Changes in discharged water quality from abandoned uranium mines near Kalna

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Abstract. Various genetic types of uranium minerals (infiltrated, hydrothermal, etc.) have been found in the region of Stara Planina. Uranium minerals in granitic rocks that build up the area of Kalna in central Stara Planina are selected for their importance and the degree of exploration. The analyzed levels of the natural radioactive and trace elements in water and fluvial deposits from a general area of the closed mines are presented in this paper. Relatively wide ranges of the obtained uranium concentrations in ground and surface waters are explained in this work by the presence of various geochemical barriers and by the variations in the quantity and velocity of ground water flow over the year.

Introduction

This paper is concerned with the area of abandoned mines at Kalna on Stara Planina, which was explored, where uranium ore was extracted and where water and soil are radioactive. The concentration levels of the natural radioactive uranium, radium and radon elements were measured in water bodies, fluvial deposits, humus, and spoils of the old mines. Our purpose in writing this contribution is to present the state of the natural radioactivity in the abandoned mines, where nuclear mineral ore was extracted, and in the surrounding area that could be contaminated from mine workings. The research data are used to indicate the water and soil contamination in the given area.

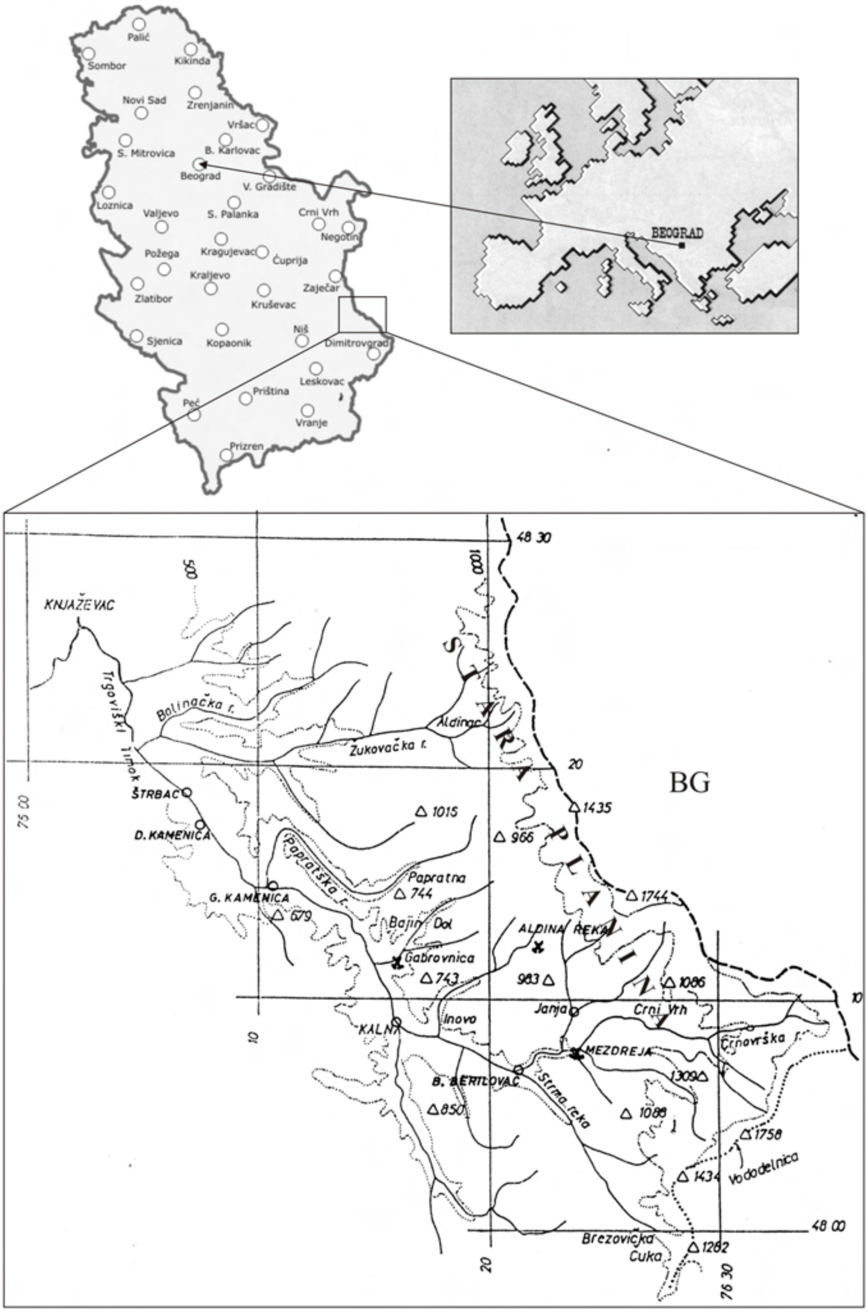

Fig. 1. Geographical location of Stara Planina and the exploration area.

Geological prospecting and exploration in the area of the old uranium mines at Kalna on Stara Planina were carried out from 1992 to 1998. The methods used in the exploration were radiometry, geochemical, hydrogeochemical, and laboratory analyses.

The geological exploration for nuclear mineral (uranium) ores near Kalna was started in 1949 when the mineral was found at Mezdreja, Gabrovnica, Srnući Do and Aldina Reka. Mine workings and ore extraction began in 1960 and discontinued in 1966. A separation plant was erected at Mezdreja. Field exploration for uranium at Kalna was discontinued in 1998. Since then, only the collected information and records have been studied.

The exploration area

The mountain of Stara Planina, situated in the extreme SE of Serbia, its ridge bounding on Bulgaria, covers a surface area of about 1100 km^2 and altitudes from 400 m to 2169 m. The Trgoviški Timok and Visočica and their many tributaries drain the mountain. Major towns in the region are Zaječar in the north, Knjaževac in the central area, and Pirot in SE, all connected by asphalted roads. There are small mountain villages that can be reached by narrow dirt roads. After the mines were closed, local population live and work on the land.

The Kalna mines are centrally situated on Stara Planina. The Trgoviški Timok and its tributaries drain the area.

Geology and metallogeny of Kalna area

The area is made up of varied lithological complexes that differ in age, origin, mineral and petrographic compositions (Fig.2). The oldest rocks are amphibolite, gneiss and greenstone of Riphean/Cambrian age (diabase phyllite formation). During the Ordovician, these rocks were intruded by basic (gabbroid) and acidic (granitic) magmatic rocks, and during the Silurian and Devonian molasse and other sediments were deposited. Carboniferous lake sediments and volcanogenic-sedimentary products deposited later. The Mesozoic is represented by sandstone, marlstone and limestone, and the Quaternary by alluvial deposits of the Trgoviški Timok in a maximum thickness of 30 m and width about 1 km (Kovačević and Gertik 1995).

Stara Planina is characterized by a complex tectonic pattern of many regional and local fault zones. Major uranium ore occurrences and deposits are spatially associated with the granite massif of Janja, or the ore field of the same name on the western slopes of central Stara Planina. High-temperature uranium-thorium minerals and hydrothermal vein/lens uranium minerals are located in Kalna ore field. The high-temperature uranium-thorium minerals at Aldina Reka are associated with the products of serpentinite granitization in zones either in the serpentinite itself or at its contact with granite. The hydrothermal vein/lens deposits and occurrences of uranium ore (Mezdreja, Gabrovnica and Srneći Do) are associated with repeatedly activated fault zones. Minerals occur in lenticular ore bodies that build columns and complex ore veins. These are minor deposits of the estimated reserve of a few hundred tons U_3O_8 (Gertik et al. 1990).

The Gabrovnica deposit in Janja granite is an example how abundant uranium accumulations are formed by its redistribution and deposition in clayey and friable

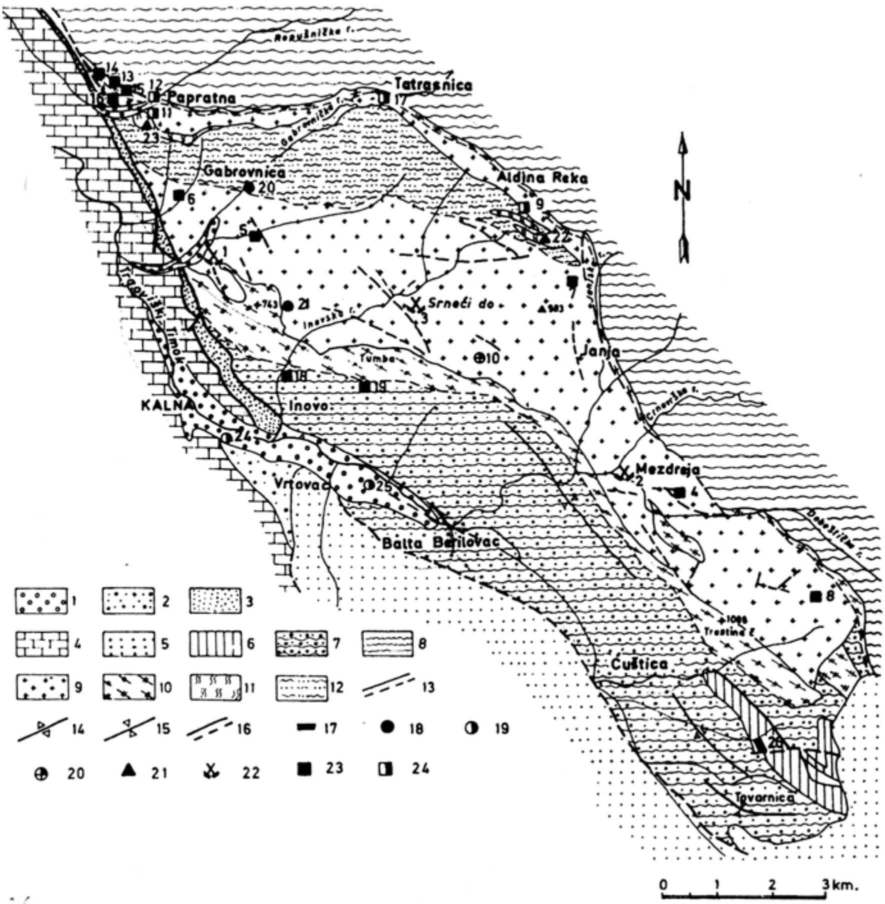

Fig. 2. Geological map of Kalna region. 1. Alluvium; 2. Sand and clay (Pl); 3. Miocene deposits; 4. Cretaceous deposits; 5. Permian deposits; 6. Carboniferous volcanogenic-sedimentary rocks; 7. Metasediment of the Inovo Series; 8. Crni Vrh Formation rocks; 9. Granitic rock; 10. Gabbroid rocks; 11. Serpentinized peridotite; 12. Gneiss; 13. Boundary; 14. Anticline axis; 15. Syncline axis; 16. Fault; 17. Black coal occurrence; 18. Au (primary) occurrence; 19. Au (alluvial) occurrence; 20. Cu and Mo occurrence; 21. Cr occurrence; 22. Uranium deposit; 23. Uranium occurrence; 24. Uranium and thorium occurrence.

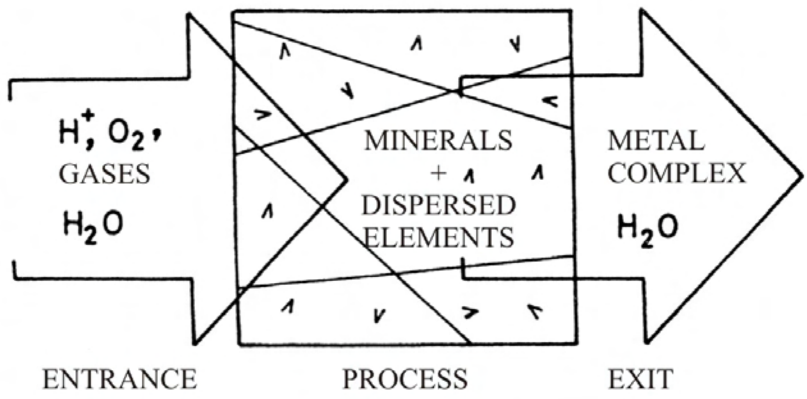

Fig. 3. Mineralized fluid formational proces.

surficial rocks of the fault zone. This process has evolved from the formation of faults to the present day (Fig.3).

One of the principal factors of uranium mobilization from granite rocks is the supply of mildly acidic aqueous solutions that altered and leached the rocks. The solutions were also oxidizing, because they contained oxygen that intensified U^{+4} oxidation and the formation of uranium ions that built complexes mainly of $Ca_2(UO_2(CO_3/_2(N_2O)$ type and a smaller amount of $Ca(UO_2(SO_4)_2(H_2O)$. These complexes are relatively easily transported by solutions (Romberger 1984). The highly migratory uranium also indicates its relatively slow deposition. For the uranium deposition in the given instance, the minerals of clays, iron oxides and organic matter in rivers are important (Gržetić and Jelenković 1995).

Generally, the mean uranium content in granites of Janja is about 6 ppm, locally up to 20 ppm, whereas the mean proportion of dissolved uranium in the granites is 3.82 ppm.

Research results

Comprehensive explorations and annual observation of uranium and characteristic elements in the area of the abandoned uranium mines of Mezdreja and Gabrovnica were carried out from 1992 to 1998 (Kovačević 1997). The collected data are given in Tales 1,2,3. Radiometric analysis of the samples from spoil dumps is not presented in this paper. The analytical results are given only for subsurface and surface waters and fluvial deposits of the Trgoviški Timok.

Table 1 shows chemical analysis of water from Mezdreja and Gabrovnica mines. The table above shows increased uranium, strontium and iron in mine water. The relatively wide ranges of some contained elements can be explained by the sampling indifferent seasons, thereby different ground water flow rates through fractures in the ore bodies and adjacent rocks (Nikić et al. 2002).

Table 1. Ranges of measured elements in pit water of Mezdreja and Gabrovnica mines.

Location	Range of measured quantities							
	U (μg/l)	Ra (Bq/l)	Fe (mg/l)	Sr (mg/l)	Pb (mg/l)	Mineral (mg/l)	pH	Ep (μS/cm)
Mezdraja	93,8-420	0,07-0,32	0,37-1,08	4,40-12,38	0,005-0,01	470-860	7,4-7,5	460-580
Gabrovnica	27,2-50,0	1,50-4,42	0,13-0,56	0,48-0,48	0,01-0,02	622-720	6,8-6,9	380-570

Table 2. Ranges of measured elements in well water of Balta Berilovac, Vrtovac, Inovo, Gornja Kamenica, Donja Kamenica, Štrbac, Baranica villages.

Location	Range of measured quantities						
	U (mg/l)	Sr (mg/l)	Cu (mg/l)	Ra (Bq/l)	Mineral. (mg/l)	pH	Ep (μS/cm)
Balta Berilovac	0,005-0,009	0,01-0,06	0,01-0,03	0,05-0,07	750-920	7,3-7,4	660-680
Vrtovci	0,001-0,002	0,01-0,03	0,01-0,02	0,09-0,20	790-938	7,0-7,1	700-740
Inovo	0,002-0,008	0,01-0,02	0,01-0,02	0,05-0,06	485-560	7,4-7,7	460-510
Gornja Kamenica	0,001-0,002	0,09-0,15	0,01-0,02	0,20-0,60	828-1020	7,3-7,5	695-870
Donja Kamenica	0,001-0,003	0,11-0,20	0,01-0,03	0,10-0,19	395-570	7,5-7,8	420-495
Štrbac	0,001-0,003	0,01-0,03	0,01-0,03	0,05-0,07	687-900	7,1-7,3	605-680
Baranica	0,001-0,003	0,01-0,02	0,01-0,02	0,11-0,20	272-360	7,4-7,6	440-460

Table 3. Radiometric data of the Trgoviški Timok alluvial deposit.

Semple	Kind of analysis: from to			
	U (ppm)	Th (ppm)	K (%)	Th/U
Fluvial deposit	1,3778-4,32672	3,38058-13,3282	0,68497-2,11951	1,63218-4,46154

Table 2 gives chemical composition of water from dug wells used for local water supply. The well water contains relatively low uranium, but increased iron. The wells are dug in the Trgoviški Timok alluvium, which is in direct hydraulic communication with the river. The alluvium consists of several alternating layers of gravel, sand and clay. Clay minerals and the organic material contained in them rapidly precipitate uranium in the marginal part of the alluvial plain. This is probably the reason for the relatively low uranium concentration in well water (Protić 1994). The sampled village wells are located in the middle of the Trgoviški Timok broad alluvial plain.

Table 3 gives radiometric data for the Trgoviški Timok alluvial deposit downstream of the mines, sampled (16 samples) at every 1000 m over a length of 16 km. The geomorphologic and hydrogeological characters of the area control the gravity flow of both surface and subsurface waters to the Trgoviški Timok. These waters carry dissolved uranium and its products to chemical barriers (clay minerals, organic material, etc.) where it is deposited. In view of the geological relationships and the hydrogeological conditions in the drainage area and the contained uranium minerals, the concentrations of radioactive elements in river deposits are not much anomalous.

Conclusion

The natural radioactive elements (uranium, thorium, radium, radon) concentration levels were measured in samples of pit water, well water and fluvial deposits. All the obtained data for the area of the old uranium mines at Kalna (Stara Planina) lead to the following conclusions. The primary source of uranium in the area is the much-fragmented granitic rocks. Fault zones are the environments of uranium deposition. Systems of fractures in granitic rocks are the flow paths of ground water that carries out uranium from the pre-formed ore bodies and the adjacent rocks. As a result, uranium and trace elements are increased in pit water. Geochemical barriers of clays and organic materials (alluvium) and the greater amounts and faster filtration of ground water control the dissolution of uranium and trace elements in ground water downstream of the mines.

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