

Alteration processes and mineralizations in the Madjarovo Ore Field

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Abstract. The style and location of hydrothermal activity varied significantly during the life time of Madjarovo system. Alteration mineralogies have confirmed the presence of epithermal (acid-sulfate and adularia-sericite) system and subjacent porphyry- and skarn styles of alteration and mineralization. The alteration zones are located in the central part of Paleogene (33-31 Ma) Madjarovo volcanic centre composed by shoshonitic and high-K calc alkaline lavas. Acid-sulfate alteration is developed in a concentric manner around the major outcrop of Madjarovo monzonitic intrusion grading outward and downward into areal propylitic alteration. Porphyry alteration and skarns are also in close space approximation to the monzonitic bodies. Adularia-sericite alteration is strongly fracture controlled and forms envelopes around veins of productive base- and precious metal mineralization. The quartz veins cross-cut the sericitic alteration in the central part of the ore field, however their mineralized part tends to be peripheral to the high-sulfidation environments. Jasperoid-like (carbonate replacement) rocks with elevated contents of Au are also in distal position from the monzonitic intrusion and show similarity to Carlin type deposit. K/Ar ages of the vein alunite (32.6 ± 1.2 Ma) and adularia (32-33 Ma), which characterize the acid-sulfate and adularia-sericite alteration respectively, are within the range of the unaltered volcanic rocks and suggest close temporal relationships between volcanism, intrusion, hydrothermal alteration and mineralization.

Fluid inclusion studies have shown that the vein mineralization was formed at a temperature interval between 210 and 280°C, salinities between 2.5 and 5.0 eq. wt.% NaCl and high fO_2 .

$\delta^{34}S$ values for sulfides are consistent with metamorphic or magmatic source. Calculated values for $\delta^{18}O_{H_2O}$ and δD_{H_2O} suggest for a meteoric origin of the mineralizing fluid with a more magmatic influence in the acid sulfate alteration. Comparison of Pb isotopes in the magmatic rocks, adularia and galena indicates that Pb source must be similar to that for monzonitic magmas.

Key words: alteration, mineralization, isotopes, Madjarovo Ore Field

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Марчев, П., С. Нокков, Р. МакКойд, Д. Желев. 1997. Променителни процеси и минерализации в Маджаровското рудно поле. — *Геохим., минерал. и петрол.*, 32, 47–58

Стилът и локализацията на хидротермалната активност варират значително по време на еволюцията на Маджаровската система. Минералогията на промените потвърждава присъствието на епитермална (кисело-сулфатна и адулар-серицитова) система и разположени под тях порфирни и скарнови промени и минерализации. Променените зони са разположени в централната част на палеогенския (33-31 Ма) Маджаровски вулкански център, изграден от шошонитови и високо-К калциево-алкални лави. Кисело-сулфатните промени са развити концентрично около главното разкритие на Маджаровската монзонитова интрузия, преминавайки навън и в дълбочина в ареални пропилити. Порфирните промени и скарните също са пространствено свърза-

ни с монцонитите. Адулар-серицитовите изменения се контролират от разломни структури, в които са вместени кварцови жили с продуктивно полиметално и златно-сребърно орудяване. Кварцовите жили пресичат кисело-сулфатния тип промени в централната част на рудното поле, но по-богатата минерализация е периферна на кисело-сулфатните промени. Заместени карбонатни скали с повишени съдържания на Au са също в дистална позиция по отношение на монцонитовата интрузия и показват сходство с тип Карлин. К/Ag възрасти на жилния алунит (32.6 ± 1.2 Ма) и адулара (32-33 Ма), показателни съответно за кисело-сулфатния и адулар-серицитовия тип изменения, попадат във възрастовия обхват на непроменените вулкански скали и подсказват за близки темпорални съотношения между вулканизма, интрузивния магматизъм, хидротермалните промени и орудяванията.

Изследването на флуидните включения показва, че жилната минерализация е формирана при температура 210 и 280°C, соленост 2.5-5.0 екв. т.% NaCl и висока fO_2 .

Данните за $\delta^{34}S$ в сулфидите са в съгласие с метаморфен или магматичен източник. Изчислените стойности за $\delta^{18}O_{H_2O}$ и δD_{H_2O} свидетелстват за метеорен източник на минерализиращите флуиди с по-силно магматично влияние в кисело-сулфатните изменения. Сравнението на изотопите на Pb в магмените скали, адулара и галенита показва, че източникът на Pb в галенита е близък до този на монцонит-латитовите магми.

Ключови думи: променителни процеси, минерализация, изотопи, Маджаровско рудно поле

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Introduction

The Madjarovo ore field (MOF) occurs 200 km ESE of Sofia and approximately 50 km south of Haskovo. The ore field occurs at an elevation of between 130 and 850 m and is characterized by steep to precipitous slopes with a local relief in excess of 700 m. It is located in the central part of the Oligocene Madjarovo volcano which is the easternmost volcanic structure of the Macedonian-Rhodope Magmatic Belt within Bulgaria.

Extensive exploration of the MOF started in 1952, although mineralogical studies in the area commenced about 90 years ago (B o n c h e v, 1905). The program involved mapping of the central and eastern part of the volcano on a scale of 1:25 000, structural studies of the ore field, trenching and drilling. In the areas of major exploration interest different specialized studies were conducted. As a result the MOF is one of the best explored ore fields in Bulgaria. 10.5 million tons of base metal ore have been mined since the beginning of mining operations. Another 6.5 million tonnes of base metal reserves and large amounts of low grade ore still exist.

Between 1980 and 1983 an exploration program was undertaken in the south part of MOF by a group from Geological Institute of Bulgarian Academy of Sciences. The major results of these studies are published in A r n a u d o v a et al. (1991). An exploration program funded by the Jambol exploration organization continued these studies during 1988-1990. This program included mapping of the whole volcano on a 1:5 000 scale, studies of the age, petrology and petrochemistry of volcanic and intrusive rocks, geochemistry of alteration, and fluid inclusions. The alteration in the area was studied by Nokov, Marchev and McCoyd (funded by Navan Resources, Eire) in 1992-1993. Preliminary results of these studies were given in annual reports of the group and M c C o y d et al. (1997) and the PhD thesis of M c C o y d (1995). An extensive gold exploration program was started recently by Jambol exploration organization in the upper part of the base metal veins. Only 8-9 major veins have been explored so far. The proven reserves are about 2 million tons grading at 3.9 g/t. Different alteration types were also sampled in order to enlarge the gold prospectives of the MOF.

The MOF was selected for this study because it contains several distinct styles of alterations and mineralizations and the geological control is good. The present paper summarizes and updates a large number of previous studies. Its main objectives are to describe different type of alteration and their relationships with the mineralization, magmatic and structural events. A detailed paper on stable isotope and fluid inclusion study of the alteration and vein mineralization will be published elsewhere.

Local geology

The Madjarovo volcano covers an area of about 120 km² in an east-west-trending sedimentary basin containing Upper Priabonian conglomerates, sandstones and coral limestones. The basement rocks crop out south, west and east of the volcanic pile and belong to the Rhodope crystalline basement. The basement comprises alternations of various high grade gneisses, schists, marbles, quartzites, migmatites and meta-ultrabasic and — basic rocks and Mesozoic low grade metamorphic rocks represented by diabases, meta-alevrolites, sandstones, breccias, argillites, chlorite-mica schists, calc-schists, quartzites and marbles. The high-grade metamorphics are intruded by Upper Cretaceous? granites (Chuchuliga type).

The volcanic activity is of predominantly fissure type which formed a shield volcano. The volcanics are dominated by large sheet-like lava flows and subordinate reworked volcanic fragmental rocks (epiclastics). Typical pyroclastic flows are not found but a tuff (Rezeda tuff), erupted from Borovitsa area and used as a tephrostratigraphic marker (I v a n o v, K o p p, 1969), underlies the Madjarovo volcanics. The latest lava flows interfinger with coral reef limestones in the vicinity of the villages Rumelia and Kochash and indicate that the periphery of the volcano was submerged up to the end of volcanism. The core of the volcano, at least in the later stages of volcano activity, probably was emergent and vegetated. This is supported by the presence of burned branches in the late epiclastics.

The unaltered volcanic rocks (M a r c h e v et al., 1989) have the composition of shoshonitic or high-K calc alkaline basic to intermediate varieties with latites being the most voluminous rock type. The most acid rocks are of quartz trachyte composition.

On the basis of measured O and Sr isotope ratios M a r c h e v et al. (1995) distinguished two sharply distinctive periods in the evolution of the Madjarovo Volcano. The first one is characterized by thick (up to 150m) latitic lava flows (sheets) alternating with 1 to 4-5 m thinner lava flows of high-K basalts, basaltic andesites and andesites. Both O and Sr isotopic ratios of the latites show highest values ($\delta^{18}\text{O}=8\text{‰}$ and $^{87}\text{Sr}/^{86}\text{Sr}=0.7086$, respectively) whereas basalts have considerably lower isotopic ratios ($\delta^{18}\text{O}=6.6\text{‰}$ and $^{87}\text{Sr}/^{86}\text{Sr}=0.7079$). Basaltic andesites and the andesites have intermediate values and on SiO_2 vs. $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ plots they form straight lines connecting basalts and latites, reflecting mixing between these two end-members.

The second period includes the last 3 consecutive lava flows ranging in composition from high-K, high-Al basalts through high-K latites to quartz-latites. They have an identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratio=0.7078 and increasing $\delta^{18}\text{O}$ from 6.6 to 7.6‰ reflecting simple closed-system fractional crystallization.

The Lower Madjarovo volcanics are intruded by monzonite, monzogabbro and syenite bodies of predominantly elongate shape which are believed to coalesce at depth (M a v r o u d c h i e v, 1959). About 11 outcrops, predominantly of monzonitic composition, are mapped in different periods. The intrusions occur mainly in the

central part of the volcano, which is dissected by the Arda River and some monzonitic plugs form spectacular steep-sided pinnacles. The largest body, named "Harman Kaja", is of monzonitic composition and crops out over approximately 1 km². It was intersected at depth in many drill holes. The Rb-Sr mineral isochrons for the bottom and top flows of the Madjarovo volcano yielded ages of 31.6 ± 1.2 Ma. and 32.3 ± 0.6 Ma, respectively (Marchev, Rogers, unpubl. data) suggesting that the whole magmatic activity lasted approximately 1-2 Ma.

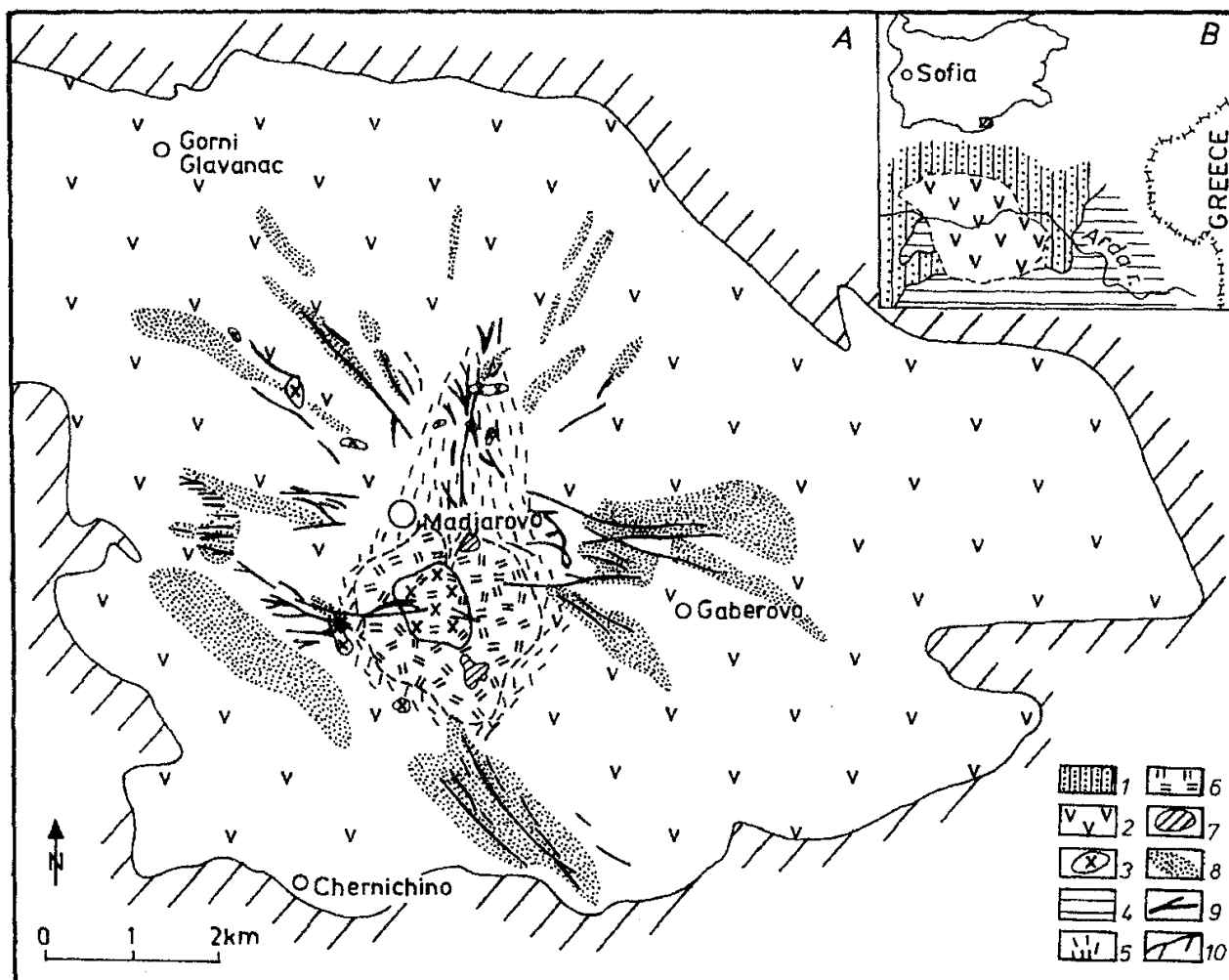


Fig.1. Geographic and geologic positions (B) and generalized geologic map of the Madjarovo volcanic centre, showing the location of major types of alteration and quartz veins (modified from Velinov, Nokov, 1991) (A)

1 – Paleogene sediments and pyroclastics; 2 – volcanics; 3 – monzonitic and sienitic subvolcanic intrusions; 4 – metamorphic basement; 5 – propylites; 6 – sericitic alteration; 7 – advanced argillic alteration; 8 – adularia-sericite alteration; 9 – base- and precious metal veins; 10 – contour of the Madjarovo volcano

Фиг. 1. Географска и геоложка позиция (B) и обобщена геоложка карта на Маджаровския вулкански център, показваща местоположението на главните типове промени и кварцовите жили (модифицирана по Веленов, Нокоев, 1991) (A)

1 – Палеогенски седименти и пирокластити; 2 – вулканити; 3 – монзонитови и сиенитови субвулкански интрузии; 4 – метаморфен фундамент; 5 – пропилити; 6 – серицитови изменения; 7 – интензивна аргилизация; 8 – адулар-серицитови изменения; 9 – жили с полиметално и златно-сребърно орудяване; 10 – граници на Маджаровския вулкан

Structure

Regional structures in the Madjarovo volcanic centre are represented by four groups of steeply dipping faults (70° - 90°) trending 80° - 100° , 320° - 340° , 350° - 10° , and 20° - 40° (A t a n a s o v, 1959). Syn- and postvolcanic (predominantly east-west-trending) faulting caused step-like collapse and formed an east-west-trending depression consisting of small horsts and grabens. The most important of these is the Arda fault, which is traced by veins No 6, 50, 49 (veins along the river), the system of veins No 32, vein No 15 and the southernmost normal fault separating the volcanics from metamorphics. Displacements of up to 200 m were established along the NW-SE-trending vein No 2 and the N-S-trending zone 3 (8). Many of the faults are filled with veins and very closely associated in space with the dyke swarms and particularly with some post-intrusive dykes, suggesting that these structures may have controlled volcanism in addition to subsequent mineralization. The extent and continuity of the major lineaments and the displacement of the prevolcanic sedimentary rocks and earliest volcanic flows along them suggest that they are related to deep basement structures that were active over an extended period of time.

Hydrothermal alterations

Hydrothermal alteration at Madjarovo has been discussed by R a d o n o v a (1960) and V e l i n o v et al. (1977). A model involving a pre-ore regional propylitisation followed by vein-controlled alteration (R a d o n o v a, 1960) was accepted by most later authors. Recently, V e l i n o v, N o k o v (1991) recognized the mineralization in the Madjarovo ore field as epithermal with simultaneous development of both acid-sulfate (high-sulfidation) and adularia-sericite (low sulfidation) type of alteration around the ores. In a recent paper N o k o v, M a l i n o v (1993) characterized the ore field as an adularia-sericite type epithermal deposit, using criteria tabulated by H e a l d et al. (1987).

A generalized map of the central part of the volcano is shown on Fig.1 and a summary of the general characteristics of the alteration is shown below.

Acid sulfate alteration, biotitization and skarns

The style and location of hydrothermal activity varied significantly during the life time of the Madjarovo system. Several possibly discrete stages of activity are indicated by different alteration mineralogies, over-printing alteration, and space relationships.

The central part of the Madjarovo volcanic centre is moderately to strongly altered over an area of 10 km^2 . The alteration is developed in a concentric manner around the largest outcrop of the Madjarovo intrusion grading outward from intense argillic alteration to propylitic alteration (Fig.1). The most intense alteration forms topographically elevated areas. Shish Tepe is the best studied among them (V e l i n o v et al., 1977), although patches of intensely silicified rocks (monoquartzites) were found in the upper part of the intrusion itself. The highest part of Shish Tepe comprises diaspore-bearing alunite quartzites and zunyite-bearing diaspore quartzites. Alunite was found to form small veins (vein-type alunite, V e l i n o v, A s l a n i a n, 1981). Vertically this alteration grades into quartz-sericitic (V e l i n o v, N o k o v, 1991) or sericitic (M c C o y d, 1995) alteration consisting of quartz-sericite-pyrite, and quartz

which is the prevailing alteration around and in the intrusion. The cericitic alteration grades outward and downward into propylitic alteration that consists of chlorite, albite, calcite, epidote \pm uralite or zeolites. Because of the large distribution of the propylitisation in the central part of the volcano, it was called by previous authors "areal" or regional propylitisation.

Spatially and, probably, temporally related to monzonitic intrusions are potassic alteration assemblages, defined by hydrothermal biotite and quartz. This type of alteration was established around two small bodies of monzonite (Patron Kaja and Kjumiurluka) which are intruded in the east-west Arda fault. Biotite was also observed in the deepest outcrops of argillic alteration around the south-east margin of the Harman Kaja intrusion. Disseminated pyrite accompanies silicate minerals. There is a similarity to other shallowly eroded high-sulfidation and porphyry deposits (e.g. Lepanto) described by Sillitoe (1993 and references in there) which show a transition from epithermal to porphyry environments. Earlier occurrences of biotitisation were reported by Velinov, Nokov (1991) but their location and metallogenic significance are not elucidated.

Hydrothermal biotite in the Patron Kaja and Kjumiurluka intrusions occurs in distinct groundmass-hosted aggregates containing fine-grained (0.1 mm), light brown biotite flakes or replacing the Fe-rich phenocrysts in the host-rock latites. Hydrothermal quartz occurs dominantly in veins and veinlets. Here, the potassic alteration grades into a propylitic alteration.

Skarn bodies of unknown size and potential have been discovered by drill-holes in close proximity to the Harman Kaja and Patron Kaja monzonitic bodies (Breskovska et al., 1976) and can be referred to the proximal skarns of Sillitoe (1993). Skarns are hosted by fine crystalline marbles and to a lesser extent by gneisses and amphibolites. Their formation is in two stages: an early anhydrous (garnet-pyroxene) stage and a late, hydrous (amphibole-epidote) stage. Skarns are overprinted by sulfide mineralization (sphalerite, galena, chalcopyrite, pyrite and hematite) which is believed to be contemporaneous with the base metal mineralization.

Adularia-sericite alteration

The second stage of hydrothermal alteration is typically of quartz-adularia-sericite type (Velinov, Nokov, 1991; Nokov, Malinov, 1993). It is strongly fracture-controlled, and forms extensive envelopes around quartz veins with an inner part of the alteration zone adjacent to the veins consisting of quartz-adularia. The average thickness of quartz-adularites in a single vein is up to 10 m, however, in the vein swarms it is considerably larger and may reach up to 100 m. Veinlets of quartz, adularia, pyrite, and sphalerite and galena are ubiquitous in the quartz-adularia zone as well as molybdenum mineralization represented by endogenous wulfenite and molybdenite (Nokov, Malinov, 1993; see also Arnauova et al., 1991). The alteration grades outward to quartz-sericite alteration with small amount illite and smectite (McCoyd, 1995) and propylitic alteration, which is comprised of a chlorite-carbonate-pyrite assemblage. Quartz-adularia alteration is especially well developed in the upper portion of the veins, whereas quartz-sericite alteration prevails in the lower parts. Low-sulfidation quartz veins cross-cut the advanced argillic alteration in the central part of the ore field, however, their mineralized parts tend to be peripheral to the high-sulfidation environments (Sillitoe, 1989, 1993).

Age of alteration

K-Ar dating of an adularia sample from quartz-sericite-adularia alteration around ore (A r n a u d o v a et al. 1991) gave an age of 32-33 Ma. A vein alunite sample from the high-sulfidation alteration was dated by M c C o y d (1995) at 32.6 ± 1.2 Ma. These data are practically the same as the age of Madjarovo volcanics cited above and within the limits of experimental errors of both Rb-Sr and K-Ar methods. The time difference between the intrusion emplacement and alunite alteration is usually less than 0.6-0.7 Ma (D a v i e s, B a l l a n t y n e, 1987; N o b l e, S i l b e r m a n, 1984) which means that the time gap between alteration-mineralization and preceding magmatic activity in a system as old as 30 Ma is irresolvable with the conventional K-Ar method. The data obtained for the fresh volcanics and the alteration minerals, however, suggest close temporal relationships between volcanism, intrusion, hydrothermal alteration and mineralization and a time gap between volcanism and vein emplacement of less than 1 Ma.

Mineralization

The following styles of mineralizations are established in the MOF: (a) intrusion-hosted stock-work/disseminated Cu-Mo mineralization; (b) skarn and non-skarn replacement deposits in carbonate wallrocks and (c) veins in both intrusions and wallrocks, however, only the low-sulfidation system is of economic importance so far.

Porphyry mineralization

The most probable position of any porphyry mineralization is north of Shish Tepe at the crosscut of the east-west fault system of vein No 32 and the south continuation of the north-south vein No 8. This area shows a Mo-Cu anomaly and visible Mo mineralization, established by A t a n a s o v, E s k e n a z i (1964). The location of this mineralization in the argillic alteration suggests that most probably this is the top of a porphyry system.

Skarn mineralization

This is also in close spatial relationship with the monzonitic intrusion. In accordance with its ore-mineral composition (lead-zinc-copper), it can be assigned to the lead-zinc skarn type of E i n a u d i et al. (1981).

Carbonate-replacement mineralization

Existence of this style of mineralization in the MOF was suggested by M a r c h e v and J e l e v (unpubl. data) after sampling the coral limestones in the eastern part of Madjarovo volcano, around "Bakurdjika", about 3-4 km from the monzonite intrusion. The area represents the easternmost continuation of a fault controlling the manganese mineralization west of the village of Kochash. The rocks are strongly silicified and, in places they look like jasperoid. Three rock chip samples were taken and all of them showed an anomalous content of Au ranging between 0.1-0.3 ppm. No visible mineralization of base-metals or manganese and no studies on accompanying elements have been carried out.

The distal position of this mineralization from the intrusion, and the accompanying decalcification and silicification are features which make it similar to Carlin-type gold deposits.

Gold in the high-sulfidation system

Sampling of the advanced argillic type alteration in the monzonitic intrusion and its host rocks shows elevated contents of Au. 21 out of 26 samples analysed carry about (>0.1 ppm) of gold. A rough estimation for the Madjarovo intrusion shows approximately 30 metric tons of Au. However, to be defined as a principal gold deposit, the porphyry copper mineralization must be richer in gold (>0.5 ppm Au) and contain at least 10 million metric tons averaging >1.5 ppm Au (Sillitoe, 1989).

Low-sulfidation mineralization

Economic base- and precious metal mineralization is restricted to the quartz veins. More than 140 quartz veins have been discovered in Madjarovo so far, about a quarter of them carry ore minerals. The average width of the veins is about 1 m, however, the major veins widen up to 30 m across. The length of the veins varies from several tens of meters up to 3-4 km.

Near the surface, the ore veins are entirely located in the volcanics, whereas in depth they cut metamorphic basement. A general zonation, very similar to current models of epithermal deposits with base metals precipitating below shallow deposited precious metals (Buchanan, 1981; Berger, Eimon, 1982), was established by Atanasov (1962) and Arnudova et al. (1991). Ore veins which cross-cut the intrusive bodies are narrow and are barren or contain minor mineralization. The mineralized interval is believed to extend up to 1500 m below the present surface.

The mineralization has been divided into 6 stages (Breskovska, Tarkian, 1993). The first stage of mineralization was found in the deepest parts of some ore veins. The major minerals (pyrite, chalcopyrite and quartz) are accompanied by accessory sphalerite, galena, Se-bearing Bi sulfosalts and bismuthinite. The second stage is comprised of hematite, thuringite, gold and quartz and subordinate pyrite, ripidolite, chlorite-montmorillonite and rare sphalerite and galena. The third stage carries the major quantity of galena and sphalerite. Less abundant are chalcopyrite, gold, pyrite, tetrahedrite, barite, hypogene anglesite, and hematite. The fourth stage is represented by different varieties of silica: quartz, chalcedony, amethyst, smoky quartz, agate, opal, jasper as well as barite, hypogene anglesite, and hematite. Sulfides are rare; they include fine-grained pyrite, chalcopyrite, galena, sphalerite, associated with various Pb-Ag-Sb- and Cl-bearing sulfosalts as well as hypogene greenockite, acanthite, native Ag and Sb, Au, electrum, and aurostibnite. Nokov, Malinov (1993) assigned wulfenite to the first stage and molybdenite to the fourth stage of mineralization. Arsenic sulfosalts, which are absent in the earlier stages, represent the fifth stage of mineralization. The major minerals are tennantite, luzonite, pearceite and As-bearing polybasite. The last stage, which is found in several veins, consists mainly of carbonates: calcite, Mn-bearing calcite, and siderite.

Gold in the low-sulfidation system

The main prospectives for gold in Madjarovo are connected with the quartz-adularia-sericite epithermal category. Most of the gold was deposited during the second and fourth mineralization stages. It occurs as small inclusions of 1-60 μm , rarely 100 μm , in quartz or base metal sulfides. In addition, invisible gold has been determined analytically in quartz and sulfides. The Ag content in the "early" gold varies between 5 and 11 wt.%, whereas in the late "gold" the Ag content is in the

range 7-22 wt.%, including electrum. A trace of Cu have also been detected in single gold grains. Only several veins (No 15, 6, part of 2, 29, 59) have sufficient data to allow a geological resource for Au to be outlined. Total estimated reserves from all veins are about 2 million tons grading at 3.9 g/t gold. In addition, vein No 6 contains 1.2 million tons Ag at 110 g/t. In more fractured rocks, usually at the cross-cut of two fault systems, stockwork-like mineralization can be developed. This consists of strongly silicified rocks and large numbers of small quartz veinlets. Horizontal dimensions of these zones are 100-150 m long and up to 50 m wide. Rare replacement crystals of sulfides (galena, sphalerite) also occur.

Three areas of this type (along vein No 43, No 15, No 16, No 5 and No 6) were explored for gold by rock chip sampling. All of the zones are anomalous in Au, but no economic mineralization has been defined. The Au contents in these zones is in the range 0.1-0.8 ppm with a mode of around 0.2 ppm.

Ore-forming environment

The measurements of Breskovska, Tarkian (1993), Nokov, Malinov (1993) of primary and pseudosecondary inclusions in quartz, amethyst, sphalerite and barite by the method of homogenization show formation temperatures of 370-150°C for different stages of mineralization. More recent measurements of quartz and barite (McCoyd, 1995) are of the same range (350-128°C) with the range of mean values from 283 down to 210°C. The inclusions in the quartz, sphalerite and barite from the upper part of the veins have lower temperatures of homogenization (250-160°C, 210-160°C, 240-150°C, respectively) (Nokov, Malinov, 1993; McCoyd, 1995) than the same minerals in the vein 43 (quartz 370-240°C and sphalerite 230-210°C; Breskovska, Tarkian, 1993) which is about 300 m lower, thus showing a clear trend of decreasing temperature from deeper to upper levels. The inclusions from that level of vein 43 also show unequivocal evidence for boiling with vapor/fluid ratios up to 65/35 in the quartz and 35/65 in the sphalerite.

Fluid inclusion studies have also shown that the Madjarovo ores were deposited from fluids of low to moderate salinity, ranging between 0.2 and 8 eq. wt.% NaCl, with a distinct frequency maximum between 2.5 and 5.0 eq. wt.%. A few exceptionally high salinity inclusions (13.6-18.4 eq. wt.%) have been found in samples from vein 6a (Breskovska, Tarkian, 1993). Small quantities of KCl are also possible. Alternating parageneses of sulfide and hematite in different stages of mineralization suggest that the sulfur and oxygen fugacity were fluctuating during evolution of the hydrothermal system. The abundant occurrence of barite, marcasite and anglesite in the upper parts of the veins indicate increased oxygen fugacity. A more precise determination of the chemical environment of early gold deposition can be achieved based on the assemblage quartz-hematite-chlorite-adularia. At 270°C this mineral assemblage can crystallize at approximately $\log fS_2 = -11$ and $\log fO_2 = -34$ and $pH = 5.5-6$. The multistage crystallization of adularia (Nokov, Malinov, 1993) indicates pH values higher than 5.5-6 for a long period of ore deposition.

Using his data for salinity and temperature of the fluids McCoyd (1995) estimated the depth of boiling below the paleosurface was approximately 300 m. Similar results (70-180 bars) for boiling fluids were obtained by Breskovska, Tarkian (1993). From purely geological consideration we suggest that the erosion to the highest preserved part of the system is approximately 200 m, which is in excellent agreement with the above estimations.

Isotopic studies

Some information regarding the sources of mineralizing fluids, sulfur for sulfides and sulfates, and Pb for galena can be derived from the preliminary studies of the O, D and sulfur isotopes of M c C o y d (1995) and M c C o y d et al. (1997) and lead isotopes of A m o v et al. (1979; 1985), and M a r c h e v, A m o v (unpubl. data).

Stable isotopes

Sixteen measurements of $\delta^{34}\text{S}$ of pyrite from veins and 8 from argillic alteration display a relatively narrow distribution with the vein range between -1.2 and $+6.8\%$ and from the alteration $+1.1$ and $+6.8\%$. The range of the sulfur isotopic composition of the ore fluid was calculated in the range -0.2 to $+5.4\%$. The data can not distinguish between an igneous (0 to $+4\%$) or metamorphic source (-6.7 to $+4.7\%$). Sulfate minerals (alunite from the advanced argillic alteration and barite from the veins) have been analyzed for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$. Alunite with $\delta^{34}\text{S}$ ($+22$ to $+25\%$) show similarity to the Summitvill deposit, Colorado (R y e et al., 1992). Barite $\delta^{34}\text{S}$ ranges from $+19$ to $+24\%$, indicating sulfate was derived from oxidation of hydrothermal sulfide.

The majority of calculated δD values for muscovite and inclusion fluids in quartz and barite lie between -60 and -80% . $\delta^{18}\text{O}$ quartz/muscovite values range from $+8.9$ to $+13.5\%$ and $\delta^{18}\text{O}$ barite data from $+6.3$ to $+11.7\%$. Calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values are consistent with a meteoric origin for the mineralizing fluid. $\delta^{18}\text{O}$ and δD measurements on mineral separates from the argillic/advanced argillic alteration show that overall distribution of alteration mineral $\delta^{18}\text{O}$ is very similar to that observed for the mineralization ($\delta^{18}\text{O} = +5.2$ to $+11.9\%$) whereas δD is slightly heavier ($\delta\text{D} = -57$ to -74%). Calculations of the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values indicate that this difference may be explained by a more magmatic influence.

Lead isotopes

Lead isotopic data in the Madjarovo ores have been studied by A m o v et al. (1979, 1985). Twenty-three samples of galena from volcanic-hosted veins and four samples from two metamorphic-hosted veins in the vicinity of the volcano were analyzed by A m o v et al. (1985). They show a remarkably uniform isotopic composition within a very narrow range: $^{206}\text{Pb}/^{204}\text{Pb} = 18.75-18.80$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.66-15.70$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.83-38.87$, very similar to the values obtained from the adularia in the alteration halo around the veins ($^{206}\text{Pb}/^{204}\text{Pb} = 18.76-18.83$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.65-15.66$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.74-38.75$). These values show a remarkable uniformity with the values obtained from the intrusive rocks and intermediate and acid volcanics ($^{206}\text{Pb}/^{204}\text{Pb} = 18.68-18.78$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.65-15.68$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.72-38.88$) and quite different from the high-Al basalts ($^{206}\text{Pb}/^{204}\text{Pb} = 19.24$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.69$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.81$) and the underlying metamorphic rocks ($^{206}\text{Pb}/^{204}\text{Pb} = 18.51-18.56$; $^{207}\text{Pb}/^{204}\text{Pb} = 15.63-15.66$; $^{208}\text{Pb}/^{204}\text{Pb} = 38.76-38.85$; M a r c h e v et al., unpubl. data).

The newly obtained whole-rock Pb isotope data partly support a magmatic origin of the lead (A m o v et al., 1985). A more precise interpretation requires the source of the lead to be similar in isotopic composition to the strongly contaminated (by crustal material) latite-syenite magmas but different from the mantle-derived basaltic magma.

Conclusions

Alteration and mineralization in the MOF is hosted by a shield type volcanic centre consisting of calc-alkaline to shoshonite lava flows and epiclastics. Geochronological data suggest an early Oligocene age of the magmatism and alteration.

The central part of the MOF is extensively altered and contains several distinct styles of alteration. Advanced argillic (quartz-alunite-pyrophyllite-diaspore and massive silicification), sericitic and propylitic alterations are developed in a concentric manner around the largest outcrop of Madjarovo monzonitic intrusion. These alteration zones formed from the leaching of rocks by low pH acid-sulfate fluids.

Spatially and, probably, temporally related to monzonitic intrusions are also potassic alteration assemblages, which show a transition from porphyry to epithermal environments, and skarn bodies of unknown size and potential.

The advanced argillic and potassic alteration are cross-cut by quartz veins of a radial distribution but their mineralized part and related quartz-adularia alteration tend to be peripheral to the high-sulfidation environment. Jasperoid-like (carbonate replacement) rocks with elevated contents of Au are also in distal position from the monzonitic intrusion and show similarity to Carlin type deposit.

Fluid inclusion data suggest temperatures of formation of 210- and 280°C and salinities between 2.0 and 4.5 eq. wt.% NaCl.

The S isotope studies can not distinguish between metamorphic and magmatic sources for the advanced argillic and vein sulfides, however O, H isotopes are consistent with a stronger magmatic input in the advanced argillic and sericitic alteration compared to the adularia-sericite alteration. The Pb isotope values indicate that the Pb was derived from the monzonitic magma which have a similar range of values.

Acknowledgements. The work is a contribution to the Project "Structure and age of the metamorphic rocks and metallogeny of the Rhodope Massif" of the bilateral cooperation between Geological Institute of BAS and Royal Society of Great Britain. An earlier version of this manuscript was improved greatly by critical comments from Ivan Velinov, Ivan Bonev, Clive Rice and Adrian Boyce.

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Accepted June 5, 1997

Одобрена на 05.06.1997 г.