

LA-ICP-MS study of malachite from copper deposits in the Rosen ore field, Burgas ore district, SE Bulgaria

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Abstract. Archaeological findings of malachite ore pieces, and objects made of malachite or copper, raise the question of where the raw material was mined. Research in this direction is a challenge in modern applied mineralogy, especially concerning minerals from the oxidation zone of copper-bearing ores. According to recent studies in this field, a complex research method, including impurity elements, will provide a better distinction between different sources. The present paper is focused on the content of impurity elements in malachite ore samples from copper deposits in the Rosen ore field, SE Bulgaria, with mining activity in the past: Propadnala Voda, Sarneshko Kladenche, Meden Rid, Korucheshme, and Rosen. The nickel concentration obtained by LA-ICP-MS analyses is above 1000 ppm (1012.80–1505.15 ppm) in all studied samples, accompanied by the following element impurities: Zn, Co, Mg, As, Sb, Fe, Ag, Au, Sn, Se, and Te. The quantitative concentrations of Zn, Co, Mg, As, Ag, and Se vary in different ranges in the examined malachites from each locality. Based on this, it seems possible to differentiate between samples of each mineralization. These data would have to be supplemented by the analyses of more malachite ore samples from the region.

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INTRODUCTION

Malachite is one of the first ores for producing copper metal and pigment for eye paint, mural painting, coloring glaze, and glass. It was a well-known raw material for making amulets, beads, and other small objects. The use of malachite and other green stones for the mentioned purposes in the Balkans goes back several millennia (Chernykh, 1978; Todorova, 1981; Todorova and Vajsov, 2001; Šljivar, 2006; Avramova, 2002). Indications of deliberate collection of pieces of copper ore are known in the prepottery Neolithic A (PPN A), around 9,500 BC, in Halan Chemi of present-day Eastern Turkey. Oxide and carbonate secondary copper ore minerals were

crushed for obtaining color pigments (Rosenberg, 1995; Zimmermann, 2011; Kunze and Pernicka, 2020a). Pieces of malachite ore are not rare in Bulgarian archaeological sites: Akladi Cheiri, Chernomorets (Leshtakov *et al.*, 2020b), Budzhaka, Sozopol (Leshtakov, 2013), Alepu (Leshtakov *et al.*, 2020a), Hadzhidimitrovo, Yambol (Petrova *et al.*, 2014), Sarnevo, Stara Zagora (Tzankova and Vasileva, 2017), Lubimets-Dana Bunar 2 (Kunze and Pernicka, 2020b), Karanovo III-IV pits (Leshtakov, 2013), and others.

One of the most famous malachite finds is from Aşağı Pinar in Turkish Thrace – high-quality malachite beads and Chalcolithic workshops (Kunze and Pernicka, 2020a). Malachite pieces,

together with fewer beads up to 8 mm in diameter and pendants, were recorded at some Vinča cultural sites in Serbia, *e.g.*, Vinča, Pločnik, Belovode, Fafos, Selevac (Antonović, 2006). In the Late Vinča horizons at Divostin were found a few perforated pendants, many discoid beads up to 7 mm in diameter, and about 100 malachite pieces (Glumac, 1988; Antonović, 2006). Reported malachite findings are fourteen beads from the Tisza cultural site Kremenjak near Čoka (Antonović, 2006) and a pendant and beads from Lepenski Vir (Antonović, 2006).

A composite string from the Late Neolithic pit field at Sarnevo, Stara Zagora, is of 47 disc-shaped beads – six of malachite and one of azurite (Bacvarov *et al.*, 2017; Alexandrova, 2017; Tzankova, 2017). At the Late Neolithic site named Budzaka were found pieces of malachite and a pendant (Leshtakov *et al.*, 2020a). Malachite beads in necklaces or bracelets were described from several tombs near Durankulak, belonging to the Hamangia culture I-II (Todorova and Vaisov, 1993; Todorova *et al.*, 2002). Kostov *et al.* (2003) studied malachite beads in a necklace from the Eneolithic necropolis Varna II. A stone pendant made of “light greenish-gray stone” and two mineral beads, blue and green, were reported from the Early Neolithic archeological site at Yabalkovo (Vasileva and Hadzhipetkov, 2014).

A complex study (archaeological, geophysical, geological, and mineralogical) in the Rosen ore field, SE Bulgaria, found evidence of mining activity far in the past (Leshtakov, 2013; Leshtakov *et al.*, 2020a, b; Rehren *et al.*, 2016, 2020; Stavrakeva and Tzankova, 2016a, b; Tzankova *et al.*, 2016; Kuntze and Pernicka, 2020a, b; Tzankova and Stavrakeva 2020a–c). All copper mines in this area ceased mining in the 1990s.

The slags found at Akladi Cheiri studied by Rehren *et al.* (2016, 2020) are by-products of the smelting of very rich copper ore, most likely almost pure malachite with only minor amounts of slag-forming gangue and associated ore minerals. The slags from an archaeological site near the village of Boyadzhiik (Yambol region) are by-products of copper-containing oxidic ore smelting (Tzankova and Stavrakeva, 2020a).

Malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ is the most common secondary mineral found in the oxidized zones of copper deposits. It is formed by weathering processes of copper ore. Common impurities reported in malachite are Ni, Co, and Zn. In smaller and variable concentrations were found Mg, As, Sb, Fe, Ag, Au, Sn, Se, and Te (Driscoll *et al.*,

2011, pp. 4, 36–39; Kunze and Pernicka, 2020b, pp. 406–407; Stavinga *et al.*, 2017, p. 6; Behrens and Girsdsies, 2010).

Malachite does form a solid solution series with three end-member minerals: glaukosphaerite $(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2$, kolwezite $(\text{Cu,Co})_2(\text{CO}_3)(\text{OH})_2$, and mcguinnessite $(\text{Cu,Mg})_2(\text{CO}_3)(\text{OH})_2$ (Driscoll *et al.*, 2011, p. 6). The chemical substitutions, strains, and stresses in the crystal structure influence the stability, reactivity, and solubility of the mineral (Driscoll *et al.*, 2011, p. 5).

The substitution of Cu by Zn on the crystal structure of synthetic malachite leads to the formation of zincian malachite $(\text{Cu}_{1-x}\text{Zn}_x)(\text{OH})_2\text{CO}_3$. Rosasite is a mineral of the chemical composition $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_2\text{CO}_3$. Rosasite-analogous minerals were also found with Mg, Ni, or Co instead of Zn (Behrens and Girsdsies, 2010).

Analyses of malachite and azurite by EMP and LA-ICP-MS indicate Zn, Pb, As, and Sb in decreasing order. Qualitative SEM and μXRF analyses defined malachite/azurite as possible hosts for Cd, Ag, and Hg (Stavinga *et al.*, 2017, p. 6).

Kunze and Pernicka (2020b) reported results from lead isotope ratios (obtained by a double-focusing mass spectrometer with inductively-coupled plasma excitation) and trace element concentrations (measured by neutron activation analysis INAA) in malachite samples from the Propadnala Voda, Sarneshko Kladenche, Meden Rid, Korucheshme, and Rosen deposits. According to them, in some situations, these two data sets combined will provide a better distinction between different sources. The authors assume that it is not possible to differentiate between the various sample locations within the Medni Rid area (listed above and the subject of the present study), but it seems to be possible to distinguish Ai Bunar and Zidarovo from Medni Rid by their higher concentrations of arsenic, antimony, and silver. They report elevated radiation levels for the ore from Propadnala Voda, compared with Varli Bryag (Kunze and Pernicka, 2020b, pp. 399, 405).

The present study focuses on the content of impurity elements in malachite ore samples from copper deposits in the Rosen ore field, SE Bulgaria, with mining activity in the past. The specificity of their content and concentration will contribute to distinguishing malachite samples from different deposits in combination with other research methods. These data can be used for comparison with impurities in copper and malachite artifacts in complex studies when searching for the source location of the raw material used.

GEOLOGICAL SETTING

The formation of copper ore deposits in the region of SE Bulgaria is associated with four Late Cretaceous volcano-plutonic centers grouped in the four ore fields of the same names: Rosen (vein copper-molybdenum), Varli Bryag (vein copper), Zidarovo and Bakadzhik (both vein copper-polymetallic). The main rock varieties of the plutons are syenites and monzonites, which intruded into trachyandesite and andesite volcanic rocks. Numerous dykes of the same composition cut across these rocks. The ore veins are of hydrothermal hypabyssal origin (Bogdanov, 1987; Popov *et al.*, 1993).

The differences in the mineral associations between ore fields in the Burgas ore region have been the subject of research by Vasilev (1960), Vasilev and Stanisheva-Vasileva (1972), Todorov (1982), and others. The Rosen ore field deposits are of the copper-molybdenum (cobalt-bearing) type. Their mineralization is predominantly chalcopyrite with less molybdenite ore, magnetite, and cobalt-bearing pyrite (Bogdanov, 1987). Chalcopyrite-pyrite mineralization and specularite are specific features of the Varli Bryag ore field deposits. Sphalerite-galena ore in non-industrial quantities and bismuth-containing sulfides and sulfosalts are included in their mineral association. The Zidarovo and Bakadzhik ore fields are copper-polymetallic with gold-silver,

bismuth, and galena-sphalerite mineralization. Molybdenum and cobalt-bearing pyrite mineralization are not typical here (Bogdanov, 1987).

The Rosen ore field is located about 20 km southeast of Burgas and covers the hills of Medni Rid and Rosen Bair (Alatepe). Ore-bearing faults are mainly developed in volcanic rocks. Almost all ore veins are embedded in them, and the ore accumulations are generally in the deep parts of the faults (Bogdanov, 1987; Popov *et al.*, 1993). The ore veins in the Rosen ore field formed deposits in a NW–SE occurrence: Propadnala Voda (Červeno Zname), Sarneshko Kladenche, Meden Rid (Bakarлак), Korucheshme (Kyumyurlaka, Stahanov), and Rosen (Fig. 1). Their mineral associations, stages of mineralization, sequence of development of ore-forming processes, and spatial distribution of minerals in individual deposits have been the subject of continuous studies, *e.g.*, Tonev (1952, 1959), Bogdanov *et al.* (1968a, b), Todorov (1968), Todorov and Laputina (1980), Vasilev (1960), Vasileva-Stanisheva and Vasilev (1981), Boyadzhiev *et al.* (2012). Only one, pulsating ore-forming process in the Rosen ore field has been recognized. More than 60 hypogene and 20 supergene minerals have been discovered and described. The endogenous mineral formation was in two successive stages, pegmatitic-pneumatolithic and hydrothermal, with the following mineral associations: apatite-feldspar, magnetite-scheelite,

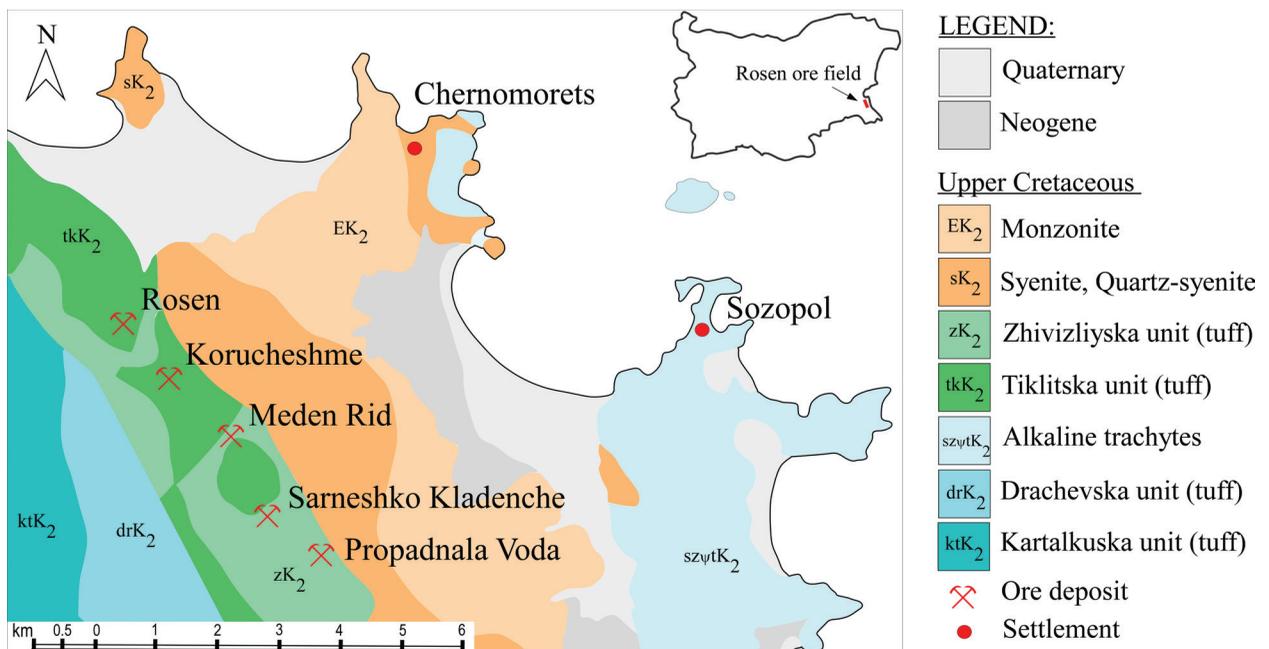


Fig. 1. Location of the studied copper deposits with mining activity in the past on the simplified geological map of the Rosen ore field (according to Petrova *et al.*, 1994, and Bogdanov, 1987, with additions).

cobalt-bearing quartz-pyrite, hematite, quartz-molybdenite, chalcopyrite-pyrite, quartz-magnetite, quartz-specularite, ankerite-dolomite, calcite and quartz-chalcedony (Bogdanov, 1987, p. 276). The minerals from the oxidation zone and secondary

sulfide enrichment are distributed in the subsurface parts of the ore veins down to 15–20 m depth. They include hydrogoethite, hydrohematite, malachite, azurite, chrysocolla, native copper, chalcocite, covellite, and others. Some rare minerals, such as il-

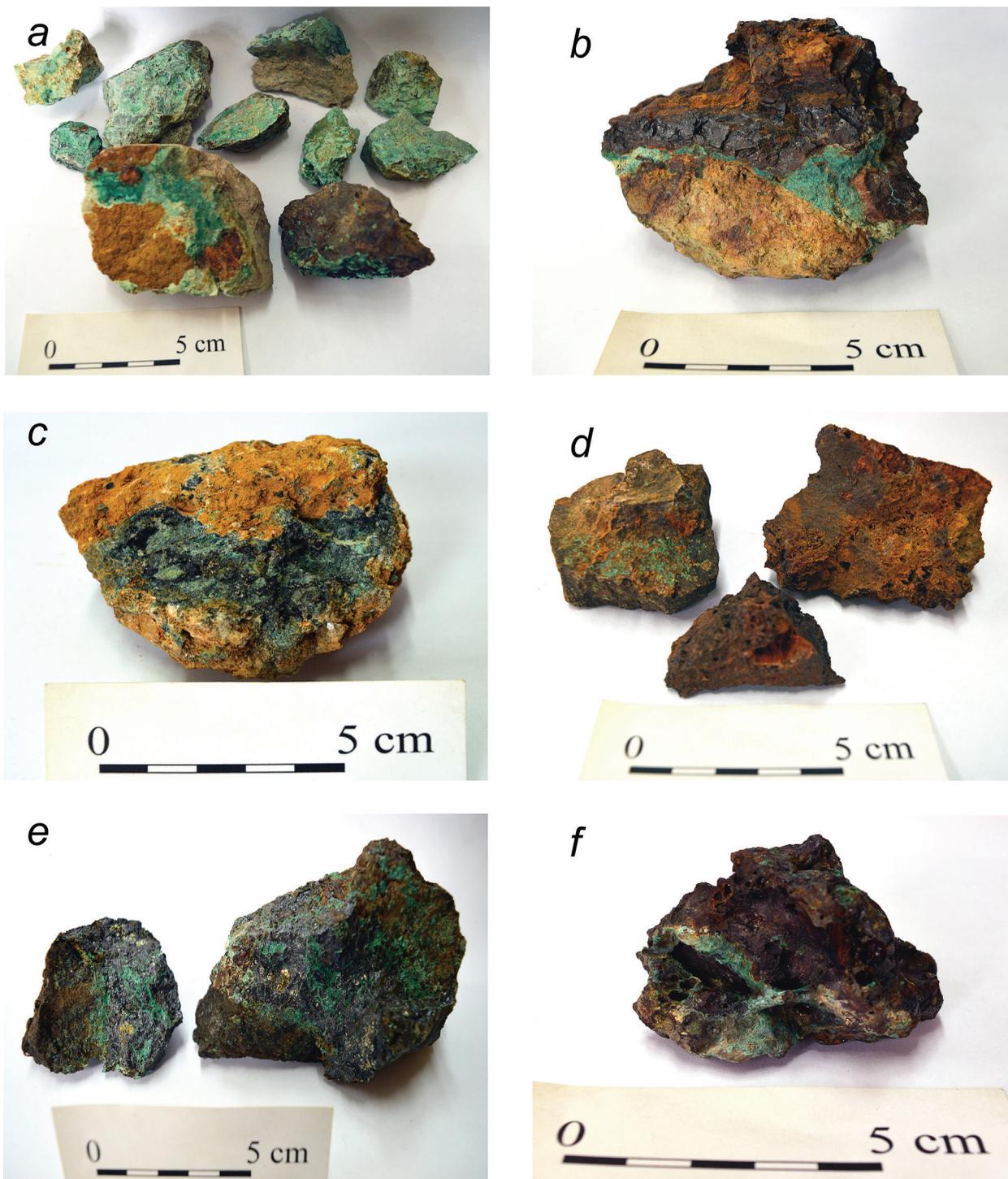


Fig. 2. Representative surface findings of malachite-bearing ore samples from the copper deposits of the Rosen ore field: a, b) Propadnala Voda; c) Sarneshko Kladenche; d) Meden Rid; e) Korucheshme (Kyumyurlaka); f) Rosen.

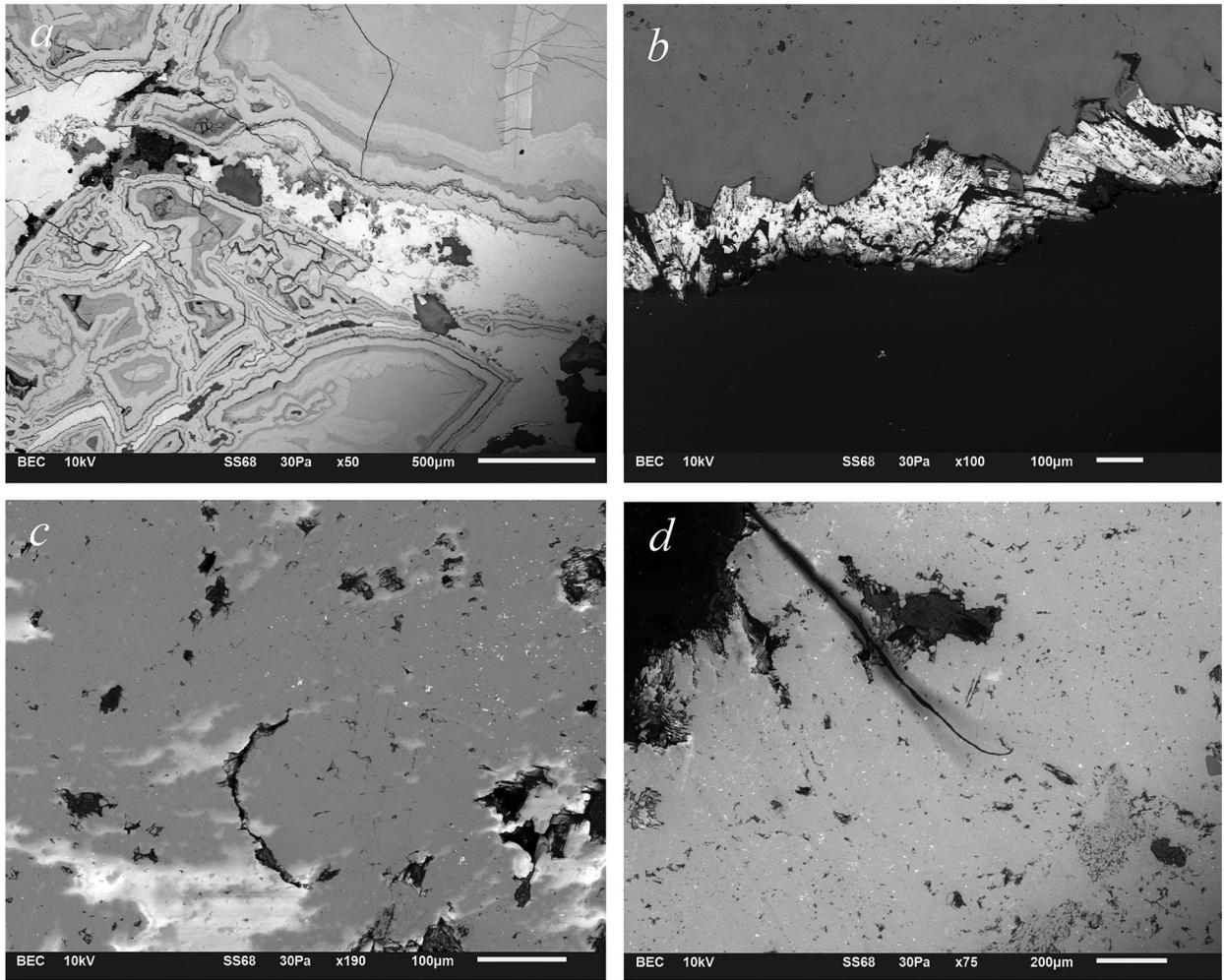


Fig. 3. Scanning electron microscope images of malachite from the Rosen ore field: *a*) malachite surrounded by aggregates of iron hydroxides, Korucheshme (Kyumyurlaka) deposit; *b*) prismatic malachite crystals, Rosen deposit; *c*) malachite with inclusions, Sarneshko Kladenche deposit; *d*) malachite with inclusions, Propadnala Voda deposit.

semannite, γ -kertschenite, vivianite, and powellite, were also found (Bogdanov, 1987; Dimitrov, 1967; Breskovska and Kiryazova, 1967).

Geochemical maps of the Burgas ore region show that the highest value of zinc anomalies repeats that of lead in the southern part of the region. The copper anomalies have a smaller areal presence, but their distribution is almost identical to that of Pb and Zn. They are located around separate volcanic-plutonic centers. The distribution of nickel anomalies in the southeastern part of the Burgas ore region, in contrast to those of most other typomorphic elements, is less frequent but more contrasting and smaller anomalies. Also noticeable are the tin anomalies, which are spatially correlated with ore fields (they are located in them) (Boyadzhiev *et al.*, 2012).

The studied malachite from the deposits in the Rosen ore field commonly forms crusts around rock

fragments and fills cracks in the rock or cavities in aggregates of iron hydroxides (Fig. 2). In polished-sections, malachite is observed surrounded by clay minerals, hydromicas, and iron hydroxides (Fig. 3a). It forms prismatic crystals when growing in voids (Fig. 3b). All examined malachite samples abound in microscopic inclusions dispersed unevenly throughout the crystals (Fig. 3c, d).

METHODOLOGY

Twenty-nine polished sections of malachite samples from the Propadnala Voda, Sarneshko Kladenche, Meden Rid, Korucheshme, and Rosen deposits were examined in reflected light with a Meiji MT9430 optical microscope equipped with a Nikon D3200 digital camera. Chemical analyses were performed

on five selected malachite samples (one from each of the listed above deposits) on the surface without alteration processes, mineral inclusions, or intergrowths.

The chemical composition of the mineral phases (malachite) was studied using a JEOL JSM 6010 Plus/LA InTouchScope™ Scanning Electron Microscope (SEM), equipped with an energy dispersive X-ray spectrometer (SDD-EDS) at the University of Mining and Geology “St Ivan Rilski”, Sofia. The microscope was operated at a low-vacuum mode (30 Pa), accelerated voltage (10 kV), scanning time 90 s, and single-point spot size 68 µm. Sample scans were transferred to NIST DTSA-II (as recommended by Ritchie, 2011; Newbury and Ritchie, 2013) software and quantitative elemental compositions was determined using a standard set for microanalysis (SPI – 53 minerals). Oxygen was calculated by cation stoichiometry and included in the matrix correction. Hydrogen was calculated by the difference from 100%.

The used LA-ICP-MS system at the Geological Institute of the Bulgarian Academy of Sciences (Sofia) consists of a 193 nm ArF excimer laser (ATLEX 300SI, Germany) linked with the ELAN DRC-e ICP-MS instrument (Perkin Elmer, Canada). The analyses were performed on 35 µm ablation pits. External standardization on NIST glass standard SRM-610 allowed linear drift correction of the spectrometer and provided the measurements of relative element concentrations. Element concentrations were transformed into true values by internal standardization through the Sills program for data reduction.

RESULTS AND DISCUSSION

The impurity elements in the studied malachite ore samples, as established by LA-ICP-MS analyses, are Ni, Zn, Co, Mg, As, Sb, Fe, Ag, Au, Sn, Se, and Te. Their concentrations are shown in Table 1. The Ni content is above 1000 ppm (from 1012.80 ppm to 1505.15 ppm) in all analyzed specimens. Contents above 1000 ppm were also measured for Zn (2025.06 ppm and 2340.16 ppm) in malachite from the Meden Rid deposit, Mg (1132.61 ppm), and Fe (1074.06 ppm, 1162.75 ppm) in malachite from the Propadnala Voda deposit. The cobalt content in malachite from the Rosen deposit (250.41–484.07 ppm) is several times higher than in samples from the Sarneshko Kladenche, Meden Rid, and Korucheshme deposits. The silver content in the specimen from Sarneshko Kladenche ranges from 8.06 ppm to 187.38 ppm. In other studied samples, it

is in a very low concentration or is below the detection limit of the equipment used, with the exception of four analyses from the Propadnala Voda deposit with a value up to 24.48 ppm. Malachites from the studied area are depleted in Sb, Au, Sn, and Te. Tin was not detected in the sample from the Propadnala Voda deposit (Table 1).

The effects of substitution of Cu by Ni, Zn, Co, and Mg have been studied by Driscoll *et al.* (2011), Behrens and Girsigsdies (2010), and others. The copper concentration in malachite depends mainly on the conditions of mineral formation, pH of the environment, and isomorphous substitutions from impurity elements. Driscoll *et al.* (2011) conducted simulated chemical weathering and leaching studies on malachite samples to identify, characterize, and model the constituents mobilized from this mineral under environmental conditions. In an acidic environment, the copper concentration in malachite samples decreases (Driscoll *et al.*, 2011, pp. 37, 40). Oxidation of sulfides is an electrochemical process in an acidic environment, sometimes with low pH values.

According to Pernicka (1999) and Kunze and Pernicka (2020b, p. 404), a relatively small number of elements are useful for discussing the provenance of archaeological copper samples, such as Ag, As, Co, Ni, Sb, Bi, Se, Te, and Au. The quantitative concentrations of Zn, Co, Mg, As, Ag, and Se vary in different ranges in the examined malachites from the Rosen ore field (Table 1). Based on this, it seems possible to make the following summary of the studied samples:

Propadnala Voda deposit – varying concentrations of Zn (24.87 ppm to 625.18 ppm), Co (16.74 ppm to 344.27 ppm), Mg (10.57–1132.61 ppm), As (<19.82 ppm to 294.19 ppm), and Se (29.98–324.86 ppm); low content of Ag (up to 24.48 ppm);

Sarneshko Kladenche deposit – low content of Zn (up to 71.07 ppm), Co (up to 28.75 ppm), As (<3.01 ppm), and Se (up to 58.82 ppm); Mg is in the range between 368.30 ppm and 611.87 ppm; varying concentrations of Ag (8.06–187.38 ppm);

Meden Rid deposit – high concentration of Zn (563.88–2340.16 ppm); low content of Co (up to 15.35 ppm), Mg (up to 86.05 ppm), As (up to 61.17 ppm), Ag (up to 1.05 ppm), and Se (<13.83 ppm);

Korucheshme deposit – low content of Zn (up to 6.98 ppm), Co (up to 0.28 ppm), Mg (up to 6.98 ppm), As (up to 2.32 ppm), Ag (<0.25 ppm), and Se (<14.43 ppm);

Rosen deposit – low concentration of Zn (up to 21.64 ppm), Mg (up to 86.20 ppm), As (up to

Table 1

Impurity element concentrations (ppm) in the studied malachite samples, obtained by LA-ICP-MS analyses; < symbol shows the detection limit of the equipment used; nd – not detected

No	Cu	Ni	Zn	Co	Mg	As	Sb	Fe	Ag	Au	Sn	Se	Te
Propadnala Voda deposit													
An. 1	530980	1371.80	25.12	23.79	23.46	49.47	<0.38	<69.00	18.64	<0.15	nd	29.98	<5.83
An. 2	530980	1351.47	25.35	18.05	<12.19	58.91	<0.45	<83.98	2.15	<0.23	nd	33.28	<5.94
An. 3	530980	1430.12	24.87	16.74	10.57	74.39	<0.35	137.00	24.48	0.16	nd	40.91	<3.41
An. 4	530980	1436.21	78.97	40.94	73.06	171.35	<0.81	<142.87	12.78	<0.25	nd	324.86	<10.96
An. 5	530980	1219.26	625.18	344.27	1132.61	<19.82	<3.89	1074.06	<2.25	<0.91	nd	119.87	<46.11
An. 6	530980	1505.15	583.75	134.36	961.61	33.57	<3.16	1162.75	<1.99	<0.89	nd	73.56	<33.58
An. 7	530980	1390.53	189.34	153.39	141.40	294.19	<1.09	373.56	<0.71	<0.39	nd	171.07	8.75
Sarneshko Kladenche deposit													
An. 1	487850	1149.23	52.59	26.64	409.25	<2.25	<0.24	<71.95	31.76	<0.11	2.63	48.38	<5.03
An. 2	487850	1184.16	57.83	28.75	424.50	<2.91	<0.44	<81.95	8.06	<0.18	<1.68	28.14	<3.31
An. 3	487850	1135.95	62.03	24.09	390.17	<2.54	<0.36	<75.94	187.38	<0.19	1.66	58.82	<7.04
An. 4	490940	1130.14	46.30	18.55	577.90	<2.47	<0.36	<73.47	71.31	0.12	1.35	54.04	<6.06
An. 5	490940	1168.43	71.07	21.71	611.87	<2.75	<0.50	<77.88	44.48	<0.17	<1.73	39.20	<5.33
An. 6	490940	1157.85	47.00	13.52	368.30	<3.01	<0.74	<82.86	60.84	<0.17	2.91	32.63	<6.98
Meden Rid deposit													
An. 1	470740	1038.88	713.18	7.05	86.05	61.17	<0.21	<46.24	1.05	<0.15	<1.45	<10.87	<3.88
An. 2	470740	1050.19	2340.16	15.35	44.79	48.45	<0.21	<47.58	0.84	<0.14	<0.97	<8.84	<5.62
An. 3	470740	1012.80	563.88	6.61	<16.82	12.98	<0.26	<47.98	0.28	<0.16	<1.19	<13.83	<5.45
An. 4	470740	1075.66	2025.06	15.02	70.35	53.71	<0.41	197.06	<0.27	<0.12	5.86	<9.59	<4.43
An. 5	470740	1086.75	936.89	7.83	20.03	13.34	<0.31	<46.48	<0.26	<0.13	<1.08	<8.76	<3.40
An. 6	470740	1130.98	742.40	7.83	27.12	19.87	<0.46	<53.74	<0.34	<0.13	1.51	<9.57	<4.78
Korucheshme deposit													
An. 1	505520	1169.21	<3.83	<0.25	<6.06	<2.31	<0.37	<62.79	<0.17	<0.15	<1.46	<9.09	<4.90
An. 2	505520	1214.91	<4.28	<0.22	<9.94	<2.79	<0.49	89.79	<0.23	<0.16	<1.75	<7.51	<5.98
An. 3	509640	1193.29	6.98	<0.26	<7.55	<2.19	<0.42	187.58	<0.25	<0.14	<1.50	<11.51	<4.03
An. 4	509640	1192.04	<4.11	<0.24	6.98	<2.16	<0.34	101.69	<0.19	<0.13	<1.27	<12.59	<4.36
An. 5	509640	1200.66	<3.22	0.28	<11.76	2.32	<0.25	<66.50	<0.21	<0.15	<1.34	<14.43	<5.65
Rosen deposit													
An. 1	574800	1329.99	21.64	484.07	86.20	<6.16	<0.47	131.84	<0.52	<0.34	9.72	<24.27	<13.70
An. 2	574800	1347.00	12.54	250.41	<13.92	8.40	<0.69	<80.29	<0.63	<0.22	2.96	<12.82	<8.22
An. 3	574800	1258.17	<6.65	306.04	53.14	13.24	<0.45	99.01	<0.44	<0.19	<1.80	<13.82	<4.65
An. 4	574800	1301.10	<7.92	279.80	23.43	8.85	<0.57	<93.88	<0.38	<0.19	<2.36	<21.88	<10.19

13.24 ppm), Ag (<0.63 ppm), Se (<24.27 ppm); Co is in the range between 250.41 ppm and 484.07 ppm.

Microinclusions with high content of P (up to 294,634.48 ppm), La (up to 1035.09 ppm), Ce (up to 991.79 ppm), Sr (up to 1085.74 ppm), Y (up to 1671.40 ppm), and U (up to 15,833.99 ppm) were analyzed in the periphery of malachite crystals from

the Propadnala Voda deposit. Earlier study on archaeological slags, representing by-products of copper sulfide ore smelting from the same region, show the presence of La, Ce, and P in all crystalline and amorphous slag phases (Stavrakeva and Tzankova, 2016b). These findings raise the question of possible REE mineralization in the Propadnala Voda deposit area.

CONCLUSION

The presented data enrich and complement the knowledge about concentrations of element impurities in malachite ore samples from copper deposits in the Rosen ore field, SE Bulgaria. Malachite from the Meden Rid deposit shows high Zn content (563.88–2340.16 ppm) and low Co content (6.61–15.35 ppm). The opposite is found in malachite from the Rosen deposit: the Zn content is low (<6.65–21.64 ppm), while the concentration of Co is high (250.41–484.07 ppm). All analyses from the Korucheshme and Sarneshko Kladenche deposits show low contents of both Zn and Co, but differ from each other in terms of Mg contents. Magnesium is high in the sample from Sarneshko Kladenche (368.30–611.87 ppm), while for malachite from the Korucheshme deposit it is low (<6.06–6.98 ppm). In addition, malachite from Sarneshko Kladenche contains silver from 8.06 ppm to 187.38 ppm. The concentrations of silver in the samples from Meden Rid, Korucheshme and Rosen deposits are most often below the detection limit of the equipment. The impurity content of malachite from Propadnala Voda varies widely. This sample differs from the others in the absence of tin (not detected) and in the relatively high content of selenium (up to 324.86 ppm) and arsenic (up to 294.19 ppm). In spite of the small number of specimens suitable for investigation, some

peculiarities have been observed in the concentrations of the various elements. It seems possible to distinguish the examined malachites of each mineralization based on the content of Zn, Co, Mg, As, Ag, and Se. However, the obtained data should be supplemented by the analyses of more malachite ore samples from the region. The results may support future complex studies on the source location of raw material for some copper and malachite artifacts.

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