СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО, год. 80, кн. 3, 2019, с. 239–241
REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY, vol. 80, part 3, 2019, p. 239–241

Национална конференция с международно участие „ГЕОНАУКИ 2019“
National Conference with international participation "GEOSCIENCES 2019"

Preliminary data on the content of W, As and U in the waters in the area of the Grantcharitza deposit, Western Rhodopes

Предварителни данни за съдържания на W, As и U във водите от района на находище Грънчарица, Западни Родопи

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Keywords: tungsten, uranium, arsenic, waters, Grantcharitsa deposit.

Introduction

The Grantcharitsa scheelite deposit (Western Rhodopes) is one of the largest and promising deposits of tungsten in Europe. It is located southwest, 18 km in a straight line, from the town of Velingrad – a modern resort town and SPA center of Bulgaria. The detailed exploration of the deposit began in 1960. Since 2009 the preparation for exploitation of the deposit has started, which has received a mixed response from the local population, worried by the possible pollution of drinking and thermal mineral waters by such elements as W, As and U. In the western part of the deposit, on the Grantcharitsa River, there are facilities for water intake into the Bistritsa derivation conduit, built in the 1950s as one of several to feed the Batak dam lake and the Batak hydroelectric power station. The Bistritsa conduit is partially used for water supply of the town of Velingrad. At present, all the activities in the Grancharitsa deposit are suspended as in 2017 the Sanitary Protection Zones have been established on the Grancharitsa River and its tributaries with boundaries that pass through the richest ores of the deposit including the oxidized ores.

In the present work, first results of the hydrochemical assessment of surface, ground and mine waters in the area of the Grantcharitsa deposit with an emphasis to W, U and As are given, as part of a systematic investigation of geochemical behavior of tungsten and other metals in the oxidation zone, soils and waters in the area of the Grantcharitza deposit, including identification of natural and anthropogenic factors causing these elements to be remobilized and to be hazardous.

Sampling places and analytical methods

Sampling. The Grantcharitsa deposits as well as the essential part of the Grantcharitsa River are located in the northen part of the Grantcharitsa granitoid body (granite-granodiorite and porphyritic granodiorite, 69–67 Ma) of the Rila-West Rhodopes batholith, in close proximity to the Babyak-Grashevo shear zone, which separates these granitoids from the younger medium- to coarse-grained biotite granite (40–35 Ma) of the West Rhodopes body (Fig. 1a) (Kamenov et al., 1999; Sarov et al., 2010).

Water quantity in the Grantcharitsa River varies in wide range depending on rain/snowfall, snowmelt and outflow into the Bistritsa derivation conduit. The water amount in the river drastically decreases after the water intake into the Bistritsa conduit (at the conflunce of Veziov Dol River into the Grantcharitza River, Fig. 1a). In 2019, five sites for water sampling in the Grantcharitza River were selected for preliminary hydrochemical assessment (Fig. 1a): №1 – reference water in the upper river about 1 km from the deposit, №3 – before facilities for water intake for the the Bistritsa derivation conduit, №4 – after facilities for water intake, №№5 and 6 – on the Central section of the deposit close to the oxidation zone. Other water samples were taken from mining waters (№2 – drainage water outflowing from prospecting gallery in the Veziov dol Valley, №№ 9 and 10 – mining water in prospecting gallery in the Kambarsko Dere Valley) (Fig. 1a). Two sites (№№ 7 and 8) were selected for ground water sampling – in northen (№7) and southern (№8) river terraces just below the oxidation zone

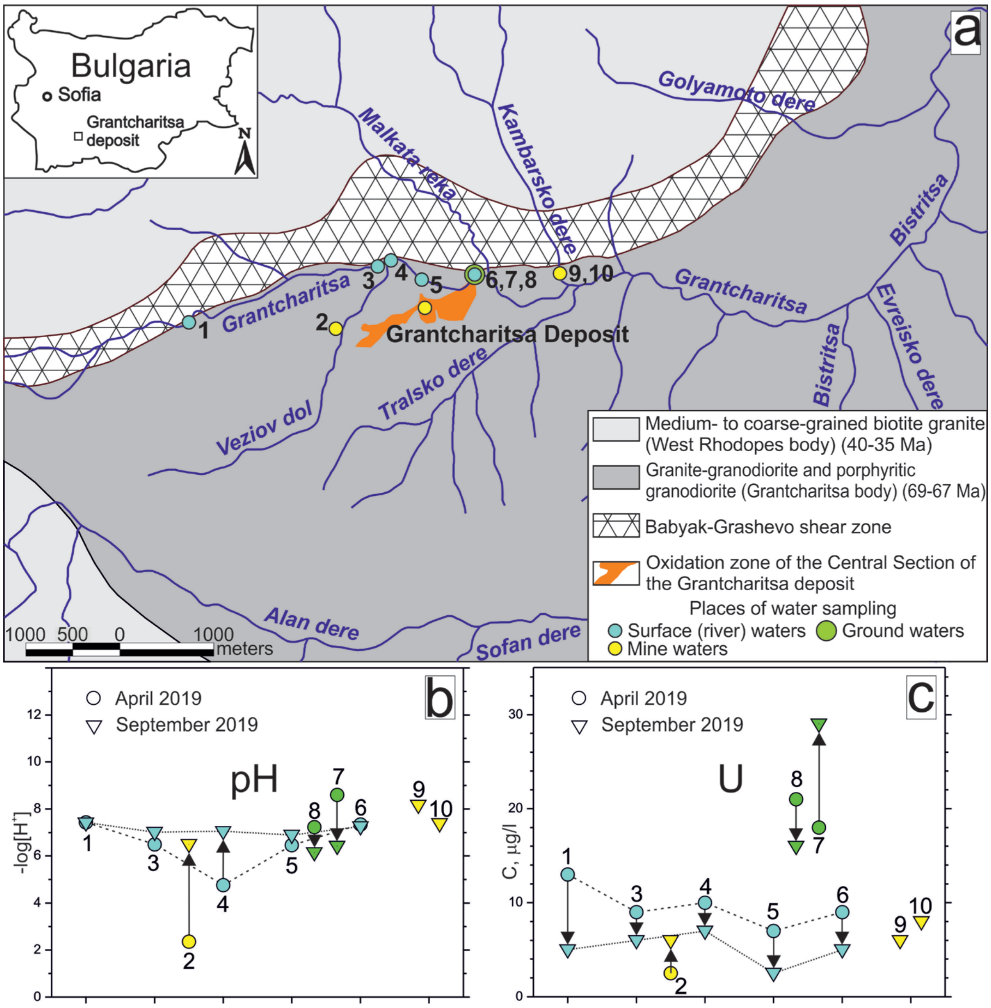

Fig. 1. *a*, sites of water sampling in the area of the Grantcharitsa deposit (modified geological map of Sarov et al. (2010); *b*, *c*, variations of pH and uranium content in waters sampled in April and September, 2019. The numbers in the graphs correspond to the sampling sites in *a*.

(near the sampling site №6) (Fig. 1a). Field works were conducted in April, 2019 (high waters due to spring snowmelt and rainfalls) and September, 2019 (low waters, dry season). In September, 2019, it was observed that the Grantcharitsa River was dried up in places, and its waters did not enter the Bistritsa conduit.

Methods. Values of pH and electroconductivity of the taken waters samples were measured in the field conditions using YSI Professional Plus handheld multiparameter meter. In laboratory conditions, the waters were analysed for As, W, Fe, Ca, Si, S, P, U, hydrocarbonates and carbonates. Measurements of As, W, Fe, Ca, Si, S, P were perfomed according to ISO 11885:2009 on a SPECTROBLUE ICP-OES spectrometer (Eurotest-Control EAD, Sofia). Natural uranium content was determined using spectrophotometric method with Arsenazo-III (DIAL Ltd, Buhovo, Sofia). Hydrocarbonate and carbonate contents were determined according to ISO 9963-1:2000 by titrimetric method (Eurotest-Control EAD, Sofia).

Preliminary hydrochemical characteristics of waters

1. *Electroconductivity and pH*. Already during field works in April and September, 2019, all sampled waters (surface, ground and mine) were recognized as low mineralized waters as was evidenced by comparatively low values of the measured water conductivity (between 44.7 and 136 µS/cm), the highest being for the mine waters (85–136 µS/cm) (fresh waters are with <500 µS/cm). The pH values for most waters were close to neutral (~7) or ranged from slightly acidic to moderately alkaline with the exception of the water samples №2 and №4 measured in April, 2019 (Fig. 1a,b). The sampling place № 2 in the Veziov Dol Valley (mine drainage water) demonstrates most drastic variation in pH –

from 2.4 (high waters in April, 2019) to 6.5 (low waters in September, 2019) and may be indicative for the quality of the Veziov Dol water in general. Fig. 1 (a, b) unequivocally evidences that the waters of the Veziov Dol River essentially increase the acidity of the Grantcharitsa waters (to pH~4.8) before their intake into the Bistritsa derivation.

2. *Content of tungsten*. As we know, there is no published data on W content in the waters in the area of the Grancharitza River so far. Our results show that, with the exception of samples №№ 9 and 10 (mine waters, gallery in Kambarsko Dere), the content of W in all other water samples is below the detection limit of the applied method (ICP-OES) – <10 µg/l. The measured content of W in samples №№ 9 and 10 is 15 µg/l. This content is lower than the maximum permissible concentation (MPC) of W in drinking water (50 µg/l) in Russia (for other countries there is no data) and essentially lower than the maximal W content in drinking water – 337 µg/l reported for the town of Fallon, Nevada (Koutsospyros et al., 2006), where at the beginning of the 21st century a childhood leukemia cluster was localized. It is noticeable that in the thermomineral waters in the region of Velingrad the content of W varies in the range 3.8–29 µg/l with a tendency to increase in the NE direction – that is, in the opposite direction from the Grancharitsa deposit (Stoyanov, Hristov, 2018).

3. *Content of arsenic.* With the exception of samples 7 and 8 (ground waters, taken in September, 2019), the presence of As in all other water samples was not established – its possible content is below the detection limit of the method used (ICP-OES) – <5 µg/l (MPC for As for the surface waters in Bulgaria is 25 µg/l). In the samples of ground waters, taken during the dry season and low waters, the measured content of As was 45 µg/l (for sample №7) and 15 µg/l (for sample №8). A significant change in the content of As in the ground waters from <5 µg/l (April) to 15 and 45 µg/l (September) is an indication of removal of As from the soil to the ground water due to the changed physicochemical conditions as shown by, for example, pH change (transition from slightly acidic to moderately alkaline medium) (Fig. 1b). It is noteworthy, that this change in the ground water does not affect the content of As (<5 µg/l) in the water of the Grantcharitsa River (site № 6).

4. *Content of uranium.* The contents of U in the studied waters are below the maximum permissible concentations approved in Bulgaria for surface waters (<40 µg/l) and for ground waters (<60 µg/l) (Fig. 1c). Several features can be noted in the geochemical behavior of U in Fig. 1c: (i) the maximum contents of U in surface waters are typical for the time of the high water (spring, April); (ii) the higest content of U in the studied surface waters is found in the reference water sample taken far away from the Grantcharitsa deposit in April, 2019, thus evidencing that the scheelite ores of the deposit most likely are not a source of uranium; (iii) in sample №7 (groundwater), U has a very similar behavior to As as a result of changes in physicochemical conditions.

Conclusion

The obtained preliminary data show that the all studied waters in the area of the Grantcharitsa deposit (surface, mine and underground) are low mineralized. It was found that W, As and U as critical chemical elements for the local inhabitants, occur in the waters of the Grantcharitsa River in low concentrations (U) or their contents are below the detection limit of the method used (W and As). The geochemical behavior of U and As found in groundwater on the terrace of the Grancharitsa River, as well as the complex evolution of W in the oxidation zone of the Grancharitsa deposit established earlier by Tarassov and Tarassova (2018), show that these three elements tend to change their solid and dissolved forms, caused by changes in physicochemical conditions. Waters, ores, soils and stream sediments should be involved in the study to elucidate in detail the geochemical behavior of these elements.

Crack waters associated with the weathered crust of granitoids are widespread in the study area. Most probably they are the reason the higher content of U in the Grantcharitsa River to be detected in the time of high water.

In future work, special attention should be paid to acid mine drainage contaminating the waters of the Veziov dol.

Acknowledgement: The study was supported by the National Science Fund of Bulgaria (Contract № KP-06-OPR 03/5, 2018).

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