probe energy density, frequency, and number of pulses) and the sample's chemical composition, mineral structure, and mineral optical transparency [6]. The results, quality, and reproducibility of an analysis of the resulting pits, play a secondary role. The reference point is the monodispersion of the aerosol obtained from a sample, estimated from the stability of the analytical mass spectrometer's signal. These factors depend on the optimization of the selected laser parameter and the correspondence between the laser characteristics and the nature of the sample.

Radiation with a wavelength of 213 nm is absorbed quite efficiently by superquartzite, but quartzite of such purity also has a number of unique characteristics that affect analysis.

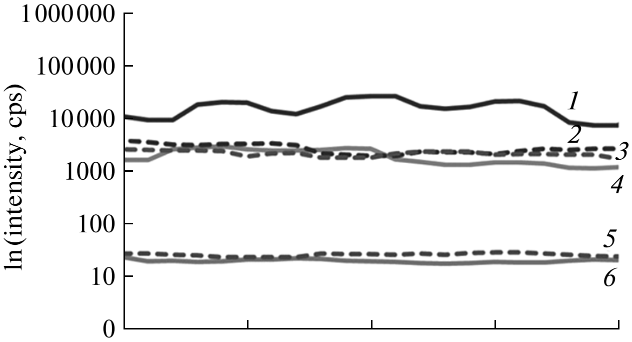

Fig. 3. Typical dependences of the relative intensities of potassium isotope lines on the laser pulse repetition frequency at intervals with different optical densities. The line intensity dependences were obtained on a NexION 300D mass spectrometer with laser platform based on an NWR-213 Nd:YAG solid-state laser. The abscissa axis is reduced to the length of the area subjected to laser ablation. Relative intensity curves *1*, *4*, and *6* were registered for the optically pure area at laser pulse repetition frequencies of 5, 3, and 1 Hz, respectively; curves *2*, *3*, *5* are for the area of GLI agglomerates at laser pulse repetition rates of 5, 3, and 1 Hz, respectively.

At this wavelength, the investigated superquartzites are virtually transparent media and interact with the laser beam mainly in optically inhomogeneous regions (the average absorption coefficient of a sample is 75% at a wavelength of 213 nm). This leads to blurring of the evaporation region and the undesired capture of excess amounts of the sample from the surrounding area. When analyzing the optically pure regions, the laser thus passes freely through them and interacts with the impurity inclusions adjacent to such grains (Fig. 2, region *1*). As a result, there is explosive expansion in the areas adjacent to a grain with the subsequent injection of material from the regions not analyzed. As was mentioned in [4], the quality of the pits depends on the laser radiation parameters in combination with features of the mineral's grain structure, chemical composition, and surface properties, along with the number of impurities and intrinsic structural defects, and the optical transparency.

As was mentioned in [7], the ratio of depth to width should be 1 : 1 or less to prevent a pit chipping and cracking upon LA. This can be achieved at laser pulse repetition frequencies of 1–3 Hz. At such low pulse frequencies, no reduction in analytical signal stability is registered, making it impossible in our case to determine the signal : noise ratio (Fig. 3, curves *1* and *2*). It was found that using a pulse repetition frequency of 10 Hz and higher results in considerable uncontrollable crumbling of the quartzite; at lower frequencies of laser radiation, however, this effect was rarely observed. This effect substantially impairs the accuracy and reproducibility of ICP-MS-LA analysis results.

Since the amount of aerosol obtained per sample is proportional to the radiation power, the amounts of superquartzite needed for mass spectrometric analysis cannot be evaporated at lower powers. Raising the radiation power helps in turn to boost the analytical signal, but local analysis is not possible under such conditions due to increased sample chipping.

It should be noted that the laser ablation of individual GLIs and their agglomerates in the superquartzite exhibited rather distinct behavior. To optimize the experimental conditions and improve data sensitivity and reproducibility, the problem of optically transparent material evaporating must be solved by properly selecting the power parameters, laser beam diameter, and regions with the optimum size of single inclusions. The optimum parameters in the available ranges were pulse repetition frequency, 5 Hz (1–20 Hz); pulse energy, 0.07 J/cm^2 (up to 6 J/cm^2); and beam diameter, 65 μm (3–110 μm).

CONCLUSIONS

Systematic experimental data were obtained on the effect the main parameters of laser radiation and sample properties have on elemental ICP mass spectrometry results. It was shown that laser ablation in each specific case exhibited rather distinct behavior, so further detailed studies are needed to improve the analytical characteristics of analyzing gas–liquid inclusions along with mineral and other impurities by means of LA-ICP-MS, and to optimize the conditions for the laser ablation of superquartzite samples and quartzes in general. The main problems of material crumbling and chipping when turning the required area of a sample into an aerosol were identified.

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