Production of pure raw quartz by enriching quartzites

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Abstract. The sedimentary metasomatic quartzites of Antonovsky deposits (Western Siberia) almost completely consist of high-density α-quartz micrograins. The grain purity is conditioned by self-purification of quartz microgranules in the process of lithification. The work proposes an effective aeromechanical technology for deep purification of quartz microgranules by applying high-temperature chemical exposure to produce commercial raw quartz.

1. Introduction
Quartz-containing rocks (quartzites, quartz sandstone, quartz sands and sand-gravels) are traditionally used as fluxing agents and raw materials for producing ferroalloys and refractory materials in chemical, glassware, building and other industries. The global production and consumption market of raw quartz is currently characterized by a consumer boom in chemically pure quartz varieties. Such an interest is associated with high technology application in producing items for semiconductor microelectronics, special materials for optical and acoustic electronics, optical fiber systems, nanomaterials, unique ceramic materials and silicon carbide (SiC) and silicon nitride (Si₃N₄)-made products for ferrous and nonferrous metallurgy, chemical industry. However, of great commercial importance is the increasing demand for crystalline silicon conditioned due to the development of helioenergetics and establishment of photoelectric plants with implemented silicon-based elements that transform solar radiation into electric energy. The principal limitation of the wide-scale application of ground solar energy systems is the high price of "solar-quality" silicon. Therefore, the current targets are both to develop new production technologies for "solar-quality" silicon, which, in its turn, would drastically reduce its cost, and to select such refined industrial silicon that would be a carbothermal renewable natural quartz, i.e. rock crystal. With due consideration Due to the limited distribution and depletion of conventional pure raw quartz (rock crystal) deposits, there is no doubt in the relevance of the problem in estimating the quality and industrial application potential of abundant quartz rocks. As quartzites have similar properties, they could be a promising source of highly-pure raw quartz materials.

In this case, quartzites of Antonovsk deposits (Kemerovo Oblast, Russia) with estimated reserves of 660 mln tons and currently used as raw source for ferrous metallurgy is of great importance. [1-3] Due to specific formation conditions, Antonovsk quartzite deposits (Kemerovo Oblast) could be a potential high-quality raw quartz source [1, 2].

2. Research Methods and Results
The results of mineralogical and geochemical studies showed that these quartzites are monomineralic rocks with rather high quartz content. Quartzites of sedimentary metasomatic origin almost completely consist of high-density $\alpha$-quartz micrograins varying from 0.01 to 50 microns, the purity of which is conditioned by quartz microgranule self-purification during lithification in the early metagenesis of quartz-hydromica-sericite series [4]. Within local areas, particularly in significant crushing zones, the hypergene processes destroy the quality characteristics of chemically pure quartzites which determine the primary industrial grades of quartzites. However such rocks do not contain poisonous or toxic elements (table 1).

| Grade / element content [10^{-4} %] | U   | Th | Yb | Sm  | La  | Hf  | Au  | Ag  | Tb  | Sc |
|-----------------------------------|-----|----|----|-----|-----|-----|-----|-----|-----|-----|
| KR-2                              | 0.2 | -  | -  | 0.5 | 0.3 | 1.3 | 0.005 | -  | -   | 0.8 |
| KF                                | 0.4 | 0.6| 0.2| 0.7 | 0.6 | 1.1 | -   | -   | -   | 1.0 |
| KSh                               | 0.4 | 0.6| 0.2| 0.8 | 0.8 | 1.2 | -   | -   | -   | 2.4 |

**Table 1.** Average content of rare, radioactive and rare-earth elements in quartzites of different industrial grades

The most pure quartzites exhibit a low quartz microgranule crystallinity degree [5, 6], lack of isomorphic replacements and impurity ions (Al, Fe, Ti, Na and other) in the $\alpha$-quartz crystal phase.

The estimation of boron and phosphorous concentrations of more than 1 ppm is of particular importance and, which, in its turn, restricts the production application of raw quartz for "solar-quality" silicon, where they are doping additives changing the conductivity type of semiconducting silicon, and quartz and special borosilicate and borophosphate glass products, whereas such elements are modifying cations.

Secondary ion mass spectrometry (SIMS) with sensitivity to practically all isotopes of $\sim$ 0.1 ppm detects boron and phosphorous in quartz grains. The isotope spectra were measured by a focused ion beam from the surface of specially prepared quartzite samples on molybdenum support, and from a quartz grain. Preliminary sample surface argon etching was applied to remove surface defects.

The panoramic SIMS spectra registered the isotopes of those chemical elements that comprise the molybdenum support (Mo$^{90}$…Mo$^{100}$, Fe$^{56}$, Sc$^{45}$, C$^{12}$, N$^{14}$ and others) and in the studied quartzites (Si$^{28}$, Al$^{27}$, K$^{39}$, O$^{16}$, Na$^{23}$ and others). The content of such elements in initial raw quartzites is 10 times higher than in granulated quartz (Malo-Kutulakskoe deposit, Yakutia). However, after crushing and purification by proposed aeromechanical separation method, the impurity element content in quartzites decreases, while in granulated quartz samples it remains unchanged. It could be assumed that the chemical impurity elements in quartzites of accessory minerals and authigenic films within intergranular space can be removed by such methods as mechanical separation and chemical etching, whereas their extraction excludes special purification methods in alloy.

Special experimental SIMS methods in relevant recording range (figures 1 and 2) were employed to detect boron and phosphorous in quartzite grains from Antonovsk. Figure 1 depicts a detailed spectrum of detected ions within the range of 9 … 17 AMU (atomic mass unit). The spectrum clearly showed the isotopes of carbon C$^{12}$ and oxygen O$^{16}$. The attempts to detect the presence of ions of boron B$^{11}$ by mathematical modeling failed.
The presence of phosphorous $^{31}$P ions (figure 2) in enriched quartzites was not detected, in spite of the fact that certain quartzites were identified in phosphorous pentoxide by chemical analysis. Atomic emission analysis and Rutherford back-scattering method also indicated the absence of phosphorous ions in enriched quartzites.

The obtained results showed that under such quartzite formation conditions the self-purification of quartzites (autolysis-accompanied crystallization) and the reverse process - infiltration of other chemical element ions into the quartzite crystal lattice did not occur.

Veined and granulated quartz due to close ion radii demonstrate the isomorphic silicon ion replacement effect by aluminum and phosphorous ions, while isomorphism was not observed in studied quartz grains in sedimentary metasomatic quartzites.

It should be noted that neutron activation analysis, spectral analysis and ICP-MS method indicated different chemical element impurity content in the initial quartzite samples which is typical for accessory minerals. Ferrum oxides, feldspar, hydromica, illite and chlorite were identified along quartz recrystallized cracks, boundary fractures and in intergranular space.

All these impurities (besides ferrum oxides) are easily removed by vibrational screening and further flushing. Ferrum oxides as authigenic films developing on the surface of quartz grains are difficult to process. In some cases, in order to satisfy the high requirements for raw quality, deep
enrichment of quartzites by a complex of mechanical, chemical, thermal and other methods should be performed. Highly pure fine-grained Antonovsk quartzites, slightly containing harmful structural impurities, could be easily enriched in contrast to monocrystalline raw materials which that require special purification in alloy.

Considering the uniqueness of the Antonovsk microquartzites formation conditions an effective aeromechanical technology was developed for profound purification under high-temperature chemical exposure. This technology has embraced the best features of existing technologies [7]. Fine raw material purification is performed for 5 …… 200 mcm grains in an aeromechanical reactor, where the material is further milled simultaneous deslurring and thermochemical treatment, which, in its turn, produces high quality quartzites with SiO$_2$ content - 99.96% and more (table 2).

| Sample name | SiO$_2$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | TiO$_2$ | Ignition loss |
|-------------|---------|-------------|-------------|---------|---------------|
| Initial quartzite | 98.89   | 0.45        | 0.3         | 0.01    | 0.35          |
| Fraction of 1 mm (enriched) | 99.58   | 0.1         | 0.3         | 0.025   | -             |
| Fraction of 0.4 mm (enriched) | 99.79   | 0.008       | 0.3         | 0.022   | 0.04          |

**Table 2.** Content alteration of certain oxides in quartzites as a result of aeromechanical separation

### 3. Conclusion

The conventional methods for enriching raw quartz decrease several-fold the total mass fraction of impurity element content, for example, electromagnetic separation – 4 -fold, electrostatic separation - 10-fold, chemical treatment-25-fold, and foam flotation - almost 100-fold. However, preliminary enrichment of rough material during extraction regional enterprises is recommended, while fine enrichment should involve the following high-tech operations: electric-impulse destruction of raw materials, high-intensity magnetic separation, ultrasonic purification of disintegrated particle surface, with further express-control of product quality and raw material loss during each technological stage.

Proposed advanced technology including aeromechanical separation under high-temperature and chemical exposure was developed for fine purification of unique Antonovsk quartzites, producing commercial-grade raw quartz after the first enrichment cycle (table 3).

| Purpose | Grade | Component content [%] | Coarseness [mm] |
|---------|-------|-----------------------|-----------------|
| Production |        | SiO$_2$ not less than | Fe$_2$O$_3$ not more than | Al$_2$O$_3$+CaO not more than |
| green SiC | top   | 99.5                  | 0.1             | 0.3             | 5.0 – 0.5         |
| black SiC | first | 99.0                  | 0.2             | 0.5             | 5.0 – 0.5         |
| Antonovsk quartzite (after the first enrichment cycle) | 99.58 | 0.100                | 0.30            | 1.0             |

**Table 3.** Technical conditions for raw quartz for the production of silicon carbide
References

[1] Ananyeva L, Ananyev Yu, Dolgov I, Korobeynikov A and Korovkin M 2001 J. Izvestaya Tomsk Polytechnic University 304 (1) 123
[2] Ananyeva L and Korovkin M J. Izvestaya Tomsk Polytechnic University 306 (3) 50
[3] Korovkin M, Ananyeva L and Antsiferova A 2012 J. Izvestaya Tomsk Polytechnic University 320 (1) 16
[4] Korovkin M and Ananyeva L 2012 Mineralogy, geochemistry and mineral resources of Asia B 2 139
[5] Korovkin M, Ananieva. L and Antsiferova A 2011 Proceedings of the 10th International Congress for Applied Mineralogy (ICAM), Trondheim, Norway 403
[6] Razva O, Anufrienkova A and Korovkin M 2014 J. Modern knowledge-intensive technologies 7-2 27
[7] Korovkin M, Ananyeva L, Antsiferova A and Ginsar V 2010 Proceedings of the 10th International Research and Practice Conference for Study, Development and Application of High Technologies in Industry, Saint-Petersburg, Russia 245