

Quartz Concentrates from Quartzites of the Eastern Sayan

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Abstract—Results from studying quartzites of the Bural–Sardyk deposit in the quartz province adjacent to Lake Baikal are presented. These quartzites are a potential source of quartz raw material. The most promising quartzites of the deposit are briefly described. The effect heat treatment has on the depth of chemical enrichment is determined. The prospects of using quartzites in the production of quartz concentrate are examined.

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INTRODUCTION

Depending on their physicochemical properties, quartz concentrates are used in the semiconducting, light engineering, fiber optical, and optical industries, along with special-purpose glass, scientific tools, and so on [1].

The strictest technical requirements are imposed on quartz concentrate used to produce transparent quartz glass. The requirements on the quality of the final quartz products are summarized in specifications TU 5726-002-1149665-97.

The most widely known company that produces extra pure quartz (EPQ) is UNIMIN (United States), with its product IOTA High-Purity Quartz (IQ). It is considered to have an almost complete monopoly in the market for EPQ (around 70% of all consumers choose this grade). The technological characteristics of this product are therefore standard.

Vein quartzes of different geological and genetic types are traditionally used to produce high and ultra-high purity quartz concentrates [2]. Such veins generally have little in the way of reserves and are of heterogeneous chemical composition. Unlike vein quartz, quartzites from the Eastern Sayan have a high degree of homogeneity and are of high purity [3, 4].

The aim of this work was to study quartzites from the Bural–Sardyk deposit as nontraditional quartz raw material for the production of quartz concentrates, and to develop ways of producing high-purity quartz concentrate.

OBJECT OF STUDY

The Bural–Sardyk deposit is confined to siliceous–carbonaceous rocks of the Irkutnaya suite that make up one of the thrust slices. Of main industrial interest are the areas of the processing of sedimentary–metamorphogenic flinty dark microquartzites,

where pale new growths of superquartzites are formed. These are characterized by almost complete monominerality and elevated chemical purity [3, 4].

Traditional microscopic studies reveal inclusions of coaly matter in superquartzites that can be traced along cracks and pointwise along the grain boundaries. In addition, we observe fluid inclusions (gas–liquid inclusions) confined either to zones of growth or to cracks that form during brittle deformation. Single inclusions of several independent mineral phases (e.g., dickite, alunite, pyrite, and muscovite) have been found in quartzites [5].

EXPERIMENTAL

Elemental composition was determined by means of inductively-coupled plasma mass spectrometry. This method is based on the preliminarily concentrating impurities by removing the principal element (silicon) in the form of tetrafluoride, producing an impurity solution in nitric acid, and subsequently measuring the intensity of the ion current (or the number of pulses per unit of time) generated during ionization of the obtained solution in the inductively-coupled plasma of a mass spectrometer [6].

Gas–liquid inclusions were studied via kinetic thermal desorption mass spectrometry and quantitative analysis of the flows of matter released into the high vacuum when a sample with a certain degree of dispersion was heated from room temperature to 1400°C with a stepwise regime of heating.

The phase composition of quartzites was determined via X-ray phase analysis, for which we used the EVA software from the Bruker DIFRAC.PLUS software package. We used a structural database to calculate the weight percent of quartz and cristobalite in each sample. Our studies were performed on a D8 Advance diffractometer with $\text{CuK}\alpha$ -radiation, a

Table 1. Content of the main impurities in gas–liquid inclusions, ppm

Sample	H ₂ O			CO ₂	CO	C _x H _x	ΣC	H ₂	HCl	H ₂ S	SO ₂
	<600°C	>600°C	total								
Kyshtym deposit, vein 175, initial [7]	56	9.7	65.7	146.2	41.7	13.5	70.4	3.62	0.02	0.09	0.15
Kyshtym deposit, vein 175, enriched [7]	4.6	9.2	13.8	1.6	3	1.1	2.6	0.24	0	0	0
Superquartzite 78/1	58.2	65.7	123.9	2.4	9.4	3.7	7.9	0.21	1.87	0.78	0.15
Superquartzite 78/2	44.5	50	94.5	1.6	5.5	1.0	3.7	0.04	1.84	0.55	0.21
Fine-grained quartzite 124/c	77.9	77.0	154.9	4.3	6.9	3.8	7.4	0.28	0.32	0.09	0.04
Superquartzite 80/1	11.1	27.8	38.9	1.3	3.6	3.0	4.5	0.10	0.02	0.16	0.01
Superquartzite 116/1	42.0	3.9	45.9	0.4	4.4	4.8	6.2	0.05	0.02	0.01	0.00
Unimin Corp Iota-standard	18.6	17.2	35.8	1.3	4.5	3.9	5.7	0.51	0.21	0.01	0.03

Goebel mirror, $V = 40$ kV, and $I = 40$ mA using the powder method.

**QUANTITATIVE STUDY
OF GAS–LIQUID INCLUSIONS
IN QUARTZITE FROM THE BURAL–SARDYK
DEPOSIT BY MEANS
OF MASS SPECTROMETRY**

Measurements were made by V. A. Kreisberg at Moscow State University's Faculty of Chemistry. Quantitative estimates of the contents of gas–liquid and gas–forming impurities were made for nine samples of quartzite grit from the Bural–Sardyk deposit via mass spectrometry. Table 1 presents the results from studying five samples:

1. Sample 78/1, hand-picked superquartzite. A 5–25 mm lump was treated with 10% hydrochloric acid for 1 h at room temperature with no thermal crushing. After grinding, a fraction of 174–450 μm was identified.

2. Sample 78/2, hand-picked superquartzite. A 5–25 mm lump was treated with 10% hydrochloric acid for 1 h at room temperature with no thermal crushing. After grinding, a fraction of 450–800 μm was identified.

3. Sample 124/c, hand-picked fine-grained quartzite. A 5–25 mm lump was treated with 10% hydrochloric acid for 1 h at room temperature with no thermal crushing. After grinding, a fraction of 174–450 μm was identified.

4. Sample 80/1, hand-picked superquartzite. A 5–25 mm lump was treated with 10% hydrochloric acid for 1 h at room temperature, followed by thermal crushing at a temperature of 900°C for 30 min. After grinding, a fraction of 174–450 μm was identified.

5. Sample 116/1, hand-picked superquartzite. A 5–25 mm lump was treated with 10% hydrochloric acid for 1 h at room temperature, followed by thermal crushing at a temperature of 900°C for 2 h. After

grinding, a fraction of 450–800 μm was identified. It was then calcined in argon at a pressure of 1.25 atm and a temperature of 1455°C for 9 h, and the calcined part was easily broken by a pestle. After grinding, a fraction of 174–450 μm was identified. The content of cristobalite was 91%.

Table 1 presents the values of water exudation at different temperatures of stepwise heating, along with the quantity of the low-temperature form of water discharged due to decrepitation and surface dehydroxylation, along with a quantity of a high-temperature form of water diffused from the structure at high temperatures, starting at 600°C. The quantity of water discharged at temperatures above 1400°C was calculated by approximating the kinetics of water discharge at 1400°C. In Table 1, the content of the two forms of water (low- and high-temperature) is calculated with respect to the correction for the partial overlapping of different forms of water at temperatures of 600–800°C and corresponds to the more accurate computer separation of these two forms. It also presents the results from earlier analyses of samples of Unimin reference quartz grit.

Quartz concentrates can be divided into 5 groups, according to the content of the high-temperature form of water: 0th group, up to 20 ppm ($\mu\text{g g}^{-1}$) of water (where ppm is parts per million by mass); 1st group, 20 to 40 ppm of water; 2nd group, 40 to 80 ppm of water; 3rd group, 80 to 150 ppm of water; and 4th group, more than 150 ppm of water. Quality quartz glass can be produced from the raw material of the first four groups (0th to 3rd) for different purposes by varying the means of melting [7].

According to the content of the high-temperature form of water, the investigated samples of quartzite grit from the Bural–Sardyk deposit belonged to the 0th group of quality (calcined cristobalitized sample of superquartzite 116/1); sample 80/1 of thermally crushed superquartzite belonged to the 1st group; and nonthermally crushed samples of fine-grained quartz-

Table 2. Temperatures and kinetics of the quartz–cristobalite phase transition, %

Type of quartz	60 min		90 min		180 min	
	1400°C					
	phase of quartz	phase of cristobalite	phase of quartz	phase of cristobalite	phase of quartz	phase of cristobalite
Fine-grained quartzite	97	3	96	4	96	4
Superquartzite	99	1	97	3	96	4
	1450°C					
Fine-grained quartzite	91	9	84	16	46	54
Superquartzite	–	–	98	2	75	25
	1500°C					
Fine-grained quartzite	60	40	57	43	9	91
Superquartzite	98	2	79	21	73	27
	1550°C					
Fine-grained quartzite	21	79	11	89	6	94
Superquartzite	75	5	55	45	–	–

ite and superquartzite 78/1, 78/2, and 124/c belonged to the 2nd group of quality.

With respect to the content of high-temperature water, cristobalitized sample of superquartzite 116/1 surpasses the Unimin reference samples of quartz and the quartz concentrate produced at the Kyshtym Mining and Processing Plant (Table 1).

PHASE TRANSITIONS

Studying the characteristics of phase transitions is an important stage in developing processes of quartz concentrate production. Due to the changes in the parameters of a crystal lattice at the temperature of phase transitions, gas–liquid inclusions actively open up.

The first phase transition recorded in quartzites of the Bural–Sardyk deposit was the transition of low-temperature α -quartz to high-temperature β -quartz, observed at 574°C. The temperature of the phase transition was measured via differential scanning calorimetry. During the $\alpha \leftrightarrow \beta$ -quartz transition, the Si–O–Si bond angle changed, resulting in an increase in specific volume (by ~4%) that was accompanied by one in the structural channels, thus leading to the partial destruction of monolithic blocks of the initial raw material. The $\alpha \leftrightarrow \beta$ -quartz transition is used in thermal crushing. Based on the results from studying the quality of the gas–liquid inclusions in the quartzite from the Bural–Sardyk deposit by means of mass spectrometry, we conclude that the process of thermal crushing in the quartzites from the Bural–Sardyk deposit was accompanied not only by a reduction in the material's strength, but also by discharges of low- and high-temperature water (Table 1). In quartzites sub-

jected to thermal crushing during the $\alpha \leftrightarrow \beta$ -quartz transition, the concentration of low-temperature water fell by more than five orders of magnitude; the concentration of high-temperature water, by more than two orders of magnitude.

The second phase transition recorded in the quartzites from the Bural–Sardyk deposit was the β -quartz– α -cristobalite transition, during which the specific volumes grew (by almost 8%) due to the increase in structural channels, which was accompanied by the opening of gas-liquid inclusions [8]. Based on our X-ray phase analysis, we concluded that neither variety of quartz from the Bural–Sardyk deposit forms a tridymite phase. The quartzites from the Bural–Sardyk deposit cristobalitize slowly in air at certain temperatures, which is typical of milk-white quartzites. The temperature range of 1650–1700°C is optimal when treating quartz raw material for the production of cristobalite [9]. Since the quartz–cristobalite transition is reconstructive, this transition has a high degree of activation and occurs slowly (these analyses were conducted by A.N. Sapozhnikov).

We can see from the data in Table 2 that the transition kinetics depends on the temperature and composition of the initial material, and that fine-grained quartzite transitions to the stage of cristobalite most effectively [10].

PRODUCTION OF QUARTZ CONCENTRATE

In developing processes for producing a quartz concentrate from the Bural–Sardyk quartzites, we considered their textural parameters and physico-

Table 3. Results from fine-grained quartzite enrichment

Analyte	Initial sample	Mass fraction of analyte, $\times 10^{-4}\%$, ppm									
		1	2	3	4	5	6	7	8	9	10
Fe	7.1	2.0	1.44	2.1	1.70	1.83	1.3	0.73	1.38	0.80	0.6
Al	65.9	67.2	51.5	51.9	53.0	59.4	55.2	9.3	9.5	8.9	9.3
Ti	2.4	2.5	2.2	2.5	1.7	1.5	1.4	1.5	1.6	2.4	1.1
Ca	4.6	3.0	1.8	2.1	2.0	2.0	2.1	1.7	2.6	1.5	1.3
Mg	4.4	3.5	2.8	3.2	3.1	3.2	3.8	1.4	1.5	1.3	1.3
Cu	0.16	0.14	0.08	0.15	0.10	0.10	0.09	0.51	0.08	0.2	0.12
Mn	0.090	0.018	0.013	0.018	0.015	0.010	0.010	0.006	0.006	0.008	0.004
Na	5.9	6.2	6.0	6.3	5.0	6.3	5.4	4.1	3.9	3.9	4.0
K	23.9	23.7	17.7	20.4	17.8	19.4	18.0	2.5	2.4	2.2	2.3
Li	0.14	0.15	0.13	0.14	0.15	0.15	0.14	0.15	0.14	0.15	0.14
Total	114.6	108.4	83.7	88.8	84.6	93.9	87.4	21.9	23.1	21.3	20.2
P	1.0	0.8	0.8	0.6	0.8	0.8	0.7	0.7	0.8	0.5	0.5
B	0.23	0.23	0.21	0.23	0.23	0.22	0.29	0.21	0.20	0.18	0.18
Total	115.8	109.4	84.7	89.6	85.6	94.9	88.4	22.8	24.1	22.0	20.8

chemical properties. Using the results from conventional optical microscopic studies and elemental analysis, we established that the quartzites from the Bural–Sardyk deposit were almost totally monomineral and were more than 99.99% quartz. We therefore omitted the flotation stage in producing a quartzite concentrate from the quartzites of the Bural–Sardyk deposit.

To evaluate the effect acids have on the depth of chemical enrichment, we chose strong mineral acids (hydrochloric, nitric, and hydrofluoric) and strong organic ethanedioic acid. We studied both the effect individual acids had on the quartzites at different concentrations and the effects of their different mixtures. All reaction mixtures of the acids were made using deionized water.

The modes of enrichment were tested on fine-grained quartzite from the same deposit. The differences between the fine-grained quartzites and the superquartzites were the grain size and the concentration of impurities.

Fine-grained quartzite was enriched according to the scheme

- (1) washing a lump in distilled water and subsequent visual control;
- (2) crushing the lump to a grain size of 5–8 mm in a quartz mortar;
- (3) grinding in a Fritsch mechanical quartz mortar for 15 min;
- (4) classifying the ground material using capron meshes, and identifying the effective size fraction with a grain size of +174–450 μm ;
- (5) washing the produced grit with a grain size of +174–450 μm in deionized water;

(6) drying in a vacuum drying box;

(7) chemical enrichment of the effective size fraction in acid solutions at 60–70°C for 2 hours.

Table 3 presents the results from our investigations: 1 is 10% ethanedioic acid (analytically pure) at room temperature with a soaking period of 16 hours; 2 is 5% ethanedioic acid (chemically pure), neutralization with deionized water, and repeated chemical enrichment in a 10% HNO_3 solution (high purity); 3 is 10% HNO_3 (high purity); 4 is a mixture of 10% HCl (high purity) and 10% HNO_3 (high purity) in a ratio of 3 : 1; 5 is a mixture of 10% HCl and 10% HNO_3 in a ratio of 3 : 1 (the acids were additionally purified via distillation); 6 is a mixture of 20% HCl (high purity) and 20% HNO_3 (high purity) in a ratio of 3 : 17 and 10% HNO_3 (high purity); 7 is a mixture of 10% HNO_3 (high purity) and 10% HF (high purity) in a ratio of 1 : 1; 8 is a mixture of 5% ethanedioic acid (chemically pure) and 10% HF (high purity) in a ratio of 1 : 1; 9 is a mixture of 10% HCl (high purity), 10% HF (high purity), and 10% HNO_3 (high purity) in a ratio of 3 : 1 : 1; and 10 is a mixture of 20% HCl (high pure) and 20% HF (high purity) in a ratio of 3 : 1).

Table 3 shows that the use of the hydrofluoric acid in the reaction mixtures during chemical enrichment of the quartzites considerably lowers the total concentration of the impurity elements, compared to processes without the of hydrofluoric acid. In this case, the mass fractions of Al, Mg, and Ka fall the most. We managed to reduce the total content of impurities by 31 ppm (27%) without using the hydrofluoric acid when quartzite was consecutively treated with solutions of the ethanedioic and nitric acids. When we used hydrofluoric acid, the total content of the impu-

Table 4. Mass fractions of impurities in the quartz concentrates, ppm

Analyte	Fe	Al	Ti	Ca	Mg	Cu	Mn	Na	K	Li	Σ10	P	B
Initial	6	27	1.7	0.8	1	0.17	0.02	3.5	6.3	0.13	46.6	0.2	0.2
Chem. enriched	0.9	4.5	0.8	0.4	0.2	0.14	0.005	2.5	0.5	0.12	10.1	0.1	0.18
Ar calcined 1450°C + chem. enriched	1.1	4	0.6	0.4	0.2	0.18	0.006	0.2	0.3	0.18	7.2	0.1	0.16
IOTA-4	0.3	8	1.4	0.7	0.07	0.004	0.01	1	0.4	0.2	12.09	0.1	0.05

urities fell by 94 ppm (82%) in the best case (a mixture of 20% HCl and 20% HF in a ratio of 3 : 1).

Our study produced a technological scheme with a number of steps: crushing a lump to a fraction size of 25 mm; classifying the lump to a fraction size of +5–25 mm; chemical etching the lump with 10% HCl; drying the lump; thermal crushing; grinding; classifying the grit to a fraction size of +174–450 μm; chemical enrichment in 20% HCl : 10% HF at a 2 : 1 liquid to solid ratio; drying the quartz grit; quality control of the quartz concentrate; and packing. The second stage of the processes included calcinating the quartz concentrate at temperatures as high as 1450°C, subsequent chemical enrichment, and drying.

The results from enriching superquartzites (done by technologist O.N. Solomein, with analysis performed by V.Yu. Ponomareva) are presented in Table 4. We can see from Table 4 that the total content of the ten regulated impurities in the concentrates obtained in the first stage of enrichment was 10 ppm; after the second stage, it was 7 ppm. We can say that during high-temperature calcinations, fluid inclusions open up and Na is exposed at the surface. Subsequent chemical enrichment allows us to reduce its concentration to 0.2 ppm, less than one-fifth of that in Unimin IOTA-4 grit.

CONCLUSIONS

The transition of low-temperature α -quartz to high-temperature β -quartz during thermal crushing not only to reduce the strength of the quartz, but also to partially discharge low- and high-temperature water. High-temperature calcination at the temperature of the onset of the β -quartz– α -cristobalite transition opens up gas–liquid inclusions due to a change in the parameters of the crystal lattice.

Using a simple scheme for the deep enrichment of nontraditional raw materials of quartzites from the Bural–Sardyk deposit, we managed to produce quartz

concentrates of ultra-high purity at the IOTA-4 level even without going through the flotation stage.

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