

# Sequential extraction of carbonaceous siltstone rock for multi-element analysis by ICP OES

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**Received:** 29<sup>th</sup> June, 2018

**Accepted:** 6<sup>th</sup> July, 2018

## Abstract

The carbonaceous siltstone rock material is a disseminated sulfide-rich sedimentary rock from a sediment-hosted gold deposit of Bakyrchik. The Bakyrchik deposit is located in Eastern Kazakhstan, which includes in Qalba gold province. The main purpose of this paper is a demonstration on chemical extraction of heavy metals from the carbonaceous siltstone rock and detection of its elemental concentrations. In the work was used a rock sample from the deposit which is a sericitized carbonaceous-siltstone rock. In sequential extraction method was selected four stages such as water soluble fraction (reaction with deionized water) for extraction of water soluble metals, reducible metal fraction (reaction with hydroxyl ammonium chloride) for extracting all reducible metals, organics and sulfides (reaction with hydrogen peroxide) for dissolution of organics and copper sulfide, and extraction of metal oxides and residual fraction (reaction with aqua regia) for extracting of all remaining metals.

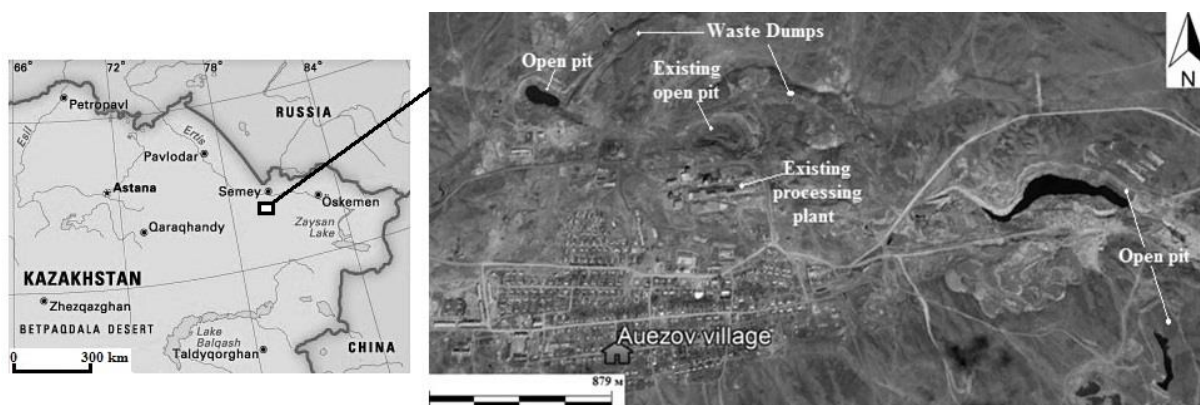
The paper comprises analytical methods for research outlooks. They are X-Ray Diffraction (determination of mineralogical composition), X-Ray Fluorescence (determination of chemical composition) and Inductively Coupled Plasma – Optical Emission Spectrometry (determination of heavy metal concentrations).

**Key words:** sequential extraction, carbonaceous siltstone rock, heavy metal, colloidal gold.

## Introduction

The Bakyrchik deposit is located in the village of Auezov, Zharma district in Northern East Kazakhstan, 110 km Southeast of the Semey city and 750 km east of the capital city of Astana (Fig.1). The deposit has 280 t (since 2014 of ore estimation) of gold reserve with average 7.7 g/t. The ore occurrence is lens forms of 120-250 m in width and 500-700 m in length (Plekhova et al. 2014). It is situated in a Bukon suite of Middle Carboniferous (Plekhova et al. 2014). The ore formation is multiple conversions of syngenetic-

sedimentogenic gold-bearing materials in near-fault dislocation-thermal meta-somatism, it is related to mineralized zone of gold-sulfide type (Umarbekova et al. 2017). Four stages of ore generation are detected at the well-studied Bakyrchik deposit (Seitkan et al. 2016): (1) preore silicification, carbonatization, sericitization, and graphitization of carbonaceous terrigenous rocks; (2) early ore stage connected with quartz, sericite and gold-bearing arsenopyrite and pyrite; (3) polymetallic stage, during which pyrite, sphalerite, chalcopyrite, galena, grey copper ore, and native gold were accumulated; and



**Fig.1.** Localization of the Bakyrchik deposit in Eastern Kazakhstan. (modified after Google Map World (left photo) and Google Earth Pro 7.3.1.4507 (32-bit) for the right photo)

(4).quartz–antimonite stage with quartz, marcasite, jamesonite, enargite. The total sulphide content of the ore varies from 0.5% to 10% (Seitkan et al. 2016).

The gold has ultra-fine microscopic forms such as ionic and colloidal (Kovalev et al. 2010). The gold mineralization is localized in thin-rhythmically laminated marl, siltstones, felsic tuffs and sandstone. The highest amount of gold-bearing arsenopyrite and pyrite is localized in a siltstone (Rafaylovich et al. 2011). This siltstone is an experimental object in the paper as metal-rich rock specimens on the sequential chemical extraction method. And the main objective of this paper is a demonstration of sequential extraction experiment for heavy metal and precious metals partitioning and indication of their metal concentrations in the samples.

## Materials and Methods

Chemical sequential extraction is an alternative approach to elements' fractions and speciation in order to know elements' existing state in the environment (Liang et al. 2016). This is widely used to study element speciation in soils, sediments, and mine wastes (Dold and Fontboté 2001; Dold 2003; Heikkinen and Räsänen 2008). In the method, solid material is partitioned into specific fractions by a sequential series of selective extractions using

appropriate reagents, and it aims to simulate the release of elements under a various environmental conditions. It provides information on the origin, mode of occurrence, bioavailability, mobilization and transport of trace elements and other elements of interest (Tessier 1979). The sequential fractionation is a frequently used approach to evaluate metal distribution into different chemical forms present in a solid phase (Beckett 1989). Tessier et al. (1979) first proposed sequential extraction method as a means for investigating the existing state of heavy metals in soils and sediments (Liang et al. 2016). Although Tessier's procedure was popularized in 1980s, many previous studies have pointed out that limited choices of reagents, redistribution during the extracting processes and lack of quality control all occurred in Tessier's procedure (Davidson et al. 1999).

In past work, sequential extraction procedures were mainly applied to sediments, soils and then it was proposed for carbonaceous sedimentary rocks (black shale) (Liang et al. 2016). Carbonaceous sedimentary rocks (black shale) occur in thin beds in many areas at various depths. They contain relatively high organic carbon content and sulfides because they were deposited under anaerobic conditions. The weathering processes of rocks were always related to acid production, acid neutralization with carbonate rocks, organic

matter degradation and the development or formation of clay minerals (Tessier et al. 1979). During the weathering processes, organic carbon is released and heavy metals are dissolved, which are important sources of environmental contamination. Change of Eh–pH, degradation and formation of organic matter, and the development of secondary mineral in the weathering process influence the transportation of elements (Tessier et al. 1979; Beckett 1989; Davidson et al. 1999).

Analytical methods used in the current work focus on determination of mineral and chemical compositions, metal distribution and metal concentration in the samples. Analyses were carried out for determination of chemical composition by X-ray fluorescence, for mineralogical composition by X-ray powder diffraction, for identification of disseminated ore mineral inclusions by scanning electron microprobe. Detection of heavy and precious metals concentrations from the leachates obtained by sequential extraction were analysed by ICP-OES. The sequential extraction procedures had four different chemical reagents such as deionized water, hydroxyl ammonium chloride, hydrogen peroxide and aqua regia. They were treated at the different temperature conditions, chemical concentration of solvents and processes such as agitation, supernatant decantation, boiling in water bath and etc. The detailed information is found it in the Table 1.

## Experiment

### *Sample description and sample preparation*

The studied rock sample (Fig.2) has sulfide ore minerals (pyrite, arsenopyrite, galena, chalcopyrite and etc.), allothigenic (quartz, muscovite), authigenic minerals (illite, siderite, smectite and ankerite (shown in the Tab.1).

The sample is a sericized carbonaceous-siltstone rock which contents quartz, sericite

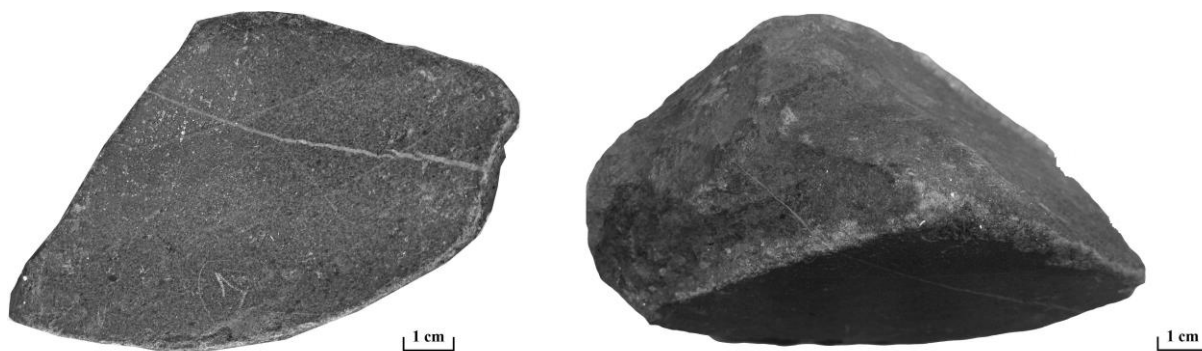
and gold-bearing arsenopyrite and pyrite. Gold-bearing sulfide minerals have been developed in the second or early stage of ore formation. The sample has a dark grey color and it is possible to see visibly disseminated sulfide minerals and quartz inclusion in micro cracks of the sample (Fig.3).

Crushed solid sample of more 50 grams (density-2.17 g/cm<sup>3</sup>) were taken from the carbonaceous siltstone rock sample with a relatively high sulfide and organic matter concentrations, for the sequential analysis. The crushed materials were passed through a 0.2-0.3 mm mesh sieve (or maximum powder) using an agate mortar and pestle. After crushing process it was weighted and 20 grams of powder sample were collected for sequential extraction experiment.

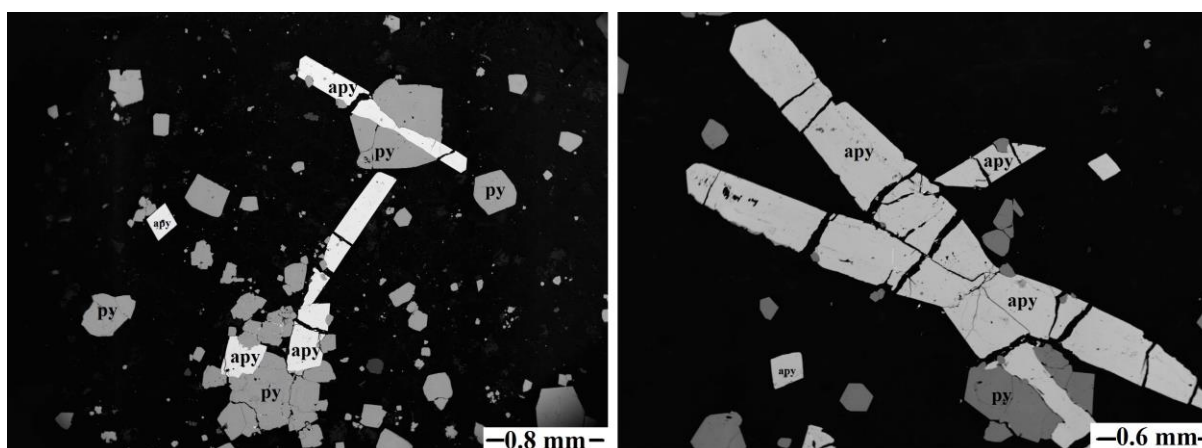
### *Instruments and chemical reagents*

Heavy and precious metals concentrations were determined with ICP-OES (720 ES made by VARIAN Inc., Arial Plasma-view, simultaneous multi-element ICP spectrometer). A reciprocating shaker equipment (LABOI) was used for agitation the first two stages, oven for drying fractions after filtration on each stage. The filtration procedure included a test tube rack (woody), funnel, two types of filtration papers such as folded filter with diameter of 24 cm (Macherey-Nagel 5160 Düren-Germany MN 615 1/4) for the first stage and 11 cm diameter of filter paper (Filtrier-Papier Nr. 589<sup>3</sup> Blauband Marke Selecta-Germany) for all remaining three stages.

There were many chemical reagents or solvents which used for dilution of interesting elements in the sample. They are a deionized water (H<sub>2</sub>O), hydroxyl ammonium chloride (NH<sub>2</sub>-OHxHCl), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and aqua regia (HNO<sub>3</sub> HCl) provided by the Chemical department of Miskolc University.



**Fig.2.** The rock sample fragment: Sericized carbonaceous-siltstone rock. (modified after a camera SMP and Photo Shop CS3)



**Fig.3.** SEM BSE images of the rock sample: Acicular-prismatic and tabular arsenopyrite associated with euhedral pyrite crystals (apy-arsenopyrite and py-pyrite). No gold inclusions have been found by EMPA, EDS (SEOL SXA 8600 Superprobe, 20 KeV and 20 mA). Analyst L. Mátè (Institute of Mineralogy and Geology, Miskolc University)

### *Sequential extraction procedures*

The sequential extraction procedure based on previous experiments (Dold and Fontboté 2001; Kulp et al. 2004; Anbar and Rouxel 2007 and etc.) is summarized in Table 1. The four-step extraction scheme for heavy and precious metals in the carbonaceous siltstone rock sample is described in detail as follows:

*Stage 1 Water soluble:* A 600 mL volume of deionized water was added to 20.1292 grams of powder sample in a plastic test bottle 1L, and mixed by manual. The plastic test bottle was shaken for 1 h at room temperature in a reciprocating shaker at 120 or 160 motions per minute. The extract of the sample was separated without vibration from the solid residues, they were decanted several hours (4

hours) and collected into plastic test tube (50 mL). The residue of the sample was washed in 1L plastic test bottle with distilled water and dried at temperature 60°C in the oven.

*Stage 2 Reducible metal:* From the residue of the sample from stage 1, 4.9751 grams were selected for the second step, 45 mL of 1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  at pH 4.5 was added and mixed manually. Then the tube was shaken 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 3 Bound to organics and sulfides:* 40,5 mL of 30 %  $\text{H}_2\text{O}_2$  was added to the residue of step 2 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 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 4 Residual:* the residue from the previous stage was used as 1.8541 grams of sample, mixed with 16.8 mL 68% HNO<sub>3</sub> – 37% HCl (1:3). Then, it was placed to water bath at 100°C water at 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 of the sequential extraction are summarized in Table 3. In total 21 elements such as heavy metals (Pb, As, Co, Zn, Cu, Cr, Mn, Fe, Sr, Ti, Ba, Bi and Zr ) light metals (Mg and Al), precious metals (Au and Ag) and other metals (Ca, K, P, and S ) in the sample of the Bakyrchik deposit (Tab.3).

## Results and Discussion

As it was mentioned before, the sample is from an early stage (or the second) ore formation,

including quartz, sericite, pyrite, arsenopyrite, gold and as well, based on results of mineralogical composition (Tab.2) and chemical composition (Tabs 2 and 3) of the sample.

*In the first stage* of the sequential extraction, little amount of metals were dissolved by deionized water. The more dissolved metals into deionized water are of Ca (155 ppm), Mg (106 ppm), K (95 ppm) and S (91 ppm). It is supposed that in the first stage easily soluble sulfates as gypsum and jarosite go into solution (Tabs 1 – 3).

*In the second stage* the solvent of hydroxyl ammonium chloride started to extract several metals in minor amounts: S (44 ppm), Al (48 ppm), Sr (54) and Mn (59 ppm), and more numbers of K (159 ppm), Ca (401 ppm), Mg (808 ppm) and Fe (1500 ppm). As far as the sample contains around 10% carbonates according to the XPRD results, the higher amount of Ca, Mg and Fe release shows the dissolution of carbonates (Tabs 2 and 3).

*In the third stage* the amounts of dissolved metals in the sample exceeded the first two stages. This solvent is strong enough to oxidize sulfides, first of all pyrite and dissolve some clay minerals. The metals are Al (250 ppm), Mn (339 ppm), K (585 ppm), Ca (693 ppm), Mg (1095 ppm), S (4272 ppm) and Fe (10345

**Tab.1.** Sequential extraction procedures with four stages. Based on previous experiments (Dold and Fontboté 2001; Kulp et al. 2004; Anbar and Rouxel 2007 and etc.)

Stage	Fraction/Bound to	Reagents	Conditions
1	Water soluble	Deionized H <sub>2</sub> O, 600ml	20.1292 g sample into the reagent, 1h agitation at room temperature; supernatant decantation.
2	Reducible metal	1M NH <sub>2</sub> OH·HCl pH 4.5, 45 ml	2h agitation at room temperature; supernatant decantation.
3	Organics and Cu-sulphides	30-35% H <sub>2</sub> O <sub>2</sub> , 40.5 ml	Heat 85°C in water bath for 1h.
4	Residual	HNO <sub>3</sub> –HCl (1:3) 16.8 ml	Bath 100 °C for 1h; (20 min); supernatant decantation.

**Tab.2.** Mineralogical and chemical compositions of the sample, based on quantitative XRPD (BRUKER D8 ADVANCE, Cu-K $\alpha$  40 kV, 40 mA) and based on WDXRF (RIGAKU Supermini 200, Pd source, 50 kV-4 mA) Analysts Dr. F. Kristály (X-Ray diffraction) and Dr. F. Moricz (X-Ray Fluorescence) (Institute of Mineralogy and Geology, Miskolc University)

Equipment	Minerals	Wt%	Equipment	Chemical elements	(%)	Chemical elements	(ppm)
X-Ray Diffraction	Muscovite	32,8	X-Ray Fluorescence	SiO <sub>2</sub>	51,5	Cu	42
	Albite	20,8		Al <sub>2</sub> O <sub>3</sub>	23,3	Zn	61
	Quartz	15,8		MgO	0,93	Pb	1304
	Amorphous	10,0		CaO	0,75	Rb	76
	Illite	8,7		Na <sub>2</sub> O	1,97	Sr	261
	Siderite	6,3		K <sub>2</sub> O	4,02	Ba	506
	Ankerite	3,3		Fe <sub>2</sub> O <sub>3</sub>	4,51	As	1537
	Smectite	2,4		MnO	0,049	Cr	101
	Annite Mica	0,1		TiO <sub>2</sub>	0,878	Co	12
					P <sub>2</sub> O <sub>5</sub>	0,125	Bi
			S	0,25	Zr	222	
			F	<0.3			

**Tab.3.** Metal concentration (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). Analyst Dr. B. Oliver (Department of Chemistry, Miskolc University)

Extracted metal distributions	Stages of the selective extraction procedures			
	1	2	3	4
Ag	2.9	0.7	1.6	27
Al	4	46	250	155
As	1.5	4	7	4050
Au	0.1	4	3	4
Ba	2	2	1	5
Bi	0.3	1.9	1.1	0.1
Ca	155	401	693	3420
Co	1.9	1.2	7	4
Cr	0.1	0.9	1.6	2
Cu	0.2	7	7	36
Fe	3	1500	13045	10400
K	95	159	585	1465
Mg	106	808	1095	15263
Mn	1.3	58	339	5517
P	2.9	0.7	1.4	2021
Pb	2	1.7	1.2	9
S	91	44	4272	5199
Sr	0.5	54	84	191
Ti	0.1	1.1	1.1	3
Zn	1.6	7	1.5	68
Zr	1.9	0.2	1.2	6

ppm). The Fe and S were continued dissolving from sulfide minerals and as well Fe from clay minerals. The Al and K, Ca and Mg might be dissolved from clay minerals and muscovite. It is remarkable that a little amount of silver and gold was also liberated in this stage, which indicates the bond of these precious elements in pyrite.

*In the last fourth stage* the most powerful aqua regia solvent dissolved almost all metals in the sample and even no-dissolving metals. In this stage As (4050 ppm), Cr (2 ppm), P (2021 ppm), Ag (27 ppm) and Au (4 ppm) were dissolved by the aqua regia solvent. The metals of Mn (5517 ppm) and Mg (15263 ppm) show sharply increasing level in this stage and sufficiently high concentrations than in the third stage. Other metals such as Al (155 ppm), Fe (10400 ppm), K (1465 ppm) and Ca (3420 ppm) are present in this stage (Tab.3).

The gold and silver were dissolved from arsenopyrite sulfide mineral in the rock sample of the Bakyrchik deposit by aqua regia solvent in the sequential extraction procedures. It means that gold and silver appear solved in arsenopyrite crystals in colloidal size. The colloidal gold was not possible to determine by electron microprobe analyzer. The sequential extraction seems an applicable method in searching of colloidal gold.

## Conclusion

The sequential extraction experiment is relatively simple in use, but it needs time especially, for drying process. This method is useful for determining the speciation of colloidal precious metal concentrations as well as for indicating concentration of toxic elements, for example As if it is released from a waste of gold deposits which may contaminate the environment during weathering.

## Acknowledgments

I thank Z.T. Umarbekova for the opportunity of sharing with sample collections. Also, my special thanks go to Dr. F. Madai for consultation and patience; and L. Mátè (EMPA), Dr. F. Kristály (X-Ray diffraction), Dr. F. Moricz (X-Ray Fluorescence) and Dr B. Oliver (ICP-OES) for their helps with analytical works.

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