Trace elements distribution in black clay sediments and dump materials (East Maritza Basin, Bulgaria)

Елементи-примеси в черни глинести седименти и насипищни материали (Източномаришки басейн, България)

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Introduction

A study of trace elements distribution in sediments and dump materials poses always many difficult questions and decisions, hence the interest of study is increasing. The black clays from East Maritza Basin (EMB) are a component in a chain: coals – coaly shales – black clays – clays with coal particles. There are many studies on the coals and coaly shales geochemistry from the basin. Узунов (1976 and references therein) clarified vanadium geochemistry during the coal-forming processes. Later Eskenazy developed EMB coal geochemistry in suites of elements, e.g. alkaline, REE, U and Th, Mo, chalcophile elements (Ескенази, 1990 and references therein). There are also data on coal and coal-bearing rock trace element geochemistry in studies of Vassilev (1993) and Костова (2005). A study and comparison of data on black clays and dump materials geochemistry will continue the chain and broad the knowledge on the elements behavior in different geological environment.

The aim of the study is to characterize the trace elements distribution and to compare the geochemical features of the sediments and dump materials, on one hand, and coals and coaly shales, on the other. A proviso should be outlined – the rocks compared are of the same, black clay, type, but not exactly the same rocks at different environment, so the comparison could not be "ideal".

Material and Methods

The black clay sediments studied are presented by three core samples from Troyanovo-2 (sedTr2) and Troyanovo-3 (sedTr3) mines of EMB. Black clay dump materials comprise three core samples from Dryanovo Dump (dDr), two surface samples from internal dump of Troyanovo-2 mine and one surface sample from Gledachevo Dump (dTr2). According to XRD data main minerals in samples studied are mixed layer illite/smectite, illite, kaolinite group minerals and quartz. Small quantities of gypsum, feldspar, and pyrite were also detected. The content of $C_{org.}$ varies from 0.94 to 9.61%. The methods for analyses used were AA for Cu, Zn, Pb, Co, Cr and Ni and ICP-MS for As, Be, Cd, Ga, Mo, V and W.

Results and Discussion

The content and behavior of Cu, Zn, Pb, V, Cr, Ni, Co, Mo and W will be discussed in detail, as they are the most interesting and variable. The number of the samples and data are not enough to present a statistically valuable estimation of the trace elements distribution, but it seems to be interesting, as it marks some tendencies. The Clarke values of Беус и Григорян (1975) and data about soil geochemistry of Gulubovo region were used to compare the data received.

The mean content of Be, Ga, Cd and As is lower than the Clarke for clays (Fig. 1), but values higher than Clarke were observed in some of the samples and the maximums were related to the black clay type.

Vanadium, Cu and Zn show mean content higher than Clarke in sediments and dump materials (Fig. 1). Lower than Clarke is the content of Zn in the core samples from Drjanovo Dump. Molybdenum also has values higher than Clarke. Tungsten shows steady tendency of values higher than Clarke in the most of the samples studied. Lead, Co and Ni content is lower than Clarke for all samples and shows regular distribution.

Most of the elements mentioned show values and tendencies of distribution in the black clay type very similar to those for coals and coaly shales. Cu and Zn have "inherited" high values from the coals and coaly shales and have retained their high values in dumps and soils (Fig. 1). The elements have analogous behavior in surface environment – they are among the more mobile of the heavy metals and the

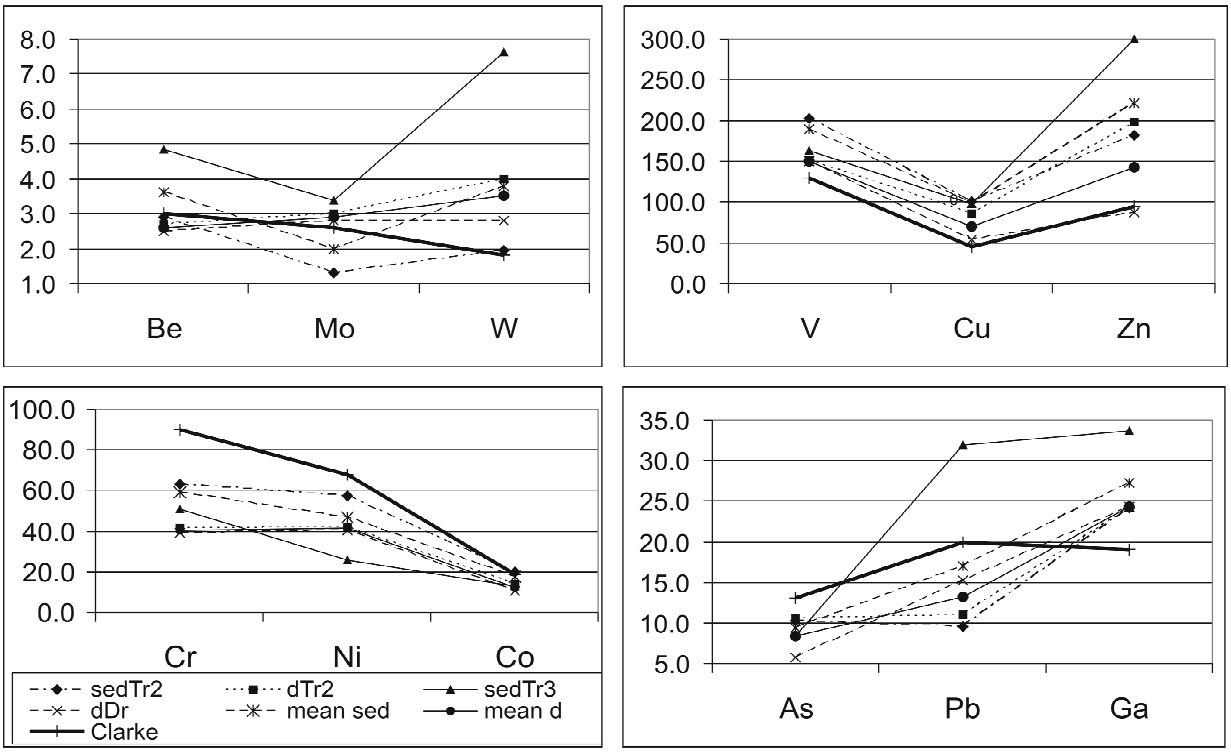

Fig. 1. Trace elements distribution in black clay sediments and dump materials from East Maritza Basin (ppm)

trend for the dump materials is to have lower values than in the sediments. Lead shows irregular distribution in sediments and dump materials, but the tendency for lower values in dumps could be marked.

In black sediments vanadium shows values higher than Clarke, but in dump materials they are nearly the Clarke values. In lignite coals of EMB vanadium content is higher than Clarke, and in the coaly shales is lower (Ескенази, 1990). The data received in this study are close to and could confirm the conclusions of Узунов (1976) – values higher than Clarke were detected in the black clays overlaying the coal seams. The tendency of decreasing values in dump materials already marked for Cu and Zn is also valid for V, Co and Ni despite the mobility of vanadium is lower than the mobility of Co and Ni. Узунов (1976) point out to the dual geochemical behavior of V strongly affected by the organic matter. The organic matter acts as a stabilizer for vanadium solutions and as a factor of its geochemical migration. Molybdenum is a tyipomorphic element for coals in EMB, i.e. its high content is organic matter dependent, and this feature is characteristic for black clays and dump materials too (Fig. 1). The geochemical behavior of W in surface environments resembles that of Mo. Usually, both elements have low mobility, very strongly dependent on pH and Eh conditions.

As concluding remarks it would be marked that the scarce number of the samples studied may not allow drawing any regularities in the elements distribution in sediments and dumps, but some steady trends could be outlined. Characteristic for dump materials of black clays are: 1 – decreasing values of a group of elements when compared to sediments: Cu, Zn, Pb, Cr, Co, Ni, As, V and Ga; 2 – two elements only (Cd and Mo) show increasing values in the black clay dump materials; 3 – tungsten shows clear differences and different trends among the sediments and dump materials, but in general is practically inert in dumps.

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