Geochemical data on contaminated beach sands of the Vromos bay, Bulgarian Black sea coast

Геохимични данни за замърсения плажен пясък на залива Вромос, български черноморски бряг

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Резюме. Изследвани са пясъци от плажа на залива Вромос, ИЮИ от гр. Бургас, замърсен с тежки метали и радиоактивни елементи от флотационния отпадък на Бургаски медни мини през периода 1954–1977 г. След почистването на плажа през 90-те години, темата остава актуална поради естествен процес на обогатяване на плажния пясък с тежки минерали от дънните седименти в залива. Данни от 2011 г. за съдържанията на главни елементи и елементи следи от 14 проби в 7 точки по протежение на плажната ивица показват обогатяване на западната част на плажа с желязо (Fe_2O_3+FeO до 24%), мед (до 1070 ppm), уран (до 32 ppm) и редки земи (∑REE до 1050 ppm). Тенденцията се свързва с натрупване на рудни минерали, тежки скалообразуващи и акцесорни минерали, както и карбонати, установени в изследваните проби или присъстващи в орудяванията от района по данни от предшестващи изследвания.

Key words: Vromos bay, beach sands, contamination, radioactivity, REE.

Introduction

The Vromos bay, situated ESE of the town of Burgas, has been contaminated by copper ore flotation tailings of increased U content. From 1954 to 1977 the total waste of approximately 8 000 000 t of the Burgas copper mines was dumped in the sea. Part of the waste formed a costal layer 1300 m long, 120 m wide and 2–3 m thick (Vapirev et al., 1993). The sand mass (black sand) was dominated by magnetite and contained up to 60 wt.% Fe_2O_3+FeO (Rojdestvensky, 1979). The increased specific activity of radionuclides was associated with increased contents of ^{238}U and ^{226}Ra (Dimitrov et al., 1994) due to the presence of U-minerals in the ore (Antonova, 1988). Numerous research projects in the period from 1979 to 1993 followed by contaminated sands removal from 1991 to 1998 resulted in decrease of total activity (^{238}U, ^{226}Ra, ^{232}Th, ^{40}K) from 74–10 175 Bq/kg in 1979 to 83–400 Bq/kg in 1998 (Bonev, 2003). The environmental problems remain however because of sea dynamics favoring natural process of placer formation and coastal sand enrichment with heavy minerals. Previous studies do not consider in details sands mineralogy and geochemistry.

Data on radioactive elements bearing minerals and bulk sand contents of U and other radioactive elements are scarce or not available in official scientific publications. We present preliminary geochemical results for major and trace elements in the Vromos bay beach sands.

Materials and methods

A set of 14 sand samples was collected from 7 points along the beach in April 2011 to specify current lateral compositional variation at surface and deeper level (0–30 cm and 30–60 cm respectively). Between 2 and 4 kg of each sample was coned to 70 g and grinded in an agate mill. The major oxides are determined by wet chemical analysis; the trace elements are analyzed by AAA and LA-ICP-MS techniques. The rest of the sand material is prepared for mineral separation. Laser Raman spectroscopy is applied for identification of minerals in selected heavy fractions (dencity >3.3 g/cm^3). Samples preparation and analytical works are performed in the Sofia University “St. Kliment Ohridski” and in the Geological Institute of the Bulgarian Academy of Sciences.

Results

Field observations clearly distinguish systematic lateral change of sands color in the western part of the beach due to increasing proportion of mafic silicates and ore minerals. The grain size is uniform and dominated by fraction 0.25–0.5 mm (6% of 0.5 to 1.00 mm; 80% of 0.25 to 0.5 mm; 13% of 0.125 to 0.25 mm; 0.4% of 0.063 to 0.125 mm; and <0.1% of fraction <0.063 mm). Data on sands mineralogy show high proportion of magnetic fractions (40% in 0.5–1 mm grain size; 75% in 0.25–0.5 mm; 31% in 0.125–0.25

mm) composed of magnetite and hematite. The most widespread minerals in nonmagnetic fractions are mafic silicates (pyroxene, amphibole, biotite, epidote, allanite) and ore minerals (pyrite and chalcopyrite). Abundant carbonate minerals (calcite, siderite, magnesite, dolomite, malachite) appear in fractions of different density.

Major oxides show similar lateral distribution in both surface and deeper level of the beach sand. Noticeable increase of Fe (Fe_2O_3+FeO up to 24 wt.%) in the western part of the beach corresponds with decrease of Si, Al, Na, and K. Strong correlations distinguish two associations among major oxides: FeO–MgO–MnO–TiO_2 related to dark-colored silicate and ore minerals, and SiO_2–Na_2O–K_2O related to light colored silicates. The ratio Fe_2O_3/(Fe_2O_3+FeO) is commonly higher in deeper level samples (0.59–0.78) than in the surface level ones (0.41–0.67), suggesting different proportions of Fe^{2+}- and Fe^{3+}-bearing minerals.

Copper (107–1071 ppm) predominate among the trace elements expected in sulphide ore mineralization of the Burgas region (Zn, Pb, Ni, Co, Cr, V, and Sc). These elements do not show clear trends of lateral or depth distribution, however the highest contents of Pb, Co and Cr are found in the samples with the highest contents of Fe, Ti, Mn and Cu. Strong positive correlations between mentioned trace and major elements support a preliminary interpretation on ore minerals accumulation in the western part of the beach.

Uranium contents (12–32 ppm) are similar in surface and deeper level at each point of sampling. The lateral distribution shows the same trend of enrichment in the western part of the beach like Fe and Cu. Th/U ratio values are low (0.17–0.48) due to low and relatively constant Th contents (5–7 ppm).

The total REE contents range from 290 to 1050 ppm with the highest values in samples with Fe, Cu, and U enrichment. Chondrite normalized patterns are uniform with high LREE (La_N/Lu_N 28–119) and missing or slightly positive Eu-anomaly (Eu/Eu* 1–1.4). The proportion of La+Ce (76 to 84% of ∑REE) suggests participation of LREE minerals like bastnazite and parasite, established in the Rosen ore mineralization (Antonova, 1988), as well as allanite, found in some mineral fractions in our samples.

High correlation coefficients (0.90–0.93) between Fe, Cu, U, and LREE give evidence for a specific geochemical assemblage produced from heavy minerals accumulation on the beach of Vromos bay due to sea dynamics.

Concluding notes

The preliminary results reported here give an idea of changing sands composition of the Vromos beach after the waste removal 14 years ago. The unexpected results refer to REE enrichment in the sands. While increased contents of Fe and Cu correspond to abundant magnetite, hematite, pyrite and chalcopyrite, the minerals bearing U and REE remain yet poorly known. Our further steps focus on identification of particular minerals responsible for U and REE enrichment, as well as on comparison between radionuclide contents and specific activity data. A better understanding of the dynamic system producing heavy minerals accumulation in the area of study needs however prolonged observations based on collaboration between physics, mineralogy and geochemistry to deduce reliable temporal trends of this process.

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