Abstract

Maps of cinnabar in alluvial sediments in Bulgaria are compiled on the basis of 133 123 stream sediment pan-concentrated samples collected in the period 1945-2004. The maps are dotted to present cinnabar concentrations coded in ranks and as contours to give the frequencies of the cinnabar population among the samples studied. A model map of cinnabar distribution using the double Fourier series method is also compiled. The map shows a grouping of cinnabar in two regional stripes of the Bulgarian territory. The correlations of cinnabar in alluvial sediments are determined and its stable mineral associations are derived! The barite-cinnabar-gold association indicates the existence of epithermal mercury-gold mineralizations in Bulgaria and the necessity of further studies on cinnabar from geological and ecological viewpoint is outlined.

Key words: cinnabar, maps of cinnabar, mineral associations of cinnabar

Introduction. Historical \[1\] and ethnographical \[2\] studies show that mercury (as a metal) and cinnabar (as a mercury mineral) are known in Bulgarian lands since ancient times. The evaluation for the prospects of mercury deposits in Bulgaria reveal the presence of mercury as a trace element in sulphidic ores and of cinnabar in stream sediment pan-concentrated samples \[3-10\]. The studies in Kjustendilsko Kraishte show that mercury is contained in soil, cinnabar - in the stream sediments, and gold-mercury amalgams and mercury drops - in the gold alluvial placers \[1\].

International projects for mercury monitoring in the European atmosphere indicate that the Bulgarian atmosphere contains mercury \[12\] and that the industrial facilities of the country (coal combustion, non-ferrous metals plants) emit more than 69 t mercury per year \[13\].

This requires analysis of the distribution of cinnabar in alluvial sediments in Bulgaria.

Data. Data from stream sediment surveys, conducted in Bulgaria in the period 1945-2002 \[14\] and actualized in 2004, are used and organized in a database \[15\]. The total number of stream sediment pan-concentrated samples is 133 123, 853 of them containing cinnabar.

Methods. A distribution map of cinnabar is compiled, its concentration being coded in ranks (Fig. 1a) and a histogram of this distribution is given in Fig. 1b. The
territory of Bulgaria is divided into squares of area of 98 km$^2$ each (map sheets scaled 1:25 000) and the frequency of cinnabar-containing samples is estimated for each square. This frequency is referred to the centre of each square and a contour frequency map is drawn (Fig. 2a) using the triangle method, the frequency distribution being illustrated by a histogram in Fig. 2b.

The frequency map data are used to compile a model map by the double Fourier series method $^{[16]}$ on 625 harmonics (Fig. 2c). The model is compiled only on squares, where cinnabar was found. The parameters of the model matrix are corrected by involving a coefficient accounting for the loss of information, defined as the ratio between the model sum and that of the data. The deviation of the model from the data is compared with a normal Gauss distribution (Fig. 2d).

Correlation between the minerals and cinnabar in the samples was examined by calculating the expected number of samples ($l_{ac}$) in which cinnabar (c) and another mineral (a) are present simultaneously (assuming they do not depend on each other), and comparing the result with the observed number of samples containing cinnabar and the considered mineral ($N_{ac}$). The difference between $l_{ac}$ and $N_{ac}$ is evaluated by calculating the total Bernoulli’s probability or the Poisson’s approximation ($S_{Pi}$). If a significant difference exists between $l_{ac}$ and $N_{ac}$, at a proper confidence level $\alpha$, one accepts that the mineral (a) forms a stable mineral association with cinnabar, i.e. they are correlated (Table 1).

**Table 1**

<table>
<thead>
<tr>
<th>N</th>
<th>Mineral (a)</th>
<th>$N_a$</th>
<th>$N_{ac}$</th>
<th>$l_{ac}$</th>
<th>$S_{Pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>zircon</td>
<td>33910</td>
<td>287</td>
<td>217.282</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>scheelite</td>
<td>28644</td>
<td>267</td>
<td>183.540</td>
<td>1.000</td>
</tr>
<tr>
<td>3</td>
<td>barite</td>
<td>27508</td>
<td>368</td>
<td>176.260</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>gold</td>
<td>13637</td>
<td>228</td>
<td>87.381</td>
<td>1.000</td>
</tr>
<tr>
<td>5</td>
<td>galena</td>
<td>7940</td>
<td>101</td>
<td>50.876</td>
<td>1.000</td>
</tr>
<tr>
<td>6</td>
<td>anatase</td>
<td>5509</td>
<td>66</td>
<td>35.300</td>
<td>1.000</td>
</tr>
<tr>
<td>7</td>
<td>leucosene</td>
<td>3444</td>
<td>77</td>
<td>22.068</td>
<td>1.000</td>
</tr>
<tr>
<td>8</td>
<td>lead</td>
<td>2279</td>
<td>50</td>
<td>14.603</td>
<td>1.000</td>
</tr>
<tr>
<td>9</td>
<td>malachite</td>
<td>912</td>
<td>18</td>
<td>5.844</td>
<td>1.000</td>
</tr>
<tr>
<td>10</td>
<td>massicot</td>
<td>144</td>
<td>7</td>
<td>0.923</td>
<td>1.000</td>
</tr>
</tbody>
</table>

A lot of correlations between the minerals listed in Table 1 and cinnabar are illustrated in Fig. 3 via a circular diagram which is decomposed into clusters using the so-called each-versus-each rule which, according to us, are with the meaning of stable mineral associations of cinnabar (Fig. 3b).
Results and discussion. It was estimated that approximately 0.64% of the Bulgarian territory (about 711 km$^2$) are prospective for mercury mineralization, a fact pointing that Bulgarian territory belongs to the Mediterranean mercury planetary band [1]. The prospects are located mainly in Transko and Kjustendilsko Kraishite, Western Balkan, Southern Rila (Razlog district), Eastern Rhodopes, Sakar and Strandja (Fig. 1a). The histogram of cinnabar content in the heavy minerals concentrates samples shows a well-expressed left-asymmetry and a mode of first rank (Fig. 1b). The histogram of the cinnabar frequencies (Fig. 2b) also reveals a clear left-asymmetry. These results point to the presence of at least two types of cinnabar mineralizations - a dispersed one, of a low content of cinnabar which according to geological data is connected with non-ferrous deposits, and a second one rich in cinnabar.
model shows a grouping of cinnabar in two regional stripes: Transko Kraishte-Dospat (135° SE-NW) and Kirkovo village (Zlatograd district)-Madjarovo-Ljubimec-Elhovo (45° NE). Our model extrapolates stripes in Northern Bulgaria, where stream sediment data do not exist till now.

Table 1 presents the minerals correlated with cinnabar, namely minerals of non-ferrous ores and products of their supergene alteration (galena, lead, massicot, malachite) as well as accessory minerals (zircon, anatase, leucoxene). Other minerals-correlates of cinnabar are gold, barite and scheelite. The relationships between these minerals are presented in Fig. 3a. After decomposing the circular diagram, seven stable cinnabar mineral associations were obtained (Fig. 3b). Barite takes part in the following two associations: barite-cinnabar-gold-massicot-zircon-anatase and barite-cinnabar-lead-galena-malachite-leucoxene, scheelite - in cinnabar-gold-lead-galena-massicot-scheelite association. Five of these associations are gold-containing, a fact pointing at the presence of mercury-gold mineralizations. Another association - cinnabar-lead-galena-malachite-massicot indicates non-ferrous mineralizations without gold.

Conclusion. 1. The present study confirms that Bulgarian territory belongs to the Mediterranean mercury planetary band and that 711 km² of it is prospective for mercury deposits.

2. Cinnabar is grouped in two regional stripes: Transko Kraishte-Dospat (135° SE-NW) and Kirkovo village (Zlatograd district)-Madjarovo-Ljubimec-Elhovo (45° NE).

3. Pathfinders of cinnabar are barite, scheelite, gold, galena, lead, massicot and malachite, thus indicating the existence therein of mercury-gold and mercury-non-ferrous deposits. On the other hand, due to the cinnabar-gold correlation the former is a pathfinder for epithermal gold deposits.

4. The present study shows the necessity of further studies on cinnabar in Bulgaria in order to clarify the sources of mercury pollution and to prospect for cinnabar deposits.

REFERENCES


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