The Alshar Epithermal Au–As–Sb–Tl Deposit, Southern Macedonia


Abstract—The results of tectono-metafomatic, geological-structural, mineralogical, isotopic, and thermobarographic studies at the Alshar deposit and in the adjacent area are discussed. The data obtained show that the gold mineralization at the deposit is similar to that observed at the Carlin-type deposits in the western United States. Similar characteristics include the Au–As–Sb–Tl–Hg geological assemblage; low Pb, Zn, Cu, and Ag contents in ore; widespread jasperoid and argillic metasomatic alterations of host siliciclastic-carbonate sedimentary rocks; and the spatial relations to fault zones. At the same time, the Alshar deposit differs from the Carlin-type deposits by the following features: (1) Placerocene age of mineralization; (2) expansion of mineralization over younger volcanics; (3) a high Tl grade in ore; and (4) localization of the ore field in a long-lived central-tectonic-magmatic structure. The results obtained can be used as an exploration model.

INTRODUCTION

The complex Au–As–Sb–Tl deposit, modest in size, is unique in its mineral composition. In addition to economic Sb and As grades, the ore is substantially enriched in Tl. Furthermore, Alshar is the first Carlin-type gold deposit discovered in the Balkan Peninsula in the late 1980s (Percival et al., 1990). The economic development of the Alshar deposit was begun in 1881 by an English-French company, which received a concession from Turkey, and lasted, with short interruptions, until 1913. During this period, the ore was mined and exported to Freiberg and other German cities. High contents of thallium minerals—lorandite and vhatite—were identified at that time in ore at the smelter of Freiberg. There is no information on the quantity of ore mined at that time. Arsenic reserves at the deposit amount to 15,000 t (Boev et al., 2001–2002). Nevertheless, this element is considered now to be an undesirable admixture of Sb concentrate. The Sb mineralization was studied after World War II from 1958 to 1974: the estimated Sb reserves exceed 20,000 t with an average Sb grade of 0.5% (Boev et al., 2001–2002). The interest of industry in thallium for solar neutrino sensors in the 1980s stimulated further exploration of the northern part of the deposit (Boev et al., 2001–2002). The Alshar deposit is classified as large in terms of thallium reserves (over 500 t) and as medium according to gold and antimony reserves.

The question of why no large Carlin-type deposits have been discovered in the world despite extensive geological exploration is currently being debated. Various hypotheses pertaining to the origin of the Carlin-type deposits are also under discussion (Muntean et al., 2004). No such deposits have been discovered in Russia or other CIS countries either. Naturally, each deposit of this kind discovered beyond the western United States attracts the attention of researchers. Geological exploration performed under a project of Naxassan Ltd. detected gold (>1.0 g/t) in ore of the Alshar deposit and established that the geological, geochromatographic, and mineralogical properties of ore at this deposit, as well as the hydrothermal alteration of host rocks, are similar to those characteristic of Carlin-type gold deposits in Nevada (Percival et al., 1990; Percival and Radlko, 1994).

In recent years, a Russian–Macedonian scientific team has carried out a comprehensive study of the Alshar deposit in southern Macedonia in line with a bilateral agreement between the University of Skopje, Macedonia, and the Institute of Geology of Ore Deposits, Petrology, Mineralogy, and Geochemistry, Russian Academy of Sciences (IGEM RAS). The metamorphic characteristics, tectonic setting, and structure of the deposit and its specific genetic features are discussed in this paper on the basis of new results and data obtained by previous investigations.

TECTONIC AND METALLOGENIC OUTLINE

A complex method of forecasting based on compilation of structural–metallogenic maps on scales of 1:500,000, 1:200,000, and 1:50,000 was elaborated.
by Tomson et al. (1992) at the Laboratory of Metallogeny of Ore Districts, IGRM RAS, and applied to the territory of the Former Yugoslav Republic of Macedonia (FYROM). The interpretation of satellite images and morphostructural analysis were employed successfully for revealing the ore-concentrating structural features. The tectonic elements of the present-day topography were marked out and compared with the structural features that existed during the period of ore formation. The use of the present-day structural landforms of Macedonia for reconstruction of the tectonic elements of ore-bearing epochs became possible after substantiating their inherited evolution (Kochneva and Ronich, 1981).

A considerable part of the study area (Fig. 1) belongs to the ancient Serbo-Macedonian and Pelo-

Fig. 1. Tectonic units of Macedonia. (1) Serbo-Macedonian Massif; (2) Rhodope Varoš Graben; (3) Pelagonian Massif; (4) West Macedonian region; (5) Cenozoic metallogenic zones; (6) Variscan metallogenic zone.

sily the West and East Macedonian margins, reactivated in the Caledonian–Hercynian time and in the Cenozoic, respectively.

The joint studies allowed us to establish that present-day Macedonia comprises fold–block systems, as well as superimposed and through-type structural features. A new structural base was elaborated, and ore-controlling structural features, including superimposed ring and grabenlike depressions, were outlined on the basis of interpretation of satellite images and morphostructural analysis. The Macedonian Arch, which embraces practically the whole country, was recognized together with daughter ring structures and through fault zones that have important ore-controlling implications (Kochneva et al., 1997; Tomson et al., 1998).

In the present-day topography, the Cenozoic arched structure, 250 × 300 km² in size, is oval to rounded in plan view. Its central part is relatively subsided (down
to 1000–1500 m) and filled with Upper Cretaceous, Paleocene, and Quaternary sediments. The marginal part of the Macedonian Arch is uplifted to a height of 2000–2600 m on average. The dislocations within the arch are emphasized by the arcuate and radial arrangement of the main tributaries of the Vardar River. The main structural features of the arch are reflected in the isometric zoning of the anomalous gravity field: the central maximum is encircled by ring zones of gravity minima.

The comparison of the present-day structural grain of the territory with geological and paleostructural data shows that the main features of the Macedonian Arch are traceable since the Caledonian time. The localization of geological units of different ages suggests that the marginal belt of the arch, with fields of volcanoes and the largest ore deposits, is the most active and long-lived. Noteworthy is the widening of the marginal belt at the expense of daughter ring structures of the second rank, as is observed in the vicinity of the Kratovo–Zletovo, Tainitsite, and Alishar deposits.

The Cenozoic reactivation involved mainly the eastern part of the Macedonian Arch (Tomson et al., 1998) and is reflected in the formation of the NW-trending fault system oblique relative to the Vardar Zone and the NE-trending transverse fault zones that were active at the final stage. Three NW-trending systems that control graben-shaped troughs filled with Cenozoic sediments and one NE-trending fault zone have been outlined from interpretation of satellite images. Chains of local concentric central-type structures, many of which correspond to outcrops of Tertiary igneous rocks, are localized along the NW- and NE-trending zones. The northwestern system controls the Cenozoic metallogenic zones related to grabens (Fig. 1). The meridional fracture zones are important for localization of economic deposits. Ore fields are commonly localized at the intersections of NW-trending fault zones with meridional fracture zones and transverse northeast faults.

The special implication of meridional fracture zones for localization of large deposits has been demonstrated by many researchers. I.N. Tomson and M.I. Favorskaya traced such meridional ore-controlling systems through-out Europe. The active role of such systems in localization of ore deposits was pointed out in neighboring Bulgaria (Vaptzarov et al., 1986). It is notable that such intersections are the zones of maximal permeability and ascent of mantle material. All economic deposits of Macedonia—Kratovo–Zletovo, Sasa–Toranica, Bucium, Tainitsite, Rzanno, and Alishar—are controlled by meridional zones.

The Oligocene–Miocene metallogenic zones traceable through metamorphic sequences of the Serbo-Macedonian Massif are composed largely of Cenozoic tuffaceous–sedimentary and volcanic rocks and intruded by granitoid bodies and intermediate rocks. In total, three metallogenic zones make up an are belt that extends westward to Serbia and southeastward to Greece and Bulgaria (Fig. 1).

The specialization of metallogenic zones changes and the igneous complexes and ores become progressively younger from the southwest to the northeast. A distinct correlation between age and composition of ores is evident. The ore mineralization changes in this direction from high- to low-temperature and from relatively low-sulfide to polysulfide types. The change in the ore composition may be regarded as a result of ore matter differentiation in deep-seated chambers. Across the strike of metallogenic zones, the types of ore deposits change from magnetite skarn (Borov Dol) to porphyry copper (Buchim) and farther to copper–base metal (Kratovo–Zletovo) and base metal deposits proper (Sasa–Toranica). The age of igneous rocks in ore districts changes in the northeastern direction from 28.0–24.5 Ma (Borov Dol and Buchim) to 27.2–16.0 Ma (Kratovo–Zletovo) and 24–12 Ma (Sasa–Toranica). Thus, the progressive change in the composition of ore is a consequence of its rejuvenation and differentiation. These relationships suggest that close links exist between metallogenic zones.

A model of this system at a depth may be viewed as a low-angle common seismic focal zone inclined southwest (Tomson et al., 1998). The hypothetical focal zone could have served as a feeding channel for injection of igneous material in the northeast direction. Each new portion of magma that associated ore matter experienced compositional differentiation at a certain level of the seismic focal zone. The hanging wall of the zone moved southeastward down its dip. Particular blocks were detached along impaired zones with formation of grabens. The deep faults that bound the grabens could have reached the magmatic channel of the seismic focal zone to provoke the eruption of igneous material and to stimulate the ore formation.

The Kozuf–Arid metallogenic zone of Pliocene mineralization, which extends along the Greek–Macedonian border, occupies a special position in southern Macedonia (Fig. 1). Volcanic structures and subvolcanic calc-alkaline intrusions are confined to NE-trending neotectonic faults. Igneous rocks are represented by calc-alkaline andesite and quartz latite. All subvolcanic intrusions of the Kozuf district are of the same age, intrusions at the Alishar deposit belong to the youngest phase, dated at 5.1–3.9 Ma (Boev, 1988). The Kozuf–Arid metallogenic zone is characterized by the development of complex Au–As–Sb–TI mineralization.

It is known that metallogenic zones in orogenic domains of fold systems are linear and oriented in two directions: along the strike of sedimentary sequences and across the strike. The metallogenic zones conformable with folding control plutonic bodies and deposits of the early orogenic stage, while the transverse metallogenic zones are accompanied by the late orogenic mineralization and magmatism (Tomson and Polya-kova, 2000).
Thus, the system of northwestern zones in the Macedonian Arch may be referred to the early orogenic structural features, whereas the transverse Kozuf–Arid Zone is related to the late orogenic stage.

GEOLOGY OF THE KOZUF–ARID OR District and TECTONIC SETTING OF THE ALSHAR DEPOSIT

The Pliocene volcanic-plutonic complex of calc-alkaline laves of the Kozuf–Arid Zone was formed on a basement of Precambrian gneisses, Tertiary rocks (dominant), Jurassic ophiolites (gabbro–peridotite), and Cretaceous sequences. The Precambrian albite gneiss with sporadic lacies of amphibolite forms the oldest rocks of the Kozuf–Arid Zone. Marble blocks are sporadically incorporated in gneiss, Paleozoic schist, phyllite, metasandstone, shale, and quartzite occur locally. The Tertiary sequence occupies most of the area and is composed of two main facies: (1) marnerized limestone and dolomite and (2) mudstone and sandstone with sporadic dolerite and green schist. The Jurassic sequence consists of limestone, sandstone, shale, quartzite, chert, shale, and a severely serpentinized dunite-harzburgite complex that hosts small podiform chromite bodies. Serpentinite is exposed as narrow tracts that have tectonic boundaries with adjacent rocks. Their emplacement is related to diapiric processes. The Preteraceous sediments are represented by Barremian–Albian conglomerate and Turonian limestone. The Upper Eocene sequence is composed of basal conglomerate overlain by fly-sch mudstone (silcrete, clay, and sandstone with tecto- stone interbeds). Pliocene sedimentary and pyroclastic rocks are widespread around the Alshar deposit. They are composed of conglomerate and clayey sandstone with calcareous clay interbeds. Volcanoclastic sedimentary and pyroclastic rocks and clayey sandstone occur in some Pliocene basins north of the Alshar deposit. Quaternary sediment forms river terraces.

The Alshar deposit is located at the intersection of the Vardar and Kozuf–Arid metallogenic zones (Fig. 1) at the western flank of the Vardar Gneisses and the Polyg- nonian oolitalline mantos approximately 30 km southwest of the town of Kavadars and 3 km from the Greek-Macedonian border. The ore itself is 21 km² in area.

The tectonic setting of the ore district and the Alshar deposit itself was deduced from the results of morpho-structural analysis and interpretation of satellite images. First, the present-day structural grain of southern Macedonia was outlined. For this purpose, the traditional method of morphotectonic contour lines was used to generalize the topographic contour lines and drainage pattern. Structural features of different ranks were contoured from the analysis of present-day landforms of several orders.

The Alshar deposit is located in the upper reaches of the River R (the right tributary of the Crna River). The streams in the Rodenska River basin form a radial–centripetual pattern (Fig. 2). The branched radial rivers and creeks are surrounded by arctic ridges up to 1500 m in height. The arctic valley levees along their outer framework. Such an orographic pattern fits an endogenetic ring structure 8 x 15 km in size with a relatively stable ring structure and an elevated outer belt. This ring structure is located at the intersection of two extended diagonal through fault zones. The northwestern fault zone is an element of the Vardar Zone. Another (northeastern) fault zone was deduced from linear shale anomalies in satellite images. This fault zone is emphasized by the rectilinear valley of the Bosavica River, by the present-day slope elements, and by a chain of dome-shaped structural features up to 10 km across. In addition, a system of very young NE-trending faults controls the Plisnice lava flows here. The Alshar ring structure is surrounded by a belt of daughter domes up to 5 km across. Each of these domes is comparable with associated ore-bearing central-type structures (Fig. 2). The three second-order domes located in Greece south of the Alshar ring structure are characterized by the most complex structure and are contrastingly expressed in the present-day topography. By analogy with other regions studied previously, such structures control large ore districts and deposits (Volokov and Sidorov, 2001). The tectonic position of the Alshar deposit is emphasized by the configuration of the main structural horizons. An EC–Nw extends along the Vardar Zone and an Sb–As–Tl–Yb–Zn–Cu halo corresponds to the young NE-trending fault system that crosses the Oligocene and Miocene metallogenic zones (Fig. 2). In the opinion of Jancovic (1995), the extended and wide mineralization zone on the ore zone is related to the central region and ring structure serves as a main ore-controlling tectonic line. We also traced a latt- itudinal fault zone as a fragment of an extended system interpreted in a satellite image.

GEOLOGY OF THE DEPOSIT

The Alshar deposit is composed of various rocks (Fig. 3) that belong to three lithostratigraphic complexes.

A complex of tectonic sedimentary and metamorphic rocks. The basement of the Alshar deposit is composed of Middle and Upper Tertiary sandstone and shale accompanied by subordinate limestone, dolomite, and marble. Quartz–sericite–feldspar schists occur at the eastern flank of the deposit, whereas its central part is occupied by dolomite, marble, and less abundant limestone. Triassic dolomite dated back to 250 Ma (Lepitkova, 1995) is probably the oldest rock at the deposit. Massive marble consisting of calcite grains 0.5 mm in size and crossed by white calcite veins is widespread in the pre-Cenozoic rock complex. Tectonic blocks composed of marble are underlain by dolomite. The contact between marble and tuff in the south-

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part of the study area is locally mineralized. Crystalline schists are traced as two tracts in the eastern part of the Alshar deposit. The stratigraphic relationships between the crystalline schists and other Triassic rocks remain ambiguous. The schists consist of quartz, sericite, feldspar, and a small amount of chlorite.

Tertiary (?), carbonate and Pliocene volcanosedimentary rock complexes consisting of dolomite and pyroclastic material are widespread at the deposit. They are the main host rocks subject to hydrothermal metamorphic alteration. Tuffaceous dolomite is probably Tertiary in age and overlies with unconformity the Mesozoic basement in the north and west. The dark gray dolomite contains a variable admixture of volcanic ash. In the greater part of the deposit, the basement is overlain by Tertiary volcanicash, tuffaceous breccia, and lacustrine tufite. The normal stratigraphic succession of tuffaceous dolomite and pyroclastic rocks is suggested. The contact of the Tertiary sequence with the pre-Tertiary basement is marked by distinct unconformity and a basal unit 7–10 m thick composed of unsorted, variegated rock fragments. In many places, the contact zone is mineralized.

Volcanics are widespread at the deposit. Two stages of volcanic activity are recognized. The older stage, probably Miocene in age, is represented by subvolcanic dikes, which are completely altered at the Alshar deposit and in the Duda ore field. Rhoes of primary
rocks are retained only locally. The Ar–Ar age of plagioclase relics was determined at 12 Ma (Framitz, 1994). The younger stage corresponds to the Pliocene (Boev, 1988). Most volcanics that were formed during this stage are fresh and suitable for detailed petrographic examination. This volcanic stage was accompanied by a vigorous explosive event, which resulted in the formation of an extensive pyroclastic complex composed of tuff, tuffite, and ignimbrite. Products of Pliocene volcanic overlie the igneous rocks of the older stage, although the contact is completely obscured by hydrothermal metamorphic alteration. Lutite, trachyandesite, trachyte, andesite, and dacite were identified among the volcanic rocks (Boev and Serafimovski, 1990).

Faults at the Alshar deposit are divided into three groups: (1) near-meridional, (2) NW-trending, and (3) NE-trending. The anhydrite mine is located at the intersection of NE- and NW-trending faults. These faults served as conduits for hydrothermal mineral-forming fluids. The main near-meridional ore-controlling fault zone, 80–100 m wide, extends along the valley (Fig. 3). In the eastern wall of the valley, the main fault zone that hosts the ore mineralization is exposed as rocky outcrops. Geological sections across the valley compiled from geological and drilling data demonstrate the detailed structural of the ore body (Figs. 4, 5). The soil layer overlies a thick zone (30–50 m) of tuffaceous dolomite that underlies intense argillic alteration. The realgar-porphry mineralization is located at a transition of tuffaceous to tuffaceous mudstone and tuff. Downslope, the argillic alteration gives way to a zone (10–20 m) of anhydrite and thallium-bearing jaspilites and intensely silicified dolomite that grades deeper into much less silicified dolomite with subordinate cavernous siliceous varieties. The opposite western wall of the valley is hitherto unknown and composed of massive sediments (Figs. 3, 4). The formation of ore-controlling near-meridional faults was probably related to downdip-slip movements along the Vardar Zone. Postmineral vertical movements along this zone bounded the deposit in the west (Figs. 3, 4). The ore controlling role of the main fault zone is emphasized by intense Au and Sb anomalies as

![Diagram](image-url)
secondary geochemical halos. Figure 6 demonstrates the distinct correlation between these elements.

Several morphostructural types of orebodies are distinguished within the deposit: (1) mineralized breccia zones along contacts of subvolcanic intrusions with dolomite and tuffaceous dolomite and mineralized fault zones in carbonate rocks; (2) systems of mineralized veins and fissures in Tertiary tuffaceous dolomite and Triassic dolomite; (3) stratiform sulfide lodes hosted in tuffaceous dolomite; and (4) disseminated Sb mineralization (stibnite is prevalent) in association with gold-bearing pyrite and marcasite as stratiform bodies along the contact between the volcanosediimentary sequence and Triassic carbonate rocks and hosted in silicified volcanics and jasperoids as well. It should be noted that the geological exploration conducted at the deposit is insufficient for the ultimate estimation of reserves.

HYDROTHERMAL METASOMATIC ALTERATION OF HOST ROCKS

The hydrothermal metasomatic alteration of host rocks at the Alshar deposit covers an area of 2 km². The intensity of alteration is highly variable. The following types of metasomatic alteration are distinguishable: decalcification, silicification, argillization, and dolomitization (Percival and Radtke, 1994).

The hydrothermal activity started after deposition of most tuffs and emplacement of subvolcanic intrusions and prior to deposition of tuffite and lacustrine sediments, which overlie metasomatically altered and mineralized rocks in the northern and southwestern parts of the Alshar deposit (Percival and Radtke, 1994).

Decalcification at the Alshar deposit affects the Triassic and Tertiary dolomites. The removal of calcite from rocks is accompanied by quartz deposition and argillaceous alteration. Another process related to decalcification consists in the formation of dolomitic sand. This process accompanies silicification of dolomite, especially Tertiary in age. The dolomite altered by hydrothermal fluids is transformed into a peculiar dolomitic sand with spots and crusts of Fe oxides and unidentified green and yellow secondary minerals similar to those observed at some Carlin-type deposits in Nevada (Percival and Radtke, 1994).

Silicification at the Alshar deposit also affects Triassic and Tertiary carbonate rocks south of adits (Fig. 3). As was noted, silicification varies in intensity from weak to very high, in which case carbonate rocks are replaced by jasperoids. Silicified rocks are spatially related to variably oriented faults and fracture zones and make up stockworks and slightly silicified fracture zones. Jasperoids are usually brecciated and crossed by quartz veins and thin veinlets. The rocks are composed of fine-grained microcrystalline quartz, which obscures the primary structure of carbonate rocks. Although jasperoids are rather common in the Alshar deposit, they are second in abundance relative to slightly silicified host rocks.

Quartz veins and veinlet zones at the Alshar deposit are developed mainly in jasperoids. Thin veinlets (1–5 mm) contain disseminated pyrite, marcasite, and stibnite and local lenticular segregations of these minerals (Fig. 7a).

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In addition to veinlets, jasperoids contain cavities and caverns filled with quartz druses (individual crystals are as long as 0.5–1.0 cm; Fig. 7b) associated with albite and Ti-bearing minerals.

*Argillization.* The volcanosedimentary host rocks at the Alshar deposit underwent argillization and sensitization, intense in some places. Tufts are more sensitive to argillilc alteration than sedimentary rocks near fault and silicification zones. Argillites consist of fine-grained light clay, sericite, quartz, Fe hydroxides, jarosite, gypsum, calcite, siderite, marcasite, pyrite, red clay, and various Ti-bearing minerals (Fig. 8). A similar mineral composition is characteristic of argillilc alteration at the Carlin deposit and its counterparts in Nevada (Radljeke et al., 1980). As was noted previously, the zone of argillilc alteration is localized above jasperoids and siliceous rocks.

The oxidation zone is widely developed at the Alshar deposit. Oxidation products include secondary Fe oxides and hydroxides replacing sulfide ore and clay minerals of humic appearance developing after volcanosedimentary rocks. It may be assumed, by analogy with the Carlin and Olimpia (Yenisei Range) deposits, that oxidation of sulfides is accompanied by freeing of gold and enlargement of gold grains, which makes it possible to recover gold by cyanide leaching. Thus, the study of the oxidation zone is a top-priority task of the forthcoming stage of scientific research and geological exploration.
COMPOSITION OF ORE

The Alshar deposit comprises several orebodies and ore occurrences, which are characterized by specific assemblages of chemical elements and minerals. It is the only deposit in Macedonia that contains economic grades of Ti (0.1–0.5%), Sb (up to 2.5%), As (1.2%), and Au (>1 g/t). It should be noted that gold is distributed in ore nonuniformly. Its maximal contents (3–4 g/t on average and up to 20 g/t or higher in particular samples) were detected in jasperoid zones in the southern part of the deposit (Table 1, Fig. 9).

By analogy with the Carlin-type deposits in Nevada, Percival and Ruddle (1994) distinguish four types of economic gold ores at the Alshar deposit: (1) Au-bearing antimony jasperoid ore (Au–As–Ti), (2) siliceous gold ore (Au–Sb–Ti), (3) Au-bearing arsenic ore (Ti–Hg–Sb–Au), and (4) tellurium ore.

The more than 40 minerals that have been identified in ore at the Alshar deposit (Table 2) are combined into three mineral assemblages formed in sequence: pyrite–marcasite, stibnite, and orpiment–realgar–laserlite.

The pyrite–marcasite mineral assemblage includes pyrite, marcasite, and arsenopyrite (Fig. 7b). Pyrite, the most abundant, occurs as massive aggregates (grain size is ~0.5 mm). Pyrite is closely associated with marcasite and arsenopyrite (Fig. 10a), contains insignificant Mn and Co admixtures, and is characterized by a high As content (up to 5%), which reflects a high activity of this element in the course of ore deposition. Marcasite forms spheroids (grain size is 0.005–0.1 mm) in the silicified matrix or rims pyrite grains (Fig. 10c). Marcasite contains a smaller amount of impurities than pyrite and is characterized by low As and Sb contents. Arsenopyrite occurs as inclusions in pyrite or segregations of fine acicular crystals (Fig. 10c). Precisely such aggregates are characterized by the highest contents of invisible gold (Genkin et al., 1998). Arsenopyrite is replaced frequently by marcasite (Fig. 10b). The electron microscopic examination of several pyrite grains
from a sample of Sb-bearing jasperoid with a Au content of 21 ppm showed the enrichment of their outer zones in As and Sb (Percival and Radlke, 1994). Thereby, the content of these elements decreases distinctly toward the inner zone of mantos: from 7.1% As and 2.0% Sb in the outer zone to 0.9 and 0.07% in the intermediate zone to 0.56 and <0.07% in the inner zone, respectively. Similar examinations of pyrite from pre-

<p>| Table 1. The content of As and other elements in ores from the Alshar and Carlin deposits, ppm (Percival et al., 1990) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|</p>
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<th>Element</th>
<th>Au (ppm)</th>
<th>Ag (ppm)</th>
<th>As (ppm)</th>
<th>Sb (ppm)</th>
<th>Tl (ppm)</th>
<th>Hg (ppm)</th>
<th>Cu (ppm)</th>
<th>Pb (ppm)</th>
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</table>

Note: Samples were analyzed at the Sparks Mine Laboratory (Nevada, United States). Au and Ag were determined by assay analysis, and other elements by the atomic absorption method; n.a., not analyzed.
ary unoxidized ores from the Carlin and Cortez (Weiss and Millen, 1973; Radtke et al., 1980) and the Maisky and other (Novozhilov and Garriow, 1999) deposits have also shown that the outer rims of pyrite are enriched in As and to a lesser extent, in Sb, Au, and Hg. A recent study of pyrite from gold ore at Carlin-type deposits with secondary ion mass spectroscopy (SIMS) and photoelectron spectroscopy (Achert et al., 1993) confirmed high Au and Sb contents in the outer rims. These rims, usually 1–4 mm thick, grow over cubic and framboidal facets of pyrite crystals barren of these metals.

The stibnite mineral assemblage. Stibnite occurs as relatively large crystals 2 × 5 mm in size (Fig. 10a) and frequently cements quartz and marcasite grains (Fig. 10a), indicating its younger age in comparison with the pyrite-marcasite assemblage. Fe, Cu, and occasionally Ti are detected in stibnite as impurities.

The realgar-orpiment-lorandite mineral assemblage was formed at the final stage of the hydrothermal activity. Orpiment—the most abundant mineral—occurs as massive aggregates composed of large crystals (10–15 mm in size) that contain Fe and Cu impurities. Realgar is present as separate aggregates or intergrowths with orpiment, lorandite, and other minerals. The grains are 3–5 mm in size. Orpiment corrodes realgar. This mineral assemblage also includes various Ti minerals (Table 2). The most abundant of these, lorandite, occurs as intergrowths (up to 5 mm in size) with realgar and orpiment.

Table 2. Abundance of minerals at the Alshar deposit

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Major</th>
<th>Minor</th>
<th>Rare</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphides</td>
<td>Pyrite, marcasite, orpiment, realgar, lorandite, stibnite</td>
<td>Arsenopyrite, bornite, cinnabar, pararosegir</td>
<td>Gold</td>
</tr>
<tr>
<td>Oxides</td>
<td>Quartz, goethite, valentinite</td>
<td>Cervantite, stibicorite</td>
<td>Jankovite*</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Calcite, dolomite</td>
<td>Orpiment</td>
<td>Pinctropolite*</td>
</tr>
<tr>
<td>Sulfates</td>
<td>Barite, gypsum, melanterite</td>
<td>Fibroferrite, rosemite, starkeyite</td>
<td>Rutilite*</td>
</tr>
<tr>
<td>Arsenates</td>
<td>Molybdite</td>
<td>Pharmacolite, bornsite</td>
<td>Wulfenite</td>
</tr>
</tbody>
</table>

* Ti minerals known only from the Alshar deposit (Boev et al., 2001–2002).
FORMATION CONDITIONS OF ORE

To estimate the formation conditions of ore at the Alshar deposit, fluid inclusions in quartz and realgar have been studied with thermobarogeochemical methods. Most of the examined fluid inclusions in quartz with mosaics texture from Sb-bearing jasperoids and siliceous ore turned out to be no larger than 1 μm and thus unfit for thermometric studies. Nevertheless, the occurrence of primary marcasite in this ore makes it possible to determine the temperature of the main gold-ore stage. As is known, marcasite is usually deposited at a temperature below 200°C (Murovchik, 1992). Thus, a temperature of ~200°C may be accepted as highly probable for the main gold-ore stage at the Alshar deposit.

In addition, the microthermometric study of fluid inclusions in realgar crystals (Beran et al., 1990) yielded the following results: the homogenization temperature of primary inclusions varies from 144 to 177°C, the salinity of fluid ranges from 7.9 to 12.9 wt % NaCl equiv, and the fluid pressure reaches 1500 atm. However, it should be noted that deposition of realgar postdated the main gold-ore stage and, thus, the obtained data cannot be extrapolated to this stage.

The metalliferous hydrothermal fluids were acidic and initially characterized by a high sulfur concentration, as is evident from insignificant quantities of native sulfur and traces of solutatic activity at the deposit.

The Pb isotopic composition indicates that lead was supplied to the hydrothermal ore-forming solution from the host volcanics that occur at the Alshar deposit (Franz, 1994). Sb, As, and Ti could have been derived from the calc-alkaline magma that solidified as igneous rocks.

The S isotope composition has been studied in sulfides of the Au-bearing Sb-ore jasperoids and siliceous ore and in minerals from the zone of argillic alteration (Table 3). The δ34S value in sulfide varies from +0.351 to −5.601‰. The complete data set covers a relatively wide interval from +0.351 to −6.840‰. As can be seen
Table 3. Sulfur isotopic composition of sulfides from the Alshar deposit.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Mineral</th>
<th>δ34S, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14564</td>
<td>Stibnite</td>
<td>+0.351</td>
</tr>
<tr>
<td>2</td>
<td>14565</td>
<td></td>
<td>-0.337</td>
</tr>
<tr>
<td>3</td>
<td>14566</td>
<td></td>
<td>-0.419</td>
</tr>
<tr>
<td>4</td>
<td>14567</td>
<td></td>
<td>-4.728</td>
</tr>
<tr>
<td>5</td>
<td>14568</td>
<td></td>
<td>-5.6</td>
</tr>
<tr>
<td>6</td>
<td>14569</td>
<td></td>
<td>-7.25</td>
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<tr>
<td>7</td>
<td>14571</td>
<td></td>
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<td>8</td>
<td>14576</td>
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<td>-7.56</td>
</tr>
<tr>
<td>9</td>
<td>16</td>
<td></td>
<td>-2.74</td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td></td>
<td>-2.72</td>
</tr>
<tr>
<td>11</td>
<td>14572</td>
<td>Realgar</td>
<td>-1.64</td>
</tr>
<tr>
<td>12</td>
<td>14573</td>
<td></td>
<td>-3.77</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td></td>
<td>-0.18</td>
</tr>
<tr>
<td>14</td>
<td>21</td>
<td></td>
<td>-4.48</td>
</tr>
<tr>
<td>15</td>
<td>14574</td>
<td>Orpiment</td>
<td>-3.696</td>
</tr>
<tr>
<td>16</td>
<td>12570</td>
<td>Marcasite</td>
<td>-6.840</td>
</tr>
<tr>
<td>17</td>
<td>18</td>
<td></td>
<td>-0.67</td>
</tr>
<tr>
<td>18</td>
<td>19</td>
<td></td>
<td>-0.9</td>
</tr>
</tbody>
</table>

Note: Samples were analyzed at the Institute of Geology of Ore Deposits, Petrology, Mineralogy, and Geochemistry, Russian Academy of Sciences, analyst L.P. Nisik.

Table 4. Sulfur isotopic composition δ34S (PDD) in δ34S (SMOW) of calcite from the Alshar deposit.

<table>
<thead>
<tr>
<th>No.</th>
<th>δ34S, ‰</th>
<th>δ34S, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+2.44</td>
<td>+14.92</td>
</tr>
<tr>
<td>2</td>
<td>+3.38</td>
<td>+28.72</td>
</tr>
<tr>
<td>3</td>
<td>+2.66</td>
<td>+20.69</td>
</tr>
<tr>
<td>4</td>
<td>+3.07</td>
<td>+26.19</td>
</tr>
<tr>
<td>5</td>
<td>+3.93</td>
<td>+21.63</td>
</tr>
<tr>
<td>6</td>
<td>+2.03</td>
<td>+24.07</td>
</tr>
</tbody>
</table>

Note: Samples were analyzed at the Institute of Geology of Ore Deposits, Petrology, Mineralogy, and Geochemistry, Russian Academy of Sciences, analyst L.P. Nisik.

from Table 3, sulfur in ore minerals, particularly from younger assemblages, is notably enriched in the light isotope.

It is known that the host sedimentary rocks are usually characterized by δ34S ranging from -30 to +7‰ (Nielsen, 1979), whereas values varying from -4.0 to +4.0‰ are the most characteristic of fluids connected with granitoid magma (Ohimoto and Rye, 1979). Thus, the preliminary isotopic data suggest isotopic heterogeneity of mineral-forming fluids at the Alshar deposit. Both a deep magmatic chamber and sulfides from host rocks could have served as sources of sulfur.
typical of continental tholeiitic basaltic and alkaline volcanics from continental rift zones.

The formation of the Alshar deposit is undoubtedly related to postvolcanic hydrothermal fluids. On the basis of geological-structural, mineralogical-geochemical, and thermobarographic data, the deposit may be referred to the epithermal class. At the same time, it differs drastically from the typical epithermal Au-Ag deposits in its geological setting, the textures of ores, and their mineral composition. Thus, the Alshar deposit
Fig. 12. Oxygen and carbon isotopic compositions of calcite from Au-bearing copper porphyry and Carlin-type deposits after Roodt et al. (1980), Semeniukovski et al. (1996), and Estrah et al. (2003). Deposits: (I) Goldstrike, (II) Aishar, (III) Buchan. (1-3) Goldstrike deposits: (1) postore calcite, (2) late ore calcite, (3) mineralized late-stage. (4) late-ore calcite from the Aishar deposit; (5) late-ore calcite from the Buchan deposit.

represents a new mineral type of epithermal ore mineralization.

It is highly probable that zones of finely disseminated Au-bearing sulfides are hosted in pre-Tertiary sedimentary sequences of the Kozuf–Arid district. Such an ore material is a potentially effective transitional source for ore deposits (Sidorov and Torvqvist, 2000; Volkov et al., 2004). In this case, the formation of gold mineralization at the Aishar deposit should be regarded as a result of regeneration and redeposition of Au-bearing zones of fine sulfide disseminations in the course of multiple tectono-magmatic reactivation of primary ore-bearing zones. This model is confirmed by the morphostructural data and results of isotopic and thermobarogeochemical studies discussed in this paper. The high Ti contents in ore can be explained by the proximity of the deposit to ophiolites of the Vardar Zone. Elevated Ti contents are assumed to be characteristic of mafic and ultramafic rocks (Filimonova and Chigrin, 2002). As in other areas (Volkov et al., 2004), carbonate–siliciclastic sequences enriched in As could have served as a source for this element.

The results obtained from the study of the Aishar deposit allow us to forecast Carlin-type ore mineralization in siliciclastic-carbonate sequences of the basement beneath Paleozoic, Mesozoic, and Quaternary volcanogenic belts and in adjacent zones of tectono-magmatic reactivation. In eastern Russia, such deposits
may be expected in the Jurassic and Devonian—Carboniferous carbonate sequences of the Kaud and Akimsh-kurgen uplifts in the Chukchi Peninsula, the cratonic Omolon Terrane in Magadan oblast, and the Kelyma Terrane in eastern Yakutia, which form the basement of the Okhotsk-Chukotka, Uyanda-Yasachnaya, Kedon, and East Sibote-Alin volcanic belts.

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REFERENCES


GEOLOGY OF ORE DEPOSITS

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15. S. Letopikov, Petroloji karakteristikis na vulkanjske kapi od kovanjske na mognjeni Alshar so pescevel osev't na izotopni na zlato (Mag. Teza, Sip, 1995).


31. A. V. Volkov and A. A. Sidorov, Unique Gold-Ore Districts in Chukchi Peninsula (SVKNIIL, Magadan, 2001) [In Russian].