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DISTRIBUTION OF CINNABAR (HgS) IN ALLUVIAL SEDIMENTS IN BULGARIA

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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 6.9 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

Fig. 1. a) distribution map of cinnabar in alluvial sediments in Bulgaria. The concentrations of cinnabar in fine heavy fraction are coded in ranks, as follows: 1 - from 1 to 10 grains; 2 - from 11 to 20 grains; 3 - from 21 to 50 grains; 4 - from 51 to 100 grains; 5 - from 101 to 200 grains; 6 - from 0.001 to 0.01 wt %; 7 - over 0.01 to 0.02 wt %; 8 - over 0.02 to 0.05 wt %; 9 - over 0.05 to 0.1 wt %; 10 - over 0.1 to 0.5 wt %; 11 - over 0.5 wt %; b) histogram of cinnabar in ranks

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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).

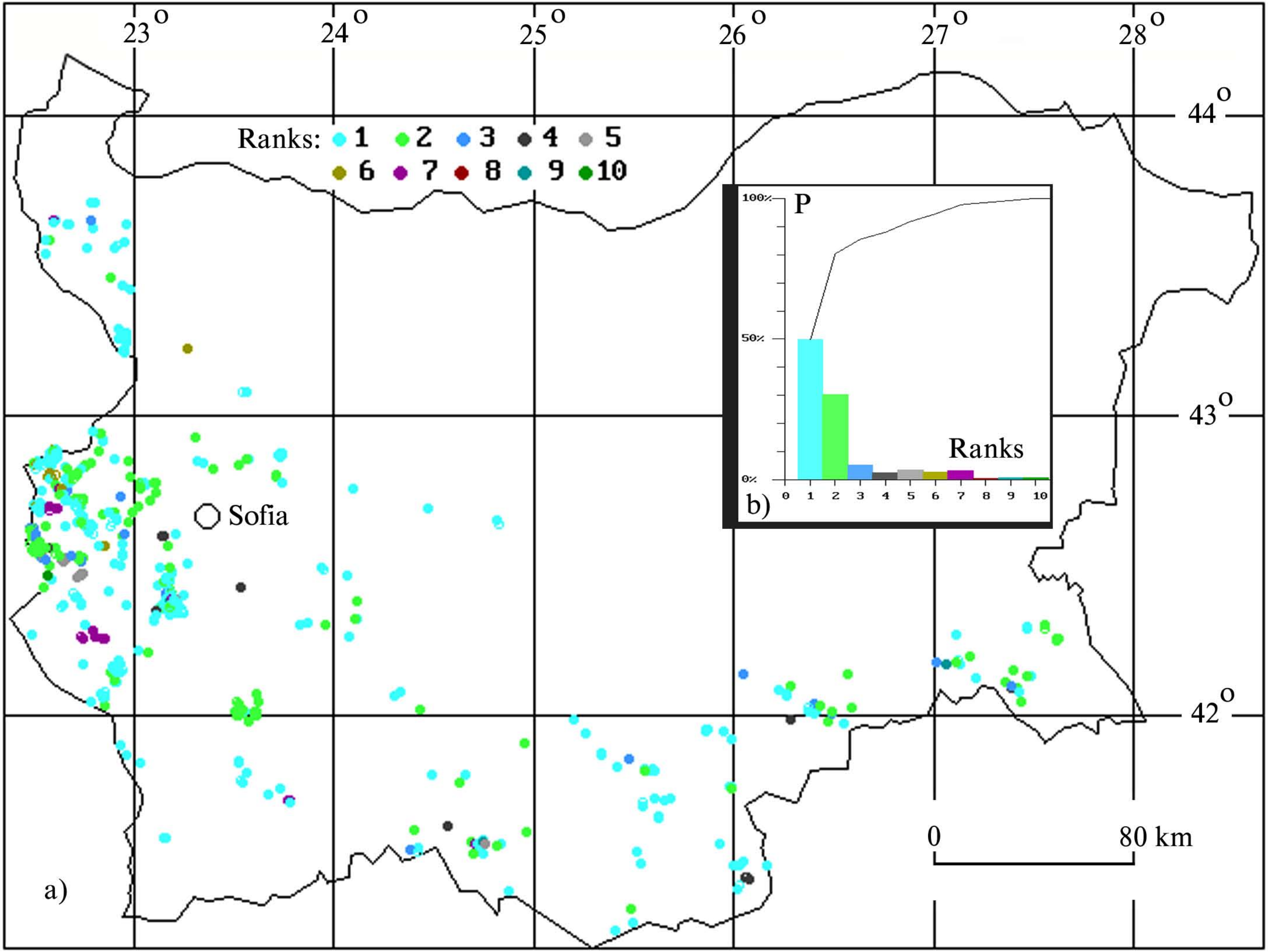
Correlation between the minerals and cinnabar in the samples was examined by calculating the expected number of samples (λ_{ac}) in which cinnabar (c) and another mineral (a) are present simultaneously (assuming they do not depend on each other), and comparing the result with the observed number of samples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

Table 1

Significant correlations between cinnabar (c) and other minerals (a): Poisson's approximation, $\alpha < 0.001$

N	Mineral (a)	N_a	N_{ac}	λ_{ac}	$\sum_{i=0}^{i=N_{ac}} P_i$
1	zircon	33910	287	217.282	1.000
2	scheelite	28644	267	183.540	1.000
3	barite	27508	368	176.260	1.000
4	gold	13637	228	87.381	1.000
5	galena	7940	101	50.876	1.000
6	anatase	5509	66	35.300	1.000
7	leucoxene	3444	77	22.068	1.000
8	lead	2279	50	14.603	1.000
9	malachite	912	18	5.844	1.000
10	massicot	144	7	0.923	1.000

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).


23°
24°
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Ranks: 1 2 3 4 5
6 7 8 9 10
Sofia
a)
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b)
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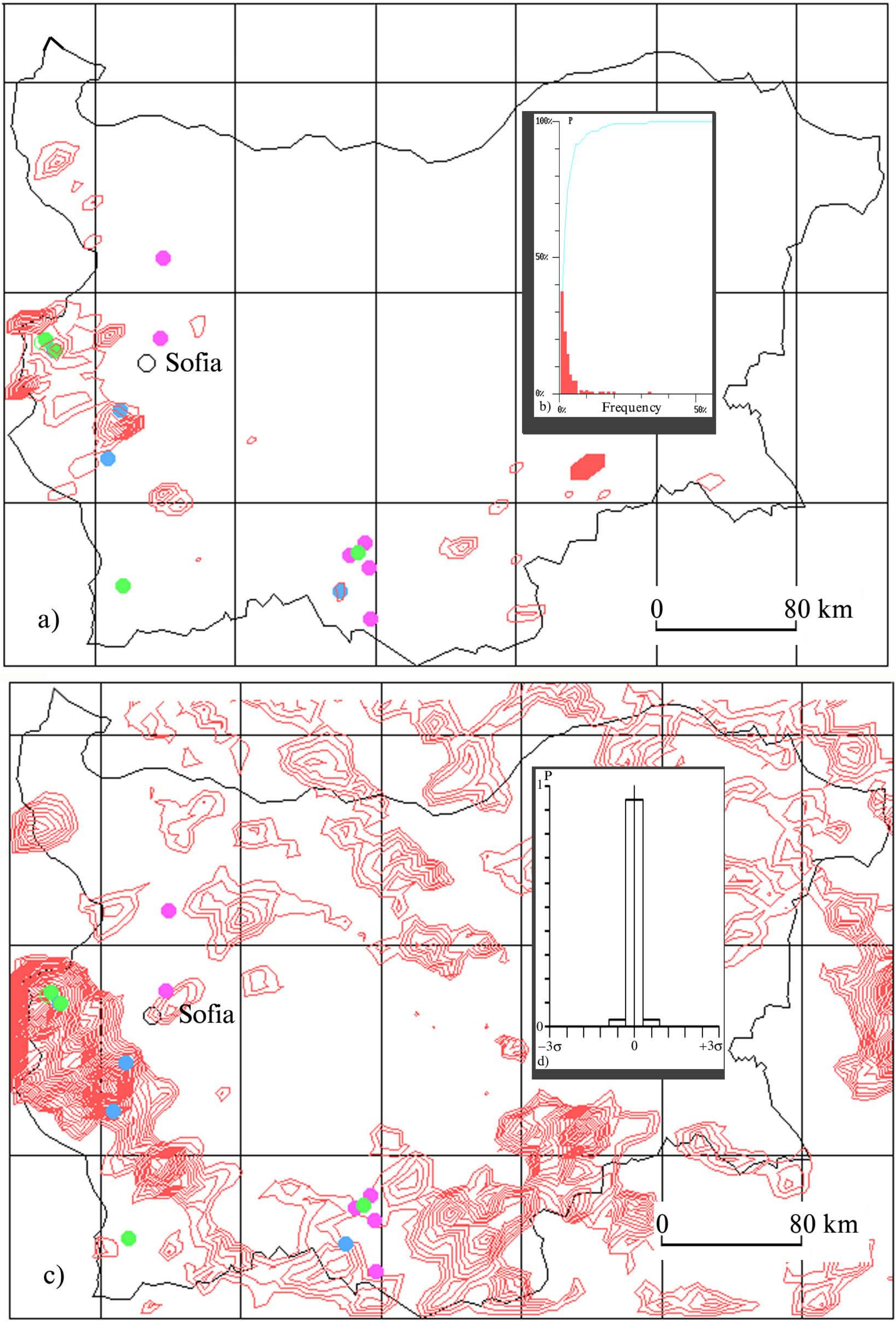
a)
Sofia
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80 km
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50%
0%
b)
0%
Frequency
50%
c)
Sofia
0
80 km
P
1
0
−3σ
0
+3σ
d)

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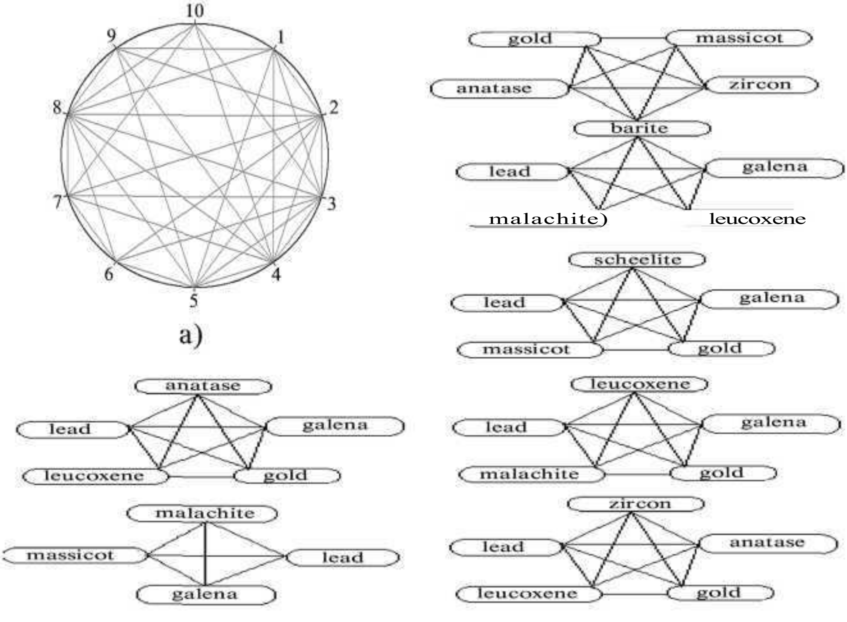
Fig. 2. a) contour frequency map of cinnabar: 1st line - 0.1 % cinnabar frequency in samples, step 2 %. Blue, green and violet circles designate indications, occurrences and deposits of cinnabar respectively or of increased concentrations of mercury in sulphidic ores; b) histogram of frequencies of samples with cinnabar; c) full Fourier-model of cinnabar; d) histogram of deviations between the model and the data

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 [11]. The prospects are located mainly in Transko and Kjustendilsko Kraishte, 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.



b)

Fig. 3. Relationships of cinnabar: a) all correlations. The numbers correspond to the minerals in Table 1; b) stable mineral associations of cinnabar

The Fourier-modelling on 171 squares shows a significant, but weak ($R = 0.24$) correlation ($T = 3.26 > 3$, $a < 0.001$) between the model and the data (Fig. 2c). The residuals obey a normal distribution ($R = 0.999$, $T >> 4.75$, $a < 0.001$), which indicates that the model is representative (Fig. 1d). The distribution of harmonics decreases quickly, namely harmonics (2-2), (4-4) and (5-5) contain 18.07% of the total amount of cinnabar, while the remaining harmonics are much weaker. The Fourier-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 assbciation - 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 km^2 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

[1] Михайлова Т. Археология, 1987, № 1, 15–23. [2] Захариев Й. В: Сб. за народни умотворения и народопис, София, Изд. БАН, 1918, св. 32, 144–155. [3] Озерова Н. А. Ртуть и эндогенное рудообразование, Москва, Наука, 1986, 232. [4] Тодоров Т., В. П. Федорчук. В: Достижения болгарской геологии, София, Техника, 1986, 197–206. [5] Димитров Р., Р. Маринова, Д. Брашнарова, Н. Гюров. Изв. ГИ на БАН, сер. рудни и нер. пол. изк., 1972, № 31, 137–141. [6] Атанасов В. Год. ВМГИ, **14**, 1969, св. 2, 7–15. [7] Id. Miner. Mag., **40**, 1975, No 11, 233–237. [8] Atanasov V., G. Kirov. Amer. Mineral., **58**, 1973, No 1-2, 11–15. [9] Колковски Б. В: Оловно-цинковите находища в България, София, Техника, 1988, 37–64. [10] Мънков С. Ibid., 1988, 90–113. [11] Витов О. В: Изв. Ист. музей Кюстендил, 2002, № 6, 335–350. [12] Pirrone N., I. Hedgecock. In: RMZ – Materials and Geoenvironment, **48**, 2001, No 1, 23–28. [13] Pacyna E., J. M. Pacyna, N. Pirrone. Atmos. Environ., **35**, 2001, No 17, 2977–3074. [14] Витов О. Геология и минерални ресурси, 2001, № 9, 19–22. [15] Id. Ibid., 1995, No 4, 6–11. [16] Davis J. Statistics and data analysis in geology. New York, John Willey & Sons Inc., 1977, 574. [17] Федорчук В. П. Геология ртути, Москва, Недра, 1983, 272.

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