

“LOOKING FOR “INVISIBLE GOLD” AND ITS CONCENTRATIONS IN ARSENIC-CONTAINING SULFIDE MINERALS OF BAKYRCHIK GOLD DEPOSITS”

Medet Junussov

PhD student

Department of Mineralogy and Petrology, Miskolc University, Hungary

INTRODUCTION

The Bakyrchik deposit comprises disseminated gold-bearing sulfide ore minerals formed in a black shale formation, located in the Qalba gold province in Eastern Kazakhstan (Fig. 1). The deposit has 280 t (since 2014 of ore estimation) of gold reserve with average 7.7 g/t [1] in a gold-containing carbonaceous-sulfide ore formation. The highest amount of gold-bearing sulfide minerals are localized in siltstones with 0.2-0.4% carbon and presence of the carbonates [2] and the total sulfide content of the ore varies from 0.5% to 10% [3]. The studied rock sample was taken from siltstone with high arsenic-bearing sulfide minerals and gold occurs in ultra-fine microscopic forms such as ionic and colloidal, included in arsenic-containing sulfide minerals. The gold-bearing sulfide minerals in the deposit are arsenic pyrite (1.81-4.86 wt% of As) and arsenopyrite. The main purpose of the paper is to determine the concentrations of Au and Ag in arsenic-containing sulfide minerals, using sequential extraction method.

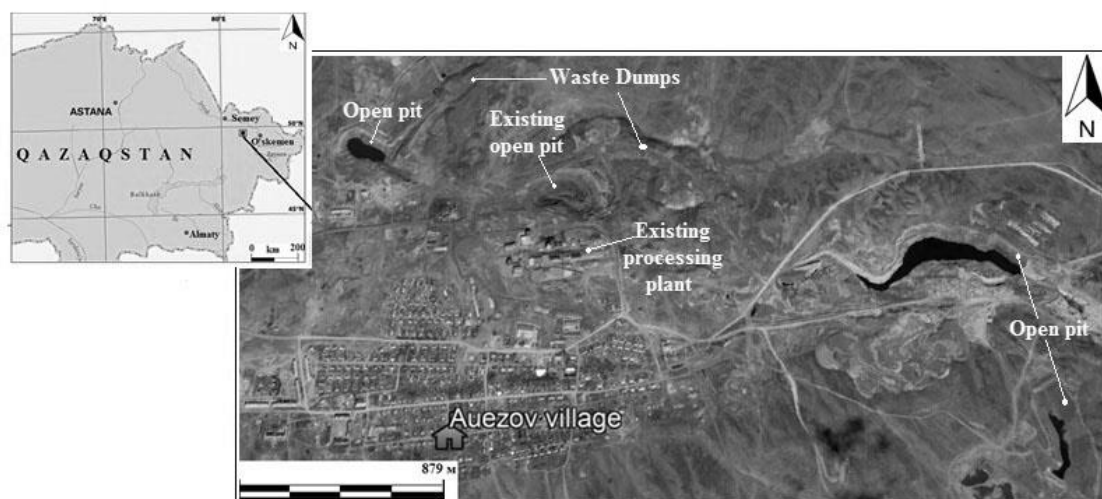


Fig. 1

Location of the Bakyrchik deposit in Eastern Kazakhstan

CHARACTERISTICS OF THE MINERALIZATION

"Invisible gold" is not detectable by optical and scanning electron microscopy, because it consists of discrete inclusions smaller than 0.1 μm in the structure of the common sulfide mineral [4]. Concentrations of invisible gold range from less than 0.5 ppm to greater than 1000 ppm in sulfide grains [4]. The gold consists either of submicroscopic metallic particles or is incorporated as “chemically bound” gold

[5, 6]. It has been assumed that gold was deposited by precipitation induced by changes in temperature, pressure, or pH of the gold-bearing fluid [7]. Concentrations vary considerably from deposit to deposit, and between discrete ore facies within a single deposit [4]. The deposit with gold-bearing sulfide minerals are concentrated in or near joints and fractures, and diminish away from these structural planes. Larger strain intensity has produced more joints and fractures resulting strong mineralization and higher gold grade [8]. Minerals that most readily act as hosts are arsenopyrite and arsenic-rich varieties of pyrite. [4]. Arsenopyrite usually contains more gold than pyrite, and the gold content of arsenic pyrites generally increases with arsenic content [9]. It is possible that gold may substitute for Fe in the lattice of arsenopyrite [10]. The arsenopyrite in acicular-prismatic form is mostly low of temperature origin [11] and it is characterized by high arsenic and high sulfur content, quite different from high-temperature arsenopyrite which is rich in arsenic and depleted in sulfur [12].

The sulfide ores of gold deposits in eastern Kazakhstan contain high and low-gold arsenopyrites, formed at different stages of ore deposition [13]. The arsenopyrite has two morphologic varieties such as acicular-prismatic (associating with invisible gold), which forms at the early productive stage of ore deposition, and late tabular arsenopyrite associated with free gold [13]. The gold-bearing arsenic pyrite and arsenopyrite minerals of the Bakyrchik deposit occur in various paragenesis and show different morphology. Morphogenetic forms of arsenic pyrite and arsenopyrite crystals have differences in shape, size and chemical concentrations. There are three morphogenetic variations of pyrites such as (1) sedimentary-digenetic globular (no gold-containing); (2) cubic form (gold-containing) recrystallized from globular pyrite in circumstances of high pressure and temperature and (3) pentagon dodecahedral pyrite (high gold-containing) which associates with arsenopyrite. Pyrite concentrates in chemogenic-terrigenous sediments of siliceous-argillaceous, calcareous and marly compositions [2]. They are included in ore formed in lenses of 120-250 m in width and 500-700 m in length and situated in the Middle Carboniferous Bukon formation [14]. The ore formation was formed in a multistage alteration of syngenetic-sedimentogenic gold-bearing materials in near-fault dislocation-thermal metasomatism, it is related to mineralized zone of gold-sulfide type [15]. The gold mineralization is localized in thin-rhythmically laminated marl, siltstones, felsic tuffs and sandstone. All occurrences of the gold-bearing mineralization are concentrated within the Qyzyl thrust zone. Carbonate and volcanogenic shales form the lower part of the stratigraphic sequence, which includes a 1500 m thick lower Carboniferous volcanoclastic sandstone containing lenses and interlayers of gritstone, conglomerate and carbonaceous-cherty siltstones. The upper part of this sequence consists of a 600-800 m thick sandstone unit with layers of carbonaceous siltstones, shales and a basal horizon of sedimentary breccia and conglomerate (Fig. 2).

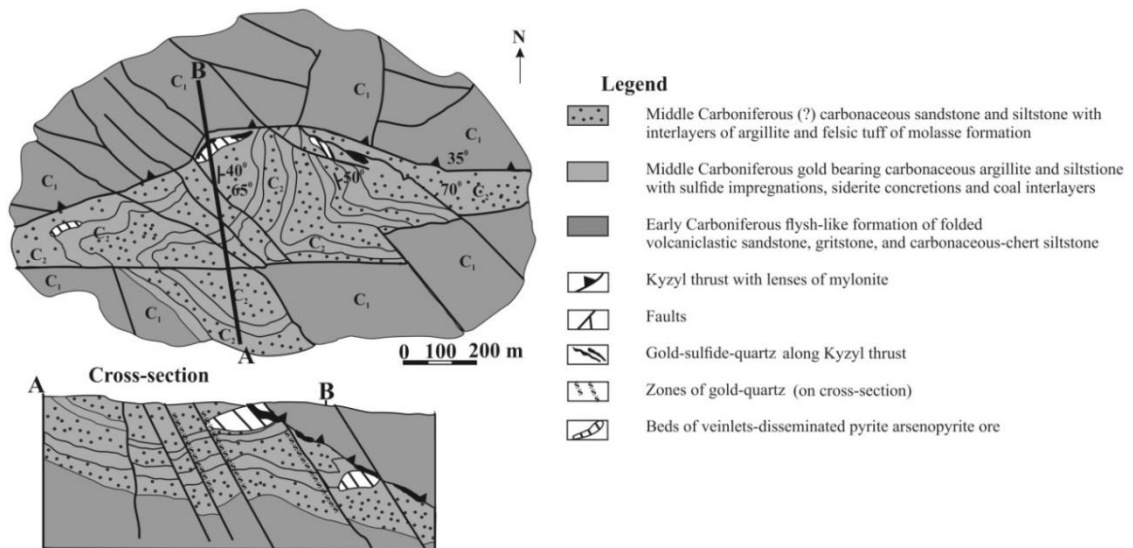


Fig. 2
Schematic geological model of the Bakyrchik deposit area
(modified after Kurbanov 1993)

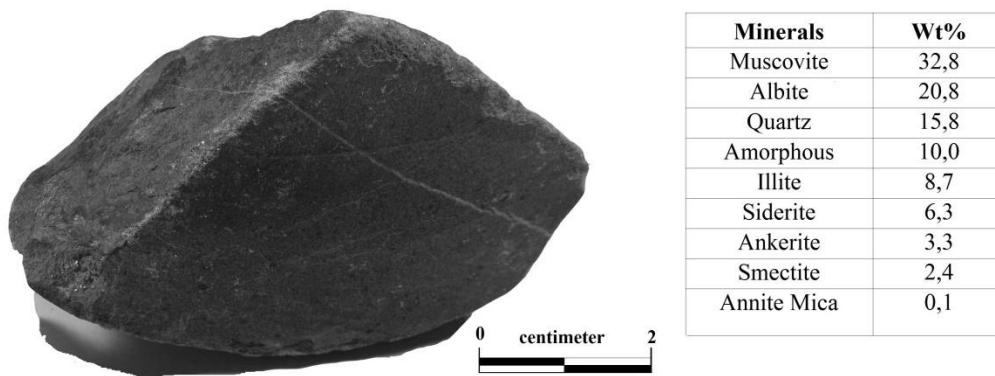


Fig. 3
Sericitized carbonaceous-siltstone rock and its mineralogical composition
measured by XRPD (BRUKER D8 ADVANCE, Cu-K α 40 kV, 40 mA)

Description of the sample: the specimen is a sericitized carbonaceous-siltstone rock which contains quartz, sericite, mica, iron-carbonate minerals and gold-bearing arsenic pyrite and arsenopyrite (LOQ). The sample has a mass of 123,3 grams, density of 2,8 g/cm³ and its color is dark grey (Fig. 3). The sample is more suitable for investigation, because it contains high concentrations of arsenic elements in sulfide minerals and it means that may be presence of gold (Fig. 4).

The rock sample (arsenic rich-sulfide sedimentary rock) and three analytical methods were used such as XRD (determination of mineralogical composition), EMPA equipment the gold and silver inclusions as well in sulfide minerals were searched and “As” concentrations were measured into surface of grains of arsenic-bearing sulfide minerals and ICP-OES equipment “Au” concentrations were determined, after dissolving with chemical reagents, using three stages with chemical reagents (the first stage-hydroxyl ammonium chloride, the second stage-

hydrogen peroxide and last one is aqua regia) for determining Au concentrations in the each stages.

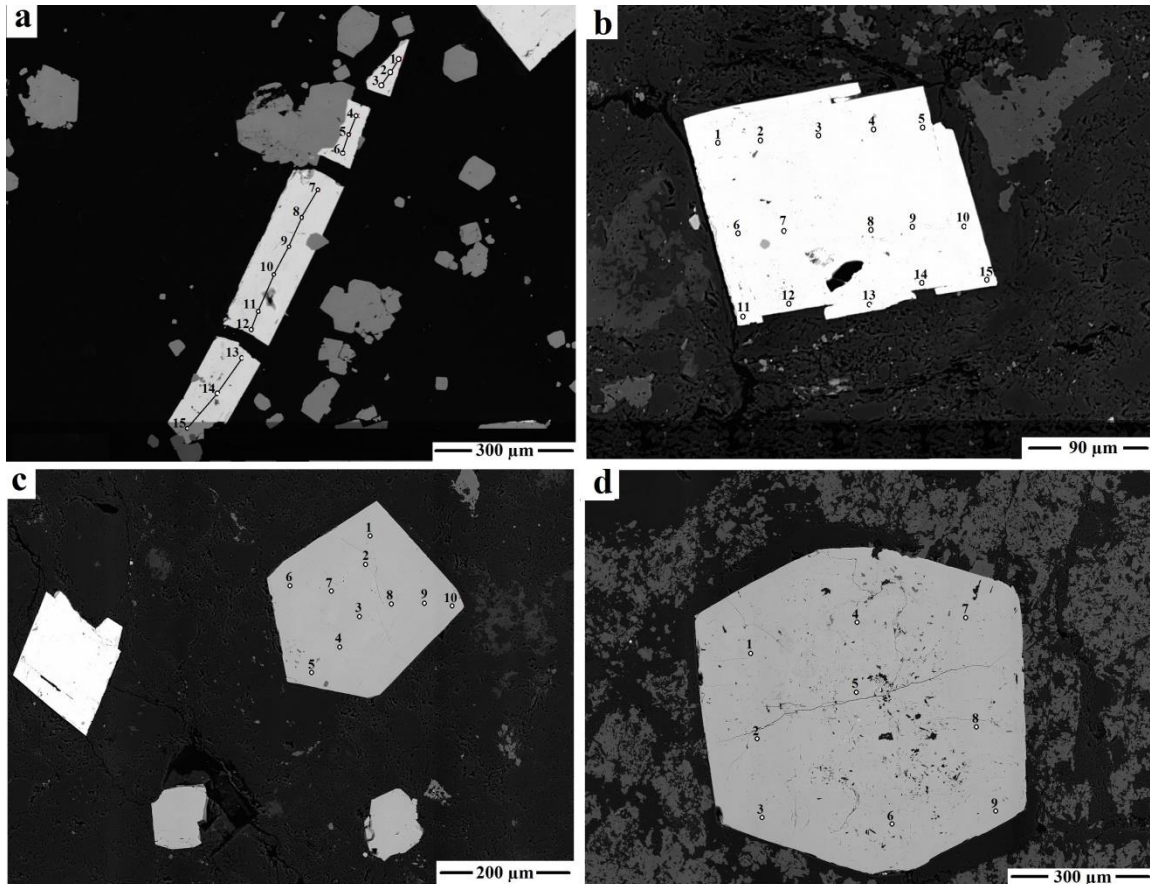


Fig. 4

SEM BSE images of Arsenic-bearing sulfide-ore minerals with EDS measurement: (a) acicular-prismatic arsenopyrite associated with cubic pyrite crystals; (b) tabular-arsenopyrite twin; (c) pentahedral pyrite crystal with tabular-arsenopyrite twin; (d) hexahedral pyrite crystal. (measured by EDS (JEOL JXA 8600 Superprobe, 20 KeV and 20 mA).

Table 1

Elemental concentration (wt%) in textures of gold-bearing sulfide minerals (no presence of gold) – measured by EDS (SEOL SXA 8600 Superprobe, 20 KeV and 20 mA)

Minerals	№	S	Fe	As	Minerals	№	S	Fe	As
Acicular-prismatic arsenopyrite	1	21.66	31.04	47.30	Pentahedral pyrite	1	54.53	42.76	2.71
	2	21.72	31.20	47.08		2	54.21	42.36	3.43
	3	21.65	31.11	47.24		3	54.10	42.48	3.42
	4	21.56	31.28	47.16		4	54.11	42.48	3.41
	5	21.79	31.09	47.13		5	55.60	42.60	1.81
	6	21.37	31.25	47.38		6	53.88	42.18	3.94
	7	21.80	31.08	47.12		7	54.89	42.67	2.44
	8	21.73	30.92	47.36		8	53.74	42.58	3.68
	9	21.92	31.20	46.89		9	54.26	42.50	3.25
	10	22.97	31.57	45.46		1	54.73	42.78	2.50

	11	23.62	31.97	44.41		0			
	12	-	-	-					
	13	23.19	31.41	45.41					
	14	22.69	31.57	45.75					
	15	21.99	31.33	46.68					
Tabular arsenopyrite	1	22.12	30.39	47.48	Hexahedral pyrite	1	53.65	42.92	4.43
	2	21.53	30.08	48.39		2	53.09	43.05	3.86
	3	21.61	30.37	48.02		3	-	-	-
	4	22.13	30.46	47.41		4	53.36	43.09	3.55
	5	21.93	30.61	47.46		5	52.10	43.03	4.86
	6	21.96	30.52	47.52		6	-	-	-
	7	-	-	-		7	52.81	43.36	3.83
	8	22.57	30.40	47.02		8	53.40	43.16	3.44
	9	22.31	30.57	47.12		9	53.98	43.31	2.70
	10	22.98	30.53	46.49					
	11	-	-	-					
	12	22.05	30.18	47.77					
	13	22.00	30.43	47.57					
	14	-	-	-					
	15	22.91	30.24	46.85					

EXPERIMENTAL PROCEDURES

The sequential extraction procedure based on previous experiments [16, 17, 18] is summarized in Table 2. The three-step extraction scheme for precious metals in the rock sample is described in detail as follows:

Experimental materials were gathered such as a test tube rack (woody), funnel and 11 cm diameter of filter paper (Filtrier-Papier Nr. 589³ Blauband Marke Selecta-Germany) for filtration procedures and an oven for drying fractions after filtration on each stage. And the chemical reagents of hydroxyl ammonium chloride ($\text{NH}_2\text{-OH}\cdot\text{HCl}$), hydrogen peroxide (H_2O_2) and aqua regia ($\text{HNO}_3\text{-HCl}$) provided by the Chemical department of Miskolc University. Precious metals concentrations were determined with ICP-OES (720 ES made by VARIAN Inc., Arial Plasma-view, simultaneous multielement ICP spectrometer).

The crushed solid sample was taken from the rock sample with a relatively arsenic rich-bearing sulfide minerals, using an agate mortar and pestle. After the crushing process it was weighted and 5 grams of powder sample were collected for the first step of sequential extraction experiment.

Table 2
Sequential extraction procedures with four stages.

Stage	Fraction	Reagents	Conditions
1	Reducible metal	1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ pH 4.5, 45 ml	2h agitation at room temperature; supernatant decantation.
2	Organics and Cu-sulfides	30-35% H_2O_2 , 40.5 ml	Heat 85 ⁰ C in water bath for 1h.
3	Residual	$\text{HNO}_3\text{-HCl}$ (1:3) 16.8 ml	Bath 100 °C for 1h; (20 min); supernatant decantation.

Stage 1 Reducible metal: 45 mL of 1M NH₂OH·HCl at pH 4.5 was added into the tube of 4.9751 grams of powder sample and mixed manually. Then the tube was shaken by a reciprocating shaker equipment (LABOI) for 2 hours at room temperature. The extract was decanted and collected into plastic test tube. Then residue was prepared for the next step by washing with distilled water and left them in the oven for drying at 60°C.

Stage 2 Bound to organics and sulfides: 40,5 mL of 30 % H₂O₂ was added to the residue of step 1 in a glass test tube. The residue of the sample was weighted and taken to this stage 4.5492 grams, mixed manually. After the mixing process the glass test tube was placed in a water bath at 85° C water for 1 hour. It had quite high reactions in the water bath and it was three times cooled by cold water and kept outside before stabilizing the reactions, then it was put back into the water bath. After this procedure it was decanted the extract and dried the residue at 60°C.

Stage 3 Residual: the residue from the previous stage was used as 1.8541 grams of sample, mixed with 16.8 mL 68% HNO₃ – 37% HCl (1:3). Then, it was placed to water bath at 100°C water for 1 hour. After finishing, the extract was filtered for more than 30 min. The residue contained silicate materials of the sample which was not dissolved by reagents.

RESULTS AND DISCUSSION

No gold inclusions in arsenic-sulfide minerals determined by microprobe analyzer, but by ICP-OES 4 ppm of Au, also 27 ppm of Ag, and As 4050 ppm were measured from the last extractive residue of the sequential extraction. The precious metals were released after dissolving completely As-bearing sulfide minerals and probably from carbonate minerals as well. It means that completely dissolving arsenic-containing sulfide minerals are given invisible gold and silver as well from their inclusions.

Table 3

Metal concentrations (ppm) after measurement of soluble extractions in each stage on the sequential extraction procedures by ICP-OES (720 ES made by VARIAN Inc., Arial Plasma-view, simultaneous multielement ICP spectrometer.)

Extracted metal distributions	Stages of the selective extraction procedures (ppm)		
	1	2	3
Ag	0.7	1.6	27
As	4	7	4050
Au	4	3	4
Fe	1500	13045	10400
S	44	4272	5199

By EMPA (EDS) results for arsenic concentrations 44.41–47.38 wt.% in acicular-prismatic arsenopyrite and the tabular arsenopyrite has As 46.49–48.39 wt.%. It means that arsenic concentration is higher in tabular arsenopyrite. In the cubic

arsenic pyrite 1.81–3.94 wt.% arsenic concentration is lower and more 2.70–4.86 wt.% in hexahedral arsenic pyrite. Due to distribution of arsenic element may propose that the inclusions of invisible gold were released more from hexahedral arsenic pyrite than cubic, more concentration of Au from tabular-arsenopyrite twin than acicular-prismatic mineral. The tabular arsenopyrite was dominated arsenic-sulfide mineral for invisible gold in the deposit of Bakyrchik.

CONCLUSION

The concentrations of invisible gold 3 ppm from arsenic pyrite and 4 ppm from arsenopyrite dissolved by reagents in the second and third stages of the sequential extraction method. In the first stage 4 ppm of invisible gold also released, but not from arsenic-sulfide minerals, might be from carbonate minerals.

It is supposed that the silver is in invisible form as well in the arsenic-bearing sulfide minerals of the sample as gold, because it was not silver inclusions under optical and electronic optical microscopes. The silver has good concentrations around 27 ppm.

According to concentrations of precious elements in the arsenic pyrite and arsenopyrite may suppose that arsenic is as a pathfinder element for invisible gold in the deposit and invisible silver as well.

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