

SEDIMENTARY-ROCK-HOSTED DISSEMINATED GOLD MINERALIZATION IN THE ALŠAR DISTRICT, MACEDONIA

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ABSTRACT

Disseminated Au-As-Sb-Tl-Hg mineralization in the Alšar district, Macedonia, is hosted in Triassic carbonate rocks, Tertiary interbedded volcanic tuff and dolomite, and Pliocene felsic tuffs. Hydrothermally altered, porphyritic, hypabyssal igneous rocks intrude both the Triassic and Tertiary rocks. Ore fluids followed major structural zones, high-angle faults and flat-lying stratigraphic features in the host rocks. Results from radiometric dating of the tuffs (<4.5–5.0 Ma) that host some of the Au-As-Sb-Tl-Hg mineralization place an upper limit on the age of that hydrothermal event and indicate that it is Pliocene in age. Hydrothermal fluids introduced large amounts of silica, iron and sulfur into, and removed calcium and magnesium from, the carbonate and volcanic rocks. These fluids also introduced arsenic, antimony, thallium, mercury, barium and gold, resulting in the formation of marcasite, pyrite, realgar, orpiment, stibnite, cinnabar, lorandite and various other Tl-bearing sulfosalt minerals, plus barite and micrometric to submicrometric particles of gold. Base-metal and silver concentrations are characteristically low, as is the case in the type locality for sedimentary-rock-hosted disseminated gold mineralization, the Carlin deposit, Nevada. Alšar is the first example of this type of precious metal mineralization to be described in Europe; it differs significantly from the typical base-metal- and silver-dominated Yugoslavian ore deposits.

Keywords: disseminated gold, sedimentary-rock-hosted, Au-As-Sb-Tl-Hg mineralization, Pliocene, realgar, stibnite, Tl-sulfosalts, Alšar, Macedonia.

SOMMAIRE

Nous signalons la présence d'une minéralisation à Au, As, Sb, Tl et Hg dans le district de Alšar, en Macédoine. Elle y est développée dans une séquence de roches carbonatées triassiques, ainsi que dans des tufs volcaniques et des dolomies tertiaires et des tufs felsiques pliocènes. Des roches ignées sub-volcaniques, porphyritiques et altérées recoupent le socle triassique et tertiaire. La phase fluide responsable a profité de zones structurales importantes, des failles à pendage abrupt et des structures stratigraphiques horizontales des roches hôtes. Les résultats d'une datation radiométrique des tufs minéralisés (<4.5–5.0 Ma) limitent l'âge de la minéralisation, qui serait donc pliocène. La circulation hydrothermale a mené à l'introduction de quantités importantes de silice, fer et soufre, et le lessivage de calcium et de magnésium des roches volcaniques et des carbonates. Elle a aussi impliqué les éléments As, Sb, Th, Hg, Ba et Au, et la formation de marcasite, pyrite, réalgar, orpiment, stibine, cinabre, lorandite et des sulfosels porteurs de Tl, en plus de baryte et de particules micrométriques à sub-micrométriques d'or. Les teneurs de métaux de base et d'argent sont faibles, tout comme dans les gisements d'or disséminé du type Carlin, au Nevada, où les roches hôtes sont sédimentaires. Alšar serait donc le premier exemple européen de ce type de minéralisation en métaux précieux, qui diffère sensiblement des gisements yougoslaves typiques, à dominance de métaux de base et d'argent.

(Traduit par la Rédaction)

Mots-clés: or disséminé, roche hôte sédimentaire, minéralisation en Au-As-Sb-Tl-Hg, pliocène, réalgar, stibine, sulfosels de thallium, Alšar, Macédoine.

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INTRODUCTION

The Alšar district is located in the Kozuf Mountains of southern Macedonia (Fig. 1), a republic in what was formerly Yugoslavia. The district was extensively mined from 1880 to 1908 for antimony (grade 2–4 wt. %), arsenic (1 wt. %) and thallium (Janković 1982).

A program of regional reconnaissance for gold was conducted in Macedonia and in other Yugoslavian republics by Nassau Limited in 1986. This work included geological and geochemical exploration of the Alšar district and resulted in the delineation of anomalous concentrations of gold (>1.0 g/t) in areas of arsenic, antimony and thallium mineralization,

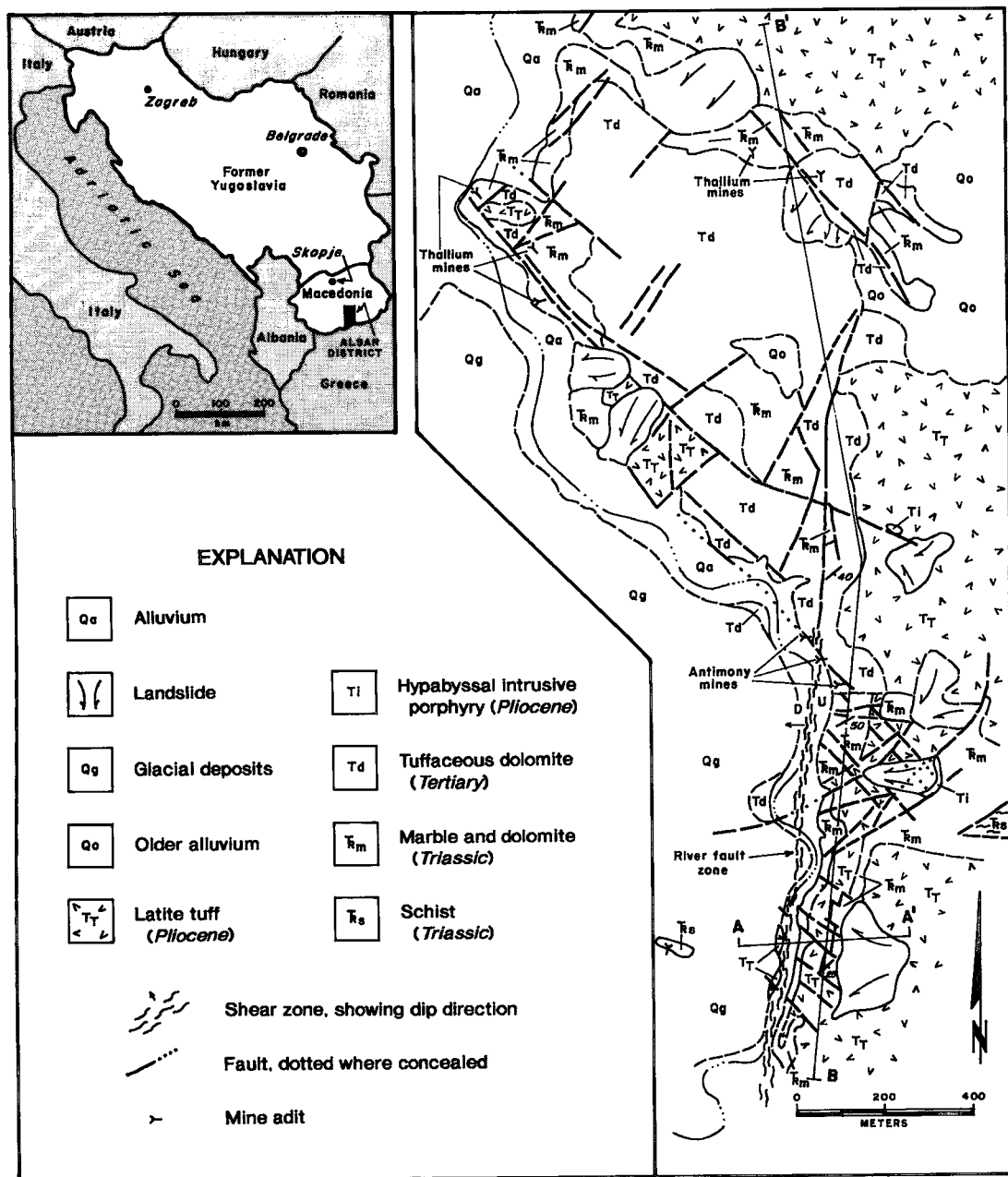


FIG. 1. Location and geological map of the Alšar mining district, Macedonia.

and also in widespread silicified zones. This paper presents the results of continuing studies of disseminated gold mineralization in the Alšar district by Nassau Ltd.

Initial results suggest that physical and chemical features of the mineralization at Alšar are similar to those that characterize many of the sedimentary-rock-hosted, disseminated (Carlin-type) gold deposits of the western U.S. (Radtke & Dickson 1974, Bagby & Berger 1985, Percival *et al.* 1988). We believe that Alšar is the first example of this type of gold mineralization to be recognized and described from Europe (Percival & Radtke 1990).

GEOLOGICAL SETTING

Regional geology

The Alšar district occurs within the Vardar Zone, a regionally extensive (700 × 80 km), north–northwest-trending tectonic suture marking the location of an extinct subduction zone (Arsovski & Ivanov 1977b). The zone is comprised of ophiolitic rocks and a complex *mélange* of metamorphosed tectonic blocks of Precambrian(?) through Mesozoic age in a cataclastic matrix. Tectonism was most intense during the Alpine Orogeny, but occurred from Upper Triassic to Paleogene time (Arsovski & Ivanov 1977b). Gabbro and granodiorite were intruded along and within the Vardar Zone during the Jurassic (Arsovski & Ivanov 1977a, Spray *et al.* 1984).

In Macedonia, the Vardar Zone separates two upper-greenschist-facies metamorphic complexes: 1) the Pelagonian Zone (to the west) and 2) the Serbo-Macedonian massif (to the east). Their borders are defined by tectonically emplaced masses of serpentinite, ophiolitic pillow lavas and metadiabase (Arsovski & Ivanov 1977b). Deposition of trench-related Triassic clastic and carbonate sediments in the Vardar Zone was followed by Cretaceous and Tertiary flysch, carbonate rocks and concluded by deposition of Neogene molasse in lacustrine basins (Arsovski & Ivanov 1977b).

Regionally extensive Pliocene (1.8–6.0 Ma) felsic to intermediate volcanic rocks of calc-alkaline to alkaline affinities covered much of the Kozuf Mountains as tuffs, flows and coeval subvolcanic intrusions (Kolios *et al.* 1980). Radiometric dating of the lower tuffs near Alšar yielded K–Ar biotite ages of 5.8 Ma (B. Boev, written comm., 1992). Several ring-radial features, suggestive of caldera-type volcanism, have been identified recently on Landsat imagery and by regional geological reconnaissance near the Alšar district (Janković & Jelenković 1990). An enrichment in large-ion lithophile elements and light rare-earth elements and high initial strontium ratios (0.7088–0.7090) in the tuffs suggest crustal contamination of a mantle-derived parent magma (Kolios *et al.* 1980, Boev 1990a, b).

Local geology

The western flank of the district is bordered by tectonically emplaced slivers of Jurassic mafic igneous rocks and serpentinite within a cataclastic matrix, typical of the Vardar Zone. Regional geological mapping by the Macedonian Geological Survey (1980) and detailed mapping by T. Percival indicate that the geology of the district is composed of two distinct chronostratigraphic units: 1) Mesozoic trench sediments, unconformably overlain by 2) Tertiary volcanic and carbonate rocks (Fig. 1).

The Mesozoic rocks include greenschist-facies marble, dolomite and minor amounts of schist, and are assigned a Triassic age by the Macedonian Geological Survey (1980). Marble is the most abundant pre-Tertiary rock (Fig. 1) and consists of gray-white to bluish gray, fine- to medium-grained equigranular calcite, with minor dispersed and interbedded detrital material. The dolomite is gray-white to tan, fine- to medium-grained and is locally recrystallized to dolomitic marble. Schist is exposed along the eastern margin of the district and is widely variable in composition; quartz–sericite, chloritic and graphitic schists are the most common.

The Tertiary unit directly above the unconformity is a massive gray-white to tan, fine-grained, micritic to sparry dolomite (Fig. 1). Variable proportions of water-laid volcanic ash and tuffaceous debris are dispersed throughout, and locally intercalated as beds within the dolomite, clearly demonstrating a volcano-sedimentary provenance. The dolomite probably was deposited in a fresh-water lacustrine basin, similar to dolomite described elsewhere in Yugoslavia (Ilich 1974, Fallick *et al.* 1991). These basins also contain dolomite and magnesite deposits of hydrothermal-sedimentary origin spatially associated with Tertiary felsic igneous rocks. Basin development occurred as a result of Miocene extensional tectonism in areas underlain by ultramafic and carbonate rocks (Ilich 1974, Fallick *et al.* 1991).

Tertiary (Pliocene) tuffaceous volcanic and volcanoclastic rocks overlie the dolomite and Mesozoic basement rocks. The lower tuff unit is dominantly latite in composition, with lesser amounts of andesite, trachyte and quartz latite. The latite is composed of light-colored ash, crystal and crystal–lithic tuff, and tuff breccia. Petrographic studies indicate that the tuffs contain varying amounts of sanidine, biotite, lesser quartz, hornblende and clinopyroxene phenocrysts in a gray aphanitic, crystalline and glassy groundmass.

In many areas these tuffs have undergone intense argillic alteration and locally are mineralized. The upper tuff unit is comprised of debris flows, felsic ash tuff and thin-bedded lacustrine volcanoclastic deposits. Hydrothermal alteration is weakly developed to nonexistent in the upper unit.

A hypabyssal intrusion cuts across both the Triassic and Tertiary rocks and is exposed as small outcrops (Fig. 1) and in underground workings in the antimony mines. The intrusion is porphyritic and contains phenocrysts of quartz, variably altered sanidine, biotite, hornblende and, rarely, clinopyroxene in a pyrite-bearing, fine-grained crystalline groundmass. Pervasive hydrothermal alteration throughout the district makes identification of rock types difficult in many areas. Several subvolcanic intrusions ranging in composition from latite to andesite occur within 1 to 3 km south and west of the intense district-wide envelope of hydrothermal alteration. These intrusions are weathered or weakly altered and exhibit textural and mineralogical features, including disseminated pyrite mineralization, similar to features of intrusive rocks at Alšar.

Structural geology

Three major steeply dipping sets of structures with distinct trends occur in the Alšar district: 1) north, 2) northwest (N40–55W), and 3) northeast (N35–50E) (Fig. 1). The structures are defined by sheared and tectonically brecciated wallrocks, gouge zones, juxtaposed stratigraphic units, topographic discontinuities, variations in intensity of hydrothermal alteration, and sulfide mineral deposition.

The river, south and immediately west of the antimony mines (Fig. 1), is underlain by a major north-trending structural zone (River Fault Zone). This zone is defined by a major topographic discontinuity between extensively altered and mineralized cliff-like outcrops on the east, in contrast to glacial-till-covered rolling hills of low relief on the west. Because of size, amount of movement, pervasive gouge and sheared matrix, and overall north–south trend, this structural zone probably is related to and formed by strike-slip movement along the Vardar zone (Smith & Spray 1984). The northwest- and northeast-trending structures formed as dilational conjugate sets of faults in response to the north–south shearing. These faults are the locus of intense fracturing and brecciation distal to the main shear-zone and served as open spaces for movement of hydrothermal fluids through reactive carbonate and tuffaceous rocks.

ALTERATION

Hydrothermal alteration features are developed in each of the rock units and are aerially extensive (1 × 2 km) throughout the Alšar district. Intensity of alteration is locally variable and ranges from weak to intense. Types of alteration include: 1) decalcification, 2) silicification, 3) argillization, 4) veining, 5) dolomitization and 6) supergene alteration.

The hydrothermal activity apparently occurred after deposition of the lowermost tuffs and emplacement of

the subvolcanic intrusions, but prior to the deposition of the unaltered tuffaceous volcanic rocks and lacustrine sediments that overlie the altered and mineralized rocks. The unaltered tuffs and sediments are exposed on the northern and southern margins of the Alšar district.

Decalcification

The process of hypogene alteration characteristic of sedimentary-rock-hosted precious metal deposits invariably begins with decalcification of the carbonate-rich host rocks (Bagby & Berger 1985, Percival *et al.* 1988). Decalcification involves the removal of calcite and dolomite from the sedimentary host-rocks by weakly acidic solutions (in a pyrite-stable field), resulting in increased porosity and permeability. Carbonate removal is accompanied by deposition of replacement silica and the formation of mineral assemblages typical of argillic alteration.

At Alšar, decalcification affected both the Triassic carbonate rocks and the Tertiary dolomitic rocks. In both units, intense silicification and argillic alteration are common and exhibit a lateral transition through variably bleached and partially decalcified rocks to fresh unaltered rock.

Sanding, a second style of decalcification that lacks accompanying silicification, is a common feature developed in the Tertiary dolomite. Sanded dolomite exhibits varying degrees of competence and commonly retains primary textural features. Intragranular corrosion by hydrothermal fluids removed the fine-grained matrix, leaving predominantly granular dolomite sand, disseminated iron oxides, iron oxide stain, and crusts and stains of an unidentified greenish to yellow secondary mineral. Similar textures have been described in altered dolomite at the Windfall sedimentary-rock-hosted gold deposit in eastern Nevada (Nolan 1962).

Silicification

Extensive hydrothermal silicification occurs in both pre-Tertiary and Tertiary rocks within and south of the antimony deposits at Alšar. The intensity of silicification varies from weak to total replacement (jasperoid) in carbonate rocks of all types. Most of the silicification in dolomitic rocks is very intense, reflecting their reactivity toward this type of alteration.

The silicified rocks are products of introduction of hydrothermal silica and replacement within and along faults and fracture zones of varying orientations (Fig. 1). The silica-bearing fluids also moved from the tectonically prepared zones outward into stratigraphic horizons with favorable permeabilities and chemical properties in both pre-Tertiary and Tertiary carbonate and volcanic rocks. End products include both weak pervasive silicification and micro-scale stockworks in fracture zones.

The jasperoids are gray to black in color and consist of fine-grained, dense microcrystalline quartz that thoroughly masks the textures of the carbonate host-rock. Features such as breccia textures, quartz veins and quartz microveins are common. Disseminated sulfides (pyrite, marcasite and rare arsenopyrite) occur within massive silica, whereas the more coarsely crystalline sulfides (stibnite and realgar) and their oxidation products (*e.g.*, stibiconite, cervantite, pararealgar, *etc.*) occur within the abundant vugs, open spaces and between breccia fragments. The silicified rocks and jasperoids at Alšar are similar to those that formed by hydrothermal alteration in sedimentary-rock-hosted disseminated precious metal deposits of the western U.S., as described by numerous authors, including Bagby & Berger (1985), Bakken & Einaudi (1986) and Percival *et al.* (1988).

Although pervasive development of jasperoid (especially in dolomitic rocks) is common in the Alšar district, much larger volumes of rocks of all types are only weakly to moderately silicified. These rocks are lighter colored and contain varying proportions of host rock affected by argillic alteration mixed with introduced silica. This type of alteration is most common in the tuffaceous volcanic rocks; in both the carbonate horizons and the tuffaceous volcanic rocks, relict host-rock textures are commonly preserved. Quartz microveinlets are ubiquitous. Sparsely distributed vugs are lined with drusy quartz and iron oxides, minor amounts of disseminated pyrite and marcasite, and rare crystals of stibnite and realgar. The quantity of metallic minerals in these less intensely silicified rocks usually is markedly less than that found in the jasperoids.

Argillic and sericitic alteration

Both volcanic and sedimentary rocks are altered to argillic and sericitic assemblages. The alteration is aerially extensive and is of varying intensity. Tuffaceous rocks are intensely altered close to faults and silicified zones, and the argillic and sericitic alteration in the tuffs is more widespread and intense than it is in the sedimentary rocks.

The moderately to intensely argillized rocks consist of varying proportions of fine-grained light-colored clays, sericite, quartz, iron oxides (limonite > hematite), jarosite, gypsum, calcite, siderite, sulfides (marcasite, pyrite, realgar, orpiment), a variety of thallium-bearing sulfosalt minerals (Table 1), and unidentified secondary minerals containing Fe + As + Tl.

Detailed studies to determine the mineralogical composition of the clay-bearing suite(s) of alteration minerals are in progress. Preliminary results of X-ray-diffraction studies of alteration assemblages suggest that the rocks affected by argillic alteration consist of varying proportions of the following minerals:

TABLE 1. HYPOGENE SULFIDE AND SULFOSALT MINERALS, ALŠAR DISTRICT, MACEDONIA

Sulfide mineral	Composition	Abundance ¹	Method ²
Arsenopyrite	FeAsS	C	B, C
Bravoite	(Ni, Fe)S ₂	R	S.J.
Cinnabar	HgS	C	B, C
Marcasite	FeS ₂	A	A, B, C
Orpiment	As ₂ S ₃	A	A, B, C
Petrite	Ag ₂ AsTe ₂	R	D
Pyrite	FeS ₂	A	A, B, C, D
Realgar	As ₂ S ₃	A	A, B, C
Stibnite	Sb ₂ S ₃	A	A, B
Bornandite*	TlAs ₂ S ₆	R	
Lorandite*	TlAs ₂ S ₆	C	A, B, C
Parguerite*	Tl(Sb, As) ₂ S ₆	R	
Pickersillite*	TlFeS ₂ S ₃	R	
Ragunite*	TlFeS ₂	R	
Rebunite*	Tl ₂ Sb ₂ As ₂ S ₂₂	R	
Simonite*	TlHgAs ₂ S ₆	R	
Vrbaitte*	Tl ₂ Hg ₂ Sb ₂ As ₂ S ₂₀	R	C

* Type locality: Alšar District, Macedonia; typical occurrence is within the thallium ore and arsenian gold ore.

1. Relative abundance of minerals: A: Abundant, C: Common, R: Rare.

2. Methods used to identify the sulfide and sulfosalt minerals: A: megascopically recognizable, in hand specimen; B: recognized in polished sections and polished thin sections; C: X-ray diffraction; D: electron-microprobe analysis. S.J.: S. Janković, written communication, 1991.

kaolinite, sericite, illite-group minerals (including celadonite), hydromicas, pyrophyllite, subordinate chlorite, ephesite (Na, Li mica) and relict(?) biotite.

Zones of argillic alteration at Alšar typically envelop hydrothermally silicified zones in both vertical and lateral directions. The intensity of argillic alteration decreases, and the mineral assemblages vary, with increasing distance from the silicified rocks. Intensely argillized kaolinite-rich rocks (*e.g.*, quartz + pyrophyllite + kaolinite + sericite, quartz + kaolinite ± calcite and quartz + kaolinite + illite) occur closest to silicified and sulfide-mineralized rocks. These assemblages are bordered by and variably mixed with sericite-rich zones comprised of quartz + sericite + pyrite (± illite + kaolinite) associated with realgar and marcasite. These zones in turn grade outward into weakly to moderately "argillic-altered" rocks containing assemblages of quartz + illite + calcite + dolomite and quartz + montmorillonite + chlorite ± hydrobiotite (in tuffaceous rocks) over distances of tens of meters. Similar assemblages of alteration minerals and spatial relations occur in Carlin-type deposits of the western U.S. (Radtke & Dickson 1974, Percival *et al.* 1988, Berger & Bagby 1991).

Veins

Veins are relatively uncommon and sparse in the Alšar district. Quartz veins are most abundant within the jasperoids and silicified rocks and occur as small (<1–5 mm) gray or colorless veins or microveinlets. Thicker veins typically contain minor amounts of dis-

seminated pyrite, marcasite, crystals of stibnite and realgar and their alteration products, formed by supergene oxidation. Veins greater than 0.5 cm wide are rare. Some late-formed quartz veins (1–3 mm) are banded, contain crystals of barite, and locally have open spaces lined with drusy intergrown quartz and barite, and crystals of gypsum and calcite. Late-formed veins of calcite are typically less than 1 cm wide and may contain crystals of stibnite, realgar and barite.

Dolomitization

Dolomitized zones within the Triassic marble show a general spatial association with the hydrothermal mineralization. However, the dolomitization is weakly developed, and the dolomite erratically distributed. The dolomitized rocks are typically lighter colored than the host marble, and are locally mottled, fine-grained, non-layered, highly jointed, contain manganese and iron oxides, and grade into undolomitized marble. Whether the dolomitization is of hydrothermal origin and associated with the mineralization event, or is the result of removal of calcium carbonate from leached dolomitic rocks by low-pH hydrothermal fluids, is unknown.

Supergene alteration

Features of supergene alteration are widespread throughout the entire Alšar district. They include: 1) oxidation of pyrite and marcasite to secondary iron oxides and sulfates, 2) acid-leaching oxidation and argillic alteration from the breakdown of iron sulfide minerals, and 3) weathering of igneous and sedimentary rocks to form secondary clay minerals typical of wet and humid environments.

MINERALIZATION

The four main types of mineralization in the district are: 1) stibnite-bearing jasperoid gold ore (+ Au + As + Tl), 2) siliceous gold ore (+ Au + Sb + As), 3) arsenian gold ore (+ Tl + Hg + Sb + Au), and 4) thallium ore. Elemental associations and hypogene sulfide minerals and assemblages of alteration minerals in these ores are similar in many ways to those found in sedimentary-rock-hosted disseminated precious metal deposits of the western U.S. (Radtke & Dickson 1974, Bagby & Berger 1985, Percival *et al.* 1988). The various types of ores at Alšar contain both common and rare sulfide and sulfosalt minerals of the As–Sb–Tl–Hg suite of elements. Identifications of these and other minerals were made by a combination of plane- and reflected-light microscopy, X-ray diffraction, electron microprobe and SEM techniques. Rieck (1993) illustrated and described all the minerals that have made this a classic locality.

Stibnite-bearing jasperoid gold ore

Stibnite-bearing jasperoids at Alšar were mined extensively for their antimony content (Janković 1979, 1982). The jasperoids are comprised of dark gray to black, fine-grained, mosaic-textured microcrystalline quartz. Most of the jasperoids are fractured or brecciated and contain veinlets and irregular masses of coarser crystalline gray to white quartz. The matrix of microcrystalline quartz contains finely disseminated sulfides (typically 1–5%), dispersed fine-grained sericite and silicified host-rock clasts containing sericite and sulfides. Pyrite, commonly the most abundant sulfide, occurs as fine (<0.5 mm) subhedral disseminated grains, larger (>0.5 mm) subhedral to euhedral crystals, aggregates of coarse-grained crystals and as pyrite and quartz + pyrite veinlets that cut across the groundmass of microcrystalline quartz. Sparse amounts of finely crystalline arsenopyrite, marcasite and stibnite are also present in the groundmass. Sparse minute anhedral grains of petzite occur encased in pyrite overgrowths.

The main stage of jasperoid formation with precipitation of silica plus small amounts of sulfide minerals preceded a later-stage event characterized by deposition of large amounts of sulfide minerals. This later hydrothermal event resulted in coarse-grained sulfide minerals infilling and lining open spaces in breccia and fracture zones within the bodies of microcrystalline quartz. Marcasite occurs in banded or layered veins and framboidal masses and can represent up to 40 vol.% of some jasperoid ores.

Stibnite, like marcasite, is dominantly a late-formed mineral. It occurs in irregularly shaped fine to coarse crystalline masses, as acicular crystals filling fractures and cementing breccia fragments, and as overgrowths on quartz crystals lining open vugs. Jasperoids commonly contain 5–20 vol.% stibnite. Realgar occurs as crystals and crystalline aggregates filling vugs and open fractures and as an overgrowth on stibnite and marcasite. These features indicate that realgar in the jasperoids formed very late in the paragenesis. The jasperoids commonly contain 1 to 3 g/t gold, and as much as 20 g/t in zones that contain more than 1% antimony (Table 2).

Siliceous gold ore

Variably silicified sedimentary rocks and tuffs occur south of the antimony adits and form a resistant ridge bordering the east side of the river (Fig. 2). The tuffs and underlying marble were weakly to moderately silicified by the introduction of microcrystalline quartz and contain variable amounts of clay minerals and sericite. Tectonic brecciation and micro-stockwork veins of quartz are common.

The abundance of all sulfide minerals is less (typically <1–3 vol.%) than that in mineralized jasperoids

TABLE 2. CHEMICAL ANALYSES OF FRESH, ALTERED AND MINERALIZED SEDIMENTARY AND IGNEOUS ROCKS, ALSAR DISTRICT, MACEDONIA

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	17	19
Major Element Concentrations in Weight Percent																			
SiO ₂	2.06	0.94	61.80	56.50	57.60	3.30	61.70	23.90	20.40	78.90	39.30	74.70	77.20	91.10	59.00	29.90	48.60	83.90	64.40
TiO ₂	0.03	0.02	0.35	0.48	0.67	0.06	0.73	0.07	0.14	0.21	0.02	0.05	0.07	0.10	0.08	0.06	0.30	0.10	0.42
Al ₂ O ₃	1.24	2.13	15.60	16.00	16.50	1.00	11.90	1.70	4.06	4.55	0.61	2.41	4.55	2.23	1.60	1.53	7.96	1.85	11.60
Fe ₂ O ₃	0.21	0.26	3.37	4.13	5.48	15.04	12.24	1.37	1.50	2.57	4.92	10.04	3.36	1.13	20.10	3.34	3.42	5.29	5.71
FeO	0.13	<0.02	1.01	1.01	2.08	0.05	0.41	0.30	0.56	1	1	1.58	0.94	0.64	1.26	1	0.93	0.50	0.55
MnO	0.02	0.03	0.04	0.09	0.08	0.08	0.05	0.06	0.08	<0.01	0.03	0.02	0.02	0.01	0.03	0.03	0.04	0.01	0.01
MgO	1.50	19.80	1.16	1.71	3.24	15.30	0.90	15.60	13.50	0.31	8.47	0.14	0.05	0.10	0.16	6.10	5.54	0.15	0.51
CaO	51.40	30.20	2.99	5.70	5.46	26.10	0.45	24.10	21.00	0.63	13.50	0.53	0.35	0.15	1.34	12.30	7.94	0.15	2.22
Na ₂ O	0.06	0.07	3.24	2.16	3.85	0.02	0.06	<0.01	<0.01	0.02	0.03	0.03	<0.01	0.03	0.01	0.10	0.03	0.02	0.06
K ₂ O	0.12	0.10	4.95	3.85	4.77	0.09	3.12	0.39	0.81	1.15	0.08	0.24	0.24	0.51	0.39	0.35	1.77	0.63	1.79
P ₂ O ₅	0.19	0.17	0.24	0.28	0.45	0.42	0.23	0.23	0.27	0.15	0.21	0.18	0.17	0.19	0.42	0.24	0.32	0.22	0.12
LOI	42.70	46.14	5.08	6.78	1.78	37.73	6.69	31.98	35.76	2.99	16.23	8.55	15.61	2.31	14.20	14.65	13.10	4.32	9.65
Total	99.53	99.86	98.82	97.68	99.88	99.19	98.52	99.73	98.14	91.48	83.40	98.66	99.26	98.57	98.73	68.60	91.41	97.20	97.09

Trace Element Abundances in Parts Per Million Except gold in Parts Per Billion

Au	<5	<5	<5	<5	<5	23	22	138	10	1266	5817	11521	21908	2646	2227	4998	81	6037	596
Ag	0.3	<0.2	<0.2	<0.2	<0.2	0.9	0.7	0.5	0.5	<0.2	0.6	0.8	0.3	1.9	1.2	0.4	0.5	3.6	0.4
As	<5	24	<5	8	5300	2.20%	1980	2.29%	2800	7800	2600	1672	946	1.33%	501	8.10%	2800	2.76%	
Ba	48	23	1170	1460	1690	29	458	26	38	139	25	108	59	2810	35	45	300	171	803
Bi	<5	7	<5	<5	<5	<5	<5	7	6	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Co	<1	<1	9	8	11	19	51	2	5	6	4	55	11	5	15	4	16	<1	
Cr	2	2	135	37	71	8	83	18	17	144	78	282	240	261	176	35	41	187	62
Cu	5	4	19	14	53	9	64	5	33	25	5	10	4	10	10	7	25	7	9
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	4.33	3.25	3.93	5.86	7.54	21.02	24.52	160.	10.09	30.80	60.0	3.51	10.98	5.66
Mo	<1	<1	<1	<1	2	12	8	1	<1	3	21	62	57	15	8	8	1	13	1
Ni	1	1	109	8	14	71	196	8	23	34	<1	184	42	15	30	<1	101	5	17
Pb	2	<2	7	40	13	4	24	8	12	12	<2	3	7	8	8	<2	18	9	48
Rb	<1	<1	258	173	195	2	201	35	66	80	8	21	24	66	25	11	182	59	143
Sb	<5	<5	<5	8	<5	31	225	897	978	5.50%	10.6%	2900	4300	345	4400	12.2%	231	1279	421
Se	<5	<5	6	<5	7	7	7	<5	9	<5	113	15	12	<5	39.0	<5	12	15	10
Sr	232	98	1155	928	1529	45	25	66	42	14	20	9	9	56	9	32	36	53	33
Te	<0.2	<0.2	<0.2	<0.2	<0.2	0.8	<0.2	6.1	2.0	8.4	2.8	10.4	5.5	13.8	34.0	3.4	<0.2	19	16
Tl	0.3	0.4	1.8	2.6	1.4	390	77	690	730	53	950	210	420	41	6900	140	95	170	420
W	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Y	10	1	12	17	20	14	19	<1	5	<1	<1	<1	<1	3	<1	<1	7	1	10
Zn	8	6	50	42	58	23	100	9	19	10	12	9	6	6	32	20	86	12	21
Zr	5	10	149	149	256	14	130	21	28	25	<1	17	20	46	10	<1	59	31	90

Sample descriptions: 1. Triassic marble; 2. Tertiary dolomite; 3. Pliocene tuff; 4. Pliocene tuff breccia; 5. Pliocene subvolcanic intrusion; 6. Argillite altered dolomite; 7. Argillite altered tuff; 8. Argillite altered and silicified marble; 9. Argillite altered and silicified tuff; 10. Argillite altered and silicified tuff; 11. Stibnite-bearing jasperoid; 12. Silicified marble gold ore; 13. Silicified dolomite gold ore; 14. Silicified tuff gold ore; 15. Arsenian gold ore; 16. Antimony ore; 17. Arsenic ore; 18. Mineralized unconformity (siliceous) ore; 19. Altered-mineral subvolcanic intrusion. Notes: Analyses by Bondar-Clegg Inc., Sparks, Nevada, U.S.A. Major oxides by ICP methods except FeO (titrimetric). Au by fire assay method with atomic absorption finish. Hg, Te and Tl by atomic absorption method. Ba, Rb, Sr, Y and Zr by X-ray fluorescence method. All other elements by ICP method.

and consists primarily of finely disseminated and crystallized pyrite with lesser stibnite and minor marcasite. Acicular stibnite and minor amounts of realgar line open fractures, breccia zones, vugs and voids. Limonite, jarosite and secondary antimony oxide minerals (including stibiconite) are common. Gold grades vary from 0.5 to 10 g/t (Table 2).

Arsenian gold ore

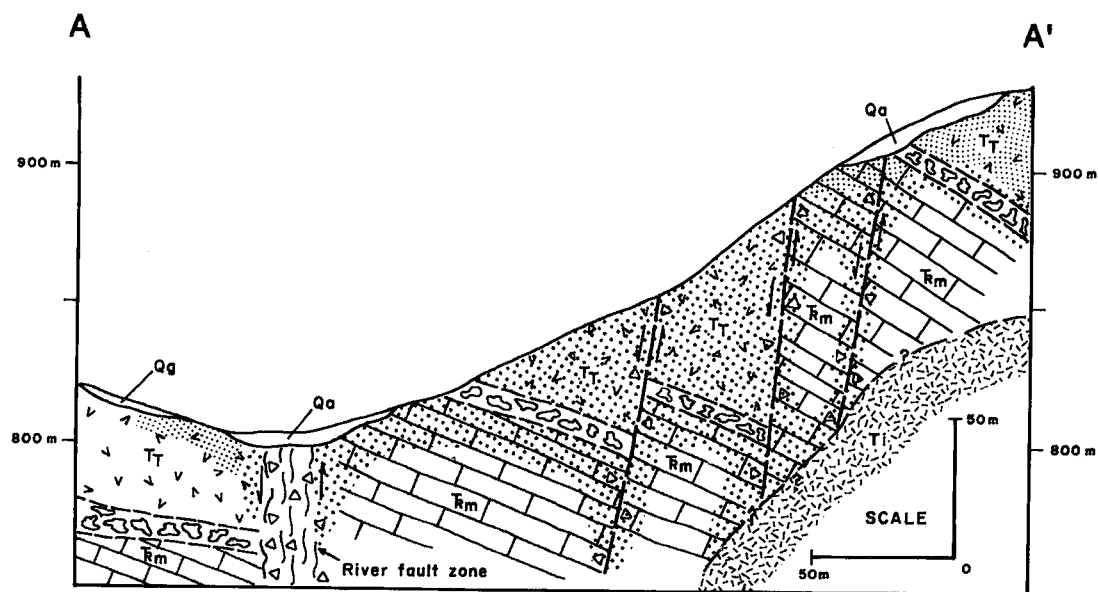
Arsenian gold ore occurs primarily in argillized tuffs, Tertiary dolomite, and rarely in Triassic carbonate rocks. The best exposures are in underground mine workings and in outcrops along the River Fault Zone (Fig. 2). This type of mineralization usually occurs in distal areas with respect to zones of hydrothermal silica. Host rocks are pervasively altered to fine-grained clay minerals and sericite mixed with limonite, jarosite, manganese oxides, gypsum and minor hydrothermal quartz. Sulfides include finely disseminated marcasite, lesser pyrite, realgar, plus sparse

amounts of orpiment, stibnite and minor thallium-bearing sulfosalts minerals. Lorandite is probably the most common Tl-bearing sulfosalt phase (Ivanov 1965, Pavicević 1988). Sulfide minerals typically comprise greater than 10 vol.% (up to 50 vol.%) of the arsenian ores.

Supergene alteration has transformed hypogene marcasite and pyrite into mixtures of yellowish, cream and greenish sulfates including melanterite, copiapite, rhomboclase(?), among other phases, and altered realgar to pararealgar, pharmacosiderite and scorodite. The gold content is usually lower (<1 to 3 g/t) than that in the siliceous ores. However, in areas of intense silicification, both primary and oxidized arsenian ores commonly contain substantial amounts of gold (3–12 g/t: unpubl. data, Nassau Ltd.).

Thallium ore

High concentrations of thallium (up to 2 wt.% Tl) occur in strongly altered carbonate and tuffaceous



EXPLANATION

	Alluvium (Quaternary)		Latite tuff (Pliocene)
	Glacial deposits (Quaternary)		Hypabyssal intrusive porphyry (Pliocene)
	Argillic alteration		Basal unconformity
	Silicification		Marble and dolomite (Triassic)
Fault, showing relative movement and brecciation			

FIG. 2. East-west cross section through the southern Alšar district.

rocks in the northern part of the district and account for a thallium resource of 1×10^5 tonnes of material with an overall grade of 0.1 wt.% Tl (Janković 1982). The ores are hosted in light-colored, friable "argillic altered" dolomitic carbonate rock and contain mixtures of orpiment, realgar, pyrite, marcasite, lorandite and rare thallium-bearing sulfosalt minerals including vrbaite, picopaulite, rebulite, simonite, bernardite,

raguinite and parapirotite (Percival & Radtke 1993). Sulfide and sulfosalt minerals (>5 to 30 vol.%) are disseminated throughout the rock, fill fractures, joints and open space between breccia fragments and, locally, massively replace the rock.

The mineralization is located along or near contact zones with the subvolcanic intrusive rocks. Arsenic and thallium commonly range from 0.02 to 1.25 wt.%,

and arsenic concentrations of up to 5 wt.% occur locally (unpubl. data, Nassau Ltd.). The concentrations of antimony usually range from 10 to 300 ppm, and those of mercury, from <1 to 200 ppm. The thallium ores analyzed to date contain only traces of gold (unpubl. data, Nassau Ltd.).

Controls on ore deposition

Structural and stratigraphic features combine to provide the primary controls of hydrothermal deposition of ore in the Alšar district. Structural features served as channelways for the movement of the hydrothermal fluids into reactive environments. Fault-induced brecciation, fracturing, shearing and regional tectonic disruption of the stratigraphic units significantly increased rock porosity and permeability, allowing fluids to permeate through large volumes of rock. The presence of stibnite-bearing jasperoids at fault intersections indicates that intersections of structures served to localize the mineralization.

Stratigraphic controls of mineralization were, in part, dependent upon structural controls. The massive, relatively impermeable and nonporous carbonate rocks are poor hosts for mineralization, except in structurally prepared zones. In contrast, extensive silicification and jasperoid gold-antimony mineralization (Table 2) occur along the basal unconformity and extend into overlying Tertiary rocks (Fig. 2). Porous and permeable clastic debris along the unconformity were silicified and mineralized to form a stratiform zone of mineralization. Highly permeable and porous ash and crystal tuffs and the reactive tuffaceous dolomitic rocks above the unconformity are extensively silicified and mineralized over large areas at and south of the antimony adits (Fig. 1).

GEOCHEMISTRY

Results of whole-rock and trace-element analyses of samples representing each of the major types of altered and mineralized rock and fresh host-rock are presented in Table 2. These samples were chosen from a suite of approximately 1500 rock samples collected from surface outcrops and underground workings, all of which had been previously analyzed for gold plus As, Sb, Hg, and Tl. The samples that were selected were re-analyzed for eleven major and minor components (shown as oxides) and twenty-three other elements plus gold.

Bulk-rock chemistry

Results of whole-rock chemical analyses of five specimens of unaltered host-rock and fourteen specimens of hydrothermally altered and mineralized rock are presented in Table 2. The data were used to calculate the relative gains and losses of major components

in the altered rocks using the "isocon" method of Grant (1986).

Three types of isocon diagrams were constructed using the Alšar chemical data (Table 2): 1) best-fit isocon among all chemical components; 2) aluminum (Al_2O_3); and 3) titanium (TiO_2) as immobile components. The titanium diagram provided the best reference isocon with respect to determinations of the chemical gains or losses for the Alšar samples, with changes in bulk composition occurring within acceptable limits among the progressively more hydrothermally altered rock-types. This is in good agreement with mass-balance studies by Kuehn (1989), Bakken & Einaudi (1989), and Kuehn & Rose (1992) at the Carlin gold deposit, Nevada. These investigators established titanium as an immobile element during hydrothermal alteration and mineralization.

Table 3 shows chemical gains and losses calculated from the isocon diagram treating Ti as an immobile element for two samples of altered marble, three samples of altered dolomite, and three samples of altered tuff. The content of SiO_2 and Fe_2O_3 increased in most of the samples of carbonate and tuffaceous parent-rocks. The brecciated carbonate rocks were an ideal host for hydrothermal replacement, resulting in substantial increases with respect to SiO_2 (to 27×) and Fe_2O_3 (to 18×). Conversely, CaO, CO_2 (high LOI in carbonates), and MgO (in dolomite and tuff) were strongly depleted.

Although only a small number of samples were analyzed, the results suggest that Na, Al, P, K and Mn were weakly to strongly depleted in dolomite and tuff, and were enriched or unchanged in altered marble (Table 3). The marble exhibits a significant increase in Mg, which corresponds to the variable dolomitic component of the marble, as documented in the field; however, this increase in Mg may have resulted from acid leaching of Ca from a dolomitic marble parent-rock, as previously discussed. Regardless of the original composition of the parent-rock (carbonate or tuff), in most cases the same suites of major elements were added and removed from rocks that have undergone similar types of hydrothermal alteration.

Detailed geological and chemical studies of the Carlin deposit, where gold mineralization is hosted in silty dolomite (or dolomitic siltstone), were published by Dickson *et al.* (1979), Radtke *et al.* (1980), and Radtke (1985). Results of these studies suggest that varying amounts of SiO_2 , total Fe, Al, and K, were introduced, and Ca, Mg and CO_2 were removed from the parent rocks during hydrothermal alteration and mineralization. However, results from more recent studies at Carlin by Bakken (1990) and Kuehn & Rose (1992) indicate that the apparent enrichments of Al, Fe, and K are due to volume losses of up to 50% as a result of carbonate removal during the hydrothermal process. Their calculations indicate that Ti and Al remain constant in all altered zones, and therefore

TABLE 3. RELATIVE ADDITIONS AND DEPLETIONS OF OXIDES USING CONSTANT TITANIUM IN HYDROTHERMALLY ALTERED AND MINERALIZED ROCKS COMPARED TO THEIR UNALTERED PARENT ROCKS, ALŠAR DISTRICT, MACEDONIA

Oxide	Marble		Dolomite			Tuff		
	A	B	A	B	C	A	B	C
SiO ₂	3.98	27.54	0.17	2.10	22.46	-0.52	1.12	4.16
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	-0.41	0.26	-0.84	-0.73	-0.39	-0.97	-0.51	-0.50
ΣFe	-0.91	18.53	17.56	0.12	3.64	0.36	-0.04	0.43
MnO	0.28	1.25	-0.11	-0.60	-0.80	-0.40	-0.58	-0.22
MgO	3.45	7.47	-0.74	-0.90	-0.99	-0.63	-0.55	-0.70
CaO	-0.80	-0.60	-0.71	-0.90	-0.99	-0.92	-0.92	-0.69
Na ₂ O	-0.92	-0.25	-0.90	-0.98	-0.96	-0.99	-0.98	-0.45
K ₂ O	0.39	0.00	-0.70	0.21	-0.31	-0.70	-0.61	-0.64
P ₂ O ₅	-0.48	0.66	-0.17	-0.76	-0.71	-0.54	-0.04	1.77

Fe as Fe₂O₃ Note: Changes are given in percent (e.g. 0.12 = 12% gain) and were calculated using the isocon method of Grant (1986).

Rock samples used for the above calculations are given below and sample numbers correspond to those in Table 2.

Marble	Dolomite	Tuffs
A. Unaltered (#1) vs. altered (#8)	A. Unaltered (#2) vs. altered (#6)	A. Unaltered (#3) vs. altered (#7)
B. Unaltered (#1) vs. altered (#11)	B. Unaltered (#2) vs. altered (#9)	B. Unaltered (#3) vs. altered (#10)
	C. Unaltered (#2) vs. altered (#13)	C. Unaltered (#3) vs. altered (#14)

were immobile, and that Ca, CO₂ and Mg were strongly depleted (-30 to -100%) and K and Fe were weakly (-10%) depleted. Silica exhibits a weak depletion (-10 to -20%) in the weakly to moderately altered zones, but was strongly (+40%) enriched in the highly altered zones.

Our results suggest that the changes in major-element chemistry in carbonate rocks at Alšar are generally similar to those at Carlin. Differences may be expected because two different hydrothermal systems reacted with compositionally different host-rocks at Carlin and Alšar.

TRACE ELEMENTS

Mineralized samples of all three rock types are strongly enriched in Au, As, Sb, Hg, Tl, and Ba relative to abundances of these elements in the unaltered parent-rocks (Table 2). These elements were introduced by the hydrothermal fluids and were deposited primarily as stibnite – realgar – orpiment – arsenopyrite – lorandite – cinnabar in association with quartz, pyrite and marcasite. In the assemblage of hypogene minerals, arsenic occurs as realgar, orpiment and arsenopyrite, antimony as stibnite, mercury as cinnabar, and thallium as lorandite and other but less

abundant Tl–As–Sb–Hg–Fe sulfosalt minerals. Barium occurs as barite, which was deposited late in the mineral paragenesis. Contents of base metals (Cu, Pb, Zn and Mo) and Ag are low in most of the samples of altered and mineralized rocks (Table 2). These mineralogical and chemical features are similar to those accompanying ore deposition in sedimentary-rock-hosted disseminated precious metal deposits of the western U.S. (Radtke & Dickson 1974, Bagby & Berger 1985, Percival *et al.* 1988).

Some of the mineralized samples at Alšar contain anomalous amounts of Te, Se, F, Bi, Cd, Mo and Zn. Thirty samples containing more than 3 ppm Au and not included in Table 2 were analyzed by atomic absorption methods for selected elements typical of igneous-magmatic environments. Results from these analyses showed Bi (20 to 85 ppm), Cd (5 to 15 ppm), Mo (1 to 560 ppm), Zn (5 to 615 ppm) and F (33 to 1265 ppm).

Results of chemical analyses of mineral separates of stibnite, realgar and orpiment (Table 4) indicate that these three sulfide minerals can contain significant amounts of Tl, As, Au, Te and Hg (stibnite) and Tl, Sb, Au, Te, and Hg (orpiment and realgar). Similar elemental associations among arsenic and antimony sulfide minerals have been reported from the Carlin

TABLE 4. CHEMICAL DATA ON HYPOGENE ORE MINERALS FROM THE ALŠAR DISTRICT, MACEDONIA

	1	2	3	4	5	6	7	8	9	10
Au	479	345	184	81	549	1240	14	61	125	12
Ag	<0.2	3.9	<0.2	<0.2	<0.2	1.0	<0.2	<0.2	<0.2	<0.2
As	313	84	331	135	153	170	M	M	M	M
Bi	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Co	1	7	7	<1	<1	4	<1	<1	<1	<1
Cr	15	74	24	33	17	40	19	1	1	<1
Cu	7	152	88	2	2	5	3	3	1	<1
Fe(%)	0.23	0.67	0.34	0.08	0.35	0.18	0.40	1.55	0.21	0.05
Hg	2.22	16.8	3.48	1.82	2.54	2.91	4.62	0.86	3.76	15.64
Mn	25	165	1	2	3	145	28	9	31	32
Mo	3	2	9	2	10	4	<1	1	<1	<1
Ni	<1	<1	94	<1	<1	<1	1	<1	3	2
Pb	<2	<2	<2	<2	<2	<2	<2	5	<2	<2
Sb	M	M	M	M	M	M	>2000	>2000	625	234
Te	14.5	>100	5.8	<0.2	<0.2	55.6	<0.2	36.0	12.4	<0.2
Tl	100	70	>100	6	45	>100	15	38	75	>100
W	22	21	<20	24	23	<20	<20	<20	<20	<20
Zn	12	29	34	2	6	23	17	4	2	2

Analyses by Bondar-Clegg, Sparks, Nevada. Gold analyses by fire assay methods (reported in ppb); Hg, Te and Tl by atomic absorption. Ba by x-ray fluorescence, all other analyses by ICP methods, and all reported in ppm except iron (reported in percent). M=major.

SAMPLE DESCRIPTIONS

1	Stibnite (south zone)	6	Stibnite (central zone)
2	Stibnite (south zone)	7	Realgar (central zone)
3	Stibnite (south zone)	8	Realgar (central zone)
4	Stibnite (central zone)	9	Orpiment (central zone)
5	Stibnite (central zone)	10	Orpiment (north zone)

deposit (Radtke *et al.* 1973, Dickson *et al.* 1975), with solid-solution incorporation of Sb and Au in orpiment and realgar, as well as As and Au in stibnite. Detailed mineralogical studies of Alšar minerals are needed to determine whether the composition of these phases represent solid solution or minute intergrowths or inclusions of discrete minerals.

Electron-microprobe analysis of several grains of pyrite from a sample of gold-rich (21 g/t), stibnite-bearing jasperoid from Alšar reveals a distinct enrichment of As and Sb at the periphery of the grains. Three distinct zones, outer, intermediate and core, were recognized in a number of pyrite grains. Preliminary results indicate that the As and Sb content of the zoned grains decreases from the outer zone to the core. The outer zone contains 7.1% As and 2.0% Sb, the intermediate zone, 0.9% As and 0.07% Sb, and the core zone, 0.56% As and <0.07% Sb. This

zonation suggests that although arsenic and antimony are concentrated in surface coatings, both elements also occur structurally bound in pyrite.

Electron-microprobe studies of pyrite in unoxidized ores from the Carlin and Cortez deposits, Nevada, were first undertaken by Wells & Mullens (1973) and Radtke (1985). Their studies showed that pyrite contains surface coatings and internal disseminations of arsenic (arsenian pyrite), and lesser amounts of antimony, gold and mercury.

Recent studies using secondary-ion mass spectrometry, electron microscopy and X-ray photoelectron spectroscopy were done by Bakken *et al.* (1989, 1991) and by Archart *et al.* (1993) on pyrite in gold ores from the Carlin and other sedimentary-rock-hosted disseminated gold deposits in Nevada. The results of the recent studies indicate that arsenic concentrates primarily in an overgrowth (arsenian pyrite) on pyrite

and that these rims also contain high concentrations of Au and Sb. Rims are typically a few (1–4) μm thick and are formed on host pyrite grains (cubes and framboids) barren of these metals. The arsenian pyrite also can occur as narrow veinlets within, and as simple and oscillatory compositionally zoned overgrowths on barren pyrite (Arehart *et al.* 1993). Similar studies by Fleet *et al.* (1993) on pyrite from several stratiform and stratabound gold deposits also revealed that arsenian pyrite containing Au is a feature common to gold deposits of different types.

Fluid-inclusion studies and temperature of ore deposition

All fluid inclusions in ore-stage quartz in stibnite-bearing jasperoids and siliceous ores at Alšar examined to date are too small ($\leq 1 \mu\text{m}$) to permit measurements. The inclusions are hosted in microcrystalline quartz exhibiting a mosaic texture and are morphologically similar to those described by Bodnar *et al.* (1985) in similar materials from Carlin-type gold deposits in the western U.S. They also found that most inclusions of this type are too small for microthermometry, but that those inclusions that could be measured commonly homogenized at 200°C or less.

Measurements of primary liquid + vapor inclusions in realgar crystals from the Alšar district made by Beran *et al.* (1990), gave temperatures of homogenization ranging from 144 to 170°C and salinities from 7.9 to 12.9 equivalent wt.% NaCl. Because most of the realgar at Alšar probably formed very late in the hypogene paragenesis, it is tenuous to use these data to infer conditions of main-stage deposition of silica + gold.

The nearly ubiquitous presence of primary marcasite in the stibnite-bearing jasperoids and siliceous ores places general constraints on the temperature of late main-stage mineral deposition, most of which followed deposition of the earlier main-stage gold ore. Detailed studies on marcasite precipitation from hydrothermal solutions by Murowchick & Barnes (1986) and Murowchick (1992) indicate that the upper limit of marcasite deposition is 240°C (at a pH less than 5) and that marcasite is usually deposited below 200°C.

We believe that a temperature of approximately 200°C for the main-stage deposition of gold ore at Alšar is reasonable and in agreement with results from detailed studies of fluid inclusions carried out at several Carlin-type gold deposits in the western U.S. Gold deposition at the Carlin deposit occurred between 175 and 235°C from fluids containing approximately 1–3 wt.% equivalent NaCl (Radtko *et al.* 1980, Rose & Kuehn 1987, Kuehn 1989); at the Cortez deposit, it occurred between 176 and 218°C (Rytuba 1977), and at the Mercur deposit, between

220 and 270°C from fluids containing 5–8 equivalent wt.% NaCl (Jewell & Parry 1988).

DISCUSSION

Lateral zonation

Variations in mineralogy and intensity of alteration indicate that a distinct pattern of lateral zonation exists within the Alšar district (Percival & Boev 1990). Key features of this zonation are shown along a north–south cross-section through the center of the district (Fig. 3). Three units are recognized on the basis of features and location: 1) the northern area, characterized by intense widespread argillic alteration, high concentrations of As + Tl + Hg with minor associated Sb + SiO_2 + Au, 2) the central area of stibnite-bearing jasperoids with high but variable concentrations of Au, As, Tl and Hg, with a thick zone of argillic alteration occurring above and lateral to the stibnite-bearing jasperoid ores, and 3) the southern area, characterized by extensive widespread replacement-induced silicification containing low concentrations of gold and Sb + As + Tl + Hg.

Results from recent studies by Jelenković & Pavicević (1990) indicate that erosion in the northern area is less than 250 m below the paleosurface but increases to much greater depths in the southern area. The central area exhibits transitional features common to both shallow and deep erosion, with an upper zone of argillic alteration (As + Tl + Hg) similar to that in the north, underlain by stibnite-bearing jasperoids (+ Au + As + Tl + Hg). These relationships suggest that the high-level zone of argillic alteration exposed in the northern area may be underlain by a zone of replacement silicification and possible mineralization analogous to that exposed by structural juxtaposition and a deeper level of erosion in the south.

Comparison with other Yugoslavian deposits

Alšar is one of a series of mining districts that lie along the Vardar Zone between northern Greece and central Yugoslavia. Mineralization within these districts is spatially related to subvolcanic, locally porphyritic, intrusive rocks of intermediate composition. The intrusions are bordered by mineralized skarns in carbonate terranes and are commonly enveloped by one or more metalliferous zones containing Fe, \pm Cu–Mo–Pb–Zn within and marginal to the intrusive body. The contents of Au–As–Sb–Hg increase outward to form distinct zones containing these metals. These zones commonly are lacking or deficient in base metals (Janković 1974, 1977, 1982, Janković & Petković 1974).

At Alšar, the Sb–Au–As–Tl–Hg mineralization is hosted by both carbonate rocks and volcanic tuffs. Zones of intense silicification containing Sb + Au

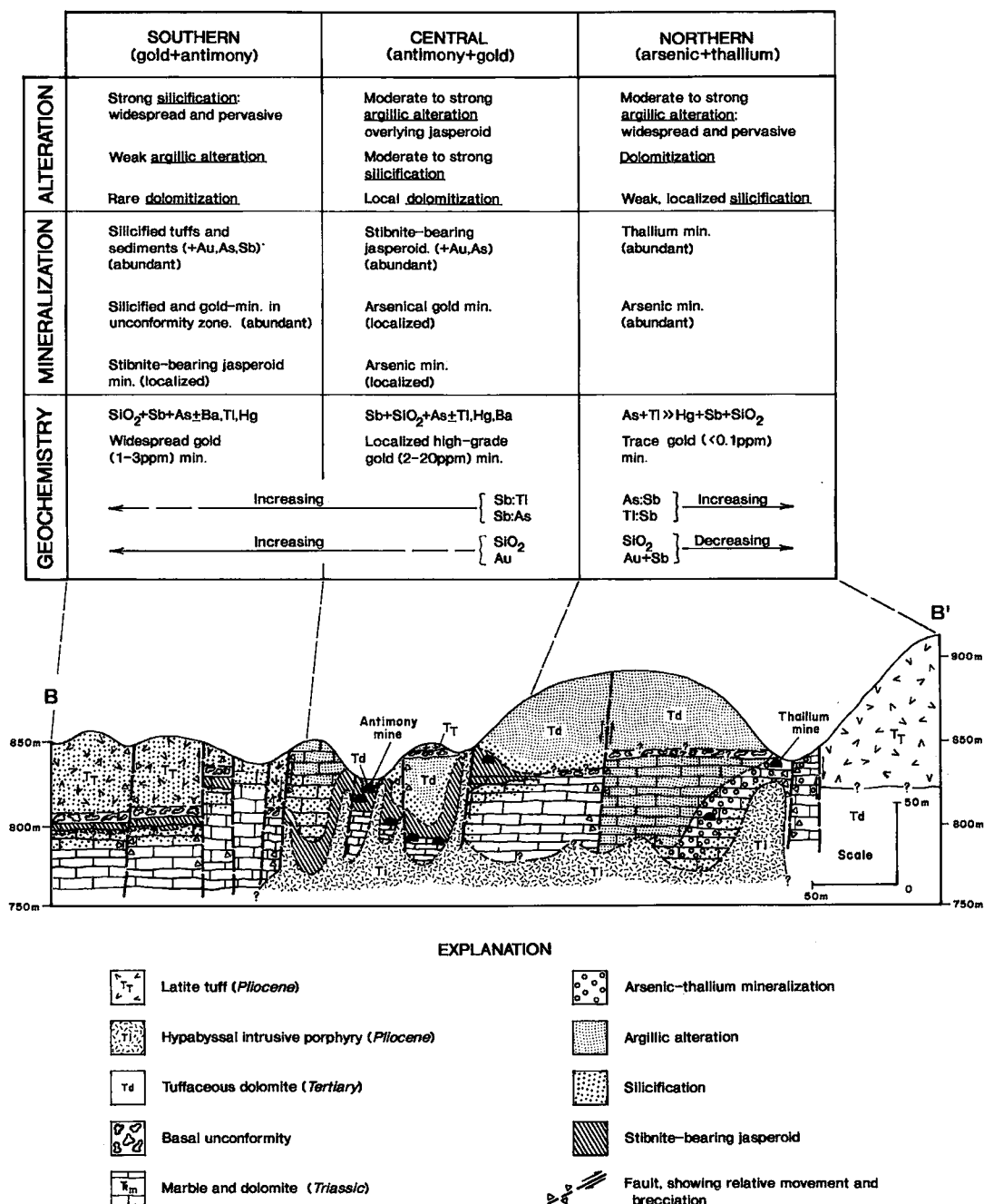


FIG. 3. North-south longitudinal section through the Alšar district showing geological, alteration and mineralization relationships among the northern, central and southern portions of the district.

formed in both rock types spatially associated with subvolcanic alkaline intrusions. The As-Sb-Tl-Au-Hg mineralization at Alšar differs markedly from

the base-metal- and Ag-dominated ore deposits typical of Yugoslavia. Base-metal mineralization has not been found to date at Alšar.

Genetic implications

Although the mineralization at Alšar is spatially related to intrusive rocks, no firm genetic tie has been established. Several lines of indirect evidence exist which, taken together, could support a possible genetic tie between intrusions and mineralization at Alšar. These are: 1) results from preliminary sulfur isotopic studies on stibnite, realgar, orpiment and marcasite, which give 0.35 to -6.84‰, implying a possible partial magmatic origin for the sulfur (Serafimovski *et al.* 1991), 2) presence of anomalous levels of As, Sb, Tl, Te, Se, F, Bi, Mo, Zn, Cd and Mn, described by Mutschler *et al.* (1985) and Sillitoe (1990) as being characteristic of deposits genetically related to alkaline intrusions, and 3) results from studies of several sedimentary-rock-hosted gold deposits in other parts of the world [Purísima Concepción, Peru: Alvarez & Noble (1988); Bau, eastern Malaysia: Percival *et al.* (1990); Bare Mountain, Nevada: Castor & Weiss (1992)] in which the authors provided some evidence to support a tie between mineralization and intrusions.

We believe that spatial associations by themselves may be suggestive of a tie or genetic association, but provide no conclusive evidence for it. An example of this is provided by Sillitoe & Bonham (1990), who attempted to establish a genetic tie for many deposits in Nevada and elsewhere, most of which lack any

proven genetic relationships.

An alternative explanation for ore genesis at Alšar would be similar to the shallow-seated hot-spring model suggested for the Carlin deposit and other deposits with similar features by Radtke & Dickson (1974), Dickson *et al.* (1979), and Radtke *et al.* (1980). Meteoric water heated by shallow-seated intrusive rocks reacted with sedimentary rocks to extract ore components and moved upward along major structures and outward through permeable rocks favorable for solution penetration and ore deposition. Although the intrusive rocks could provide ore components, the only necessary role they play is to provide heat to the surrounding rocks and meteoric waters, thereby initiating rock-water interactions and setting the waters in motion to form a convective hydrothermal cell (Dickson *et al.* 1979).

Key physical and chemical features at Alšar and those at the Carlin, Getchell and Mercur deposits in the western U.S. are summarized in Table 5. Similar features are also shared with deposits in the People's Republic of China (Cunningham *et al.* 1988, Ashley *et al.* 1991) and at Bau, eastern Malaysia (Percival *et al.* 1990).

Although many similarities in physical and chemical properties exist among the various deposits of this type, there is no guarantee that the genetic models for each of the deposits are identical. Furthermore, in spite

TABLE 5. COMPARISON OF GEOLOGICAL AND CHEMICAL FEATURES OF THE ALŠAR DISTRICT WITH THOSE OF TYPICAL CARLIN-TYPE DEPOSITS OF THE WESTERN UNITED STATES

	Alšar, Yugoslavia	Carlin, Nevada (Radtke 1985)	Getchell, Nevada (Bagby & Berger, 1985)	Mercur, Utah (Bagby & Berger, 1985)
Host Rocks	Triassic marble; Tertiary tuffaceous dolomite and Pliocene felsic tuffs	Silurian-Devonian Roberts Mountains Formation; thin-bedded, laminated silty dolomite and limestone.	Cambrian Preble Formation; carbonaceous shale, limestone and quartzite.	Mississippian Great Blue Limestone; thin-bedded, silty-limestone, mudstone, limestone and shale.
Structural Controls	Steeply dipping faults and shear zones. Relatively flat stratigraphic controls and unconformity zones.	Steeply dipping faults. Northwest trending Tuscarora Anticline. Roberts Mountain thrust fault.	Steeply dipping faults. Isoclinally folded sedimentary rocks.	Steeply dipping faults. Northwest-trending Ophir Anticline.
Associated Igneous Rocks	Pliocene latite tuffs and subvolcanic intrusions (dacite). K-Ar age dated at 5.0-4.5 m.y.	Early Cretaceous (127 m.y.) intermediate composition dikes; altered and mineralized.	Cretaceous (90 m.y.) granodiorite pluton in the Osgood Mountains. Dacite and andesite porphyry dikes; altered and mineralized.	Oligocene Eagle Hill Porphyry (31.6 m.y.) and Birds Eye Porphyry (36.7 m.y.) as dikes, sills and small stocks.
Major chemical changes in mineralized rocks	Introduced: Si, Fe, S, Mg, Au, As, Tl, Sb, Hg, Ba, F, Te, Se Removed: Ca and Mg from carbonate rocks	Introduced: Si, Fe, S, Au, As, Hg, Sb, Ba, Tl, Cu, Pb, Zn Removed: Ca, Mg	Introduced: Si, Fe, S, Au, As, Sb, Hg, Tl, F, Ba, Te, Se Removed: Ca, Mg	Introduced: Si, S, Au, As, Sb, Ba, Fe, Hg, Tl, F, Tl, Te, Se Removed: Ca, Mg
Hypogene ore mineralogy	Quartz, pyrite, marcasite, realgar, orpiment, stibnite, lorandite, arsenopyrite, barite, cinnabar, As-, Tl-, Hg- and Sb-sulfosalts. Trace: chalcocopyrite	Quartz, calcite, pyrite, arsenian-pyrite, realgar, orpiment, stibnite, cinnabar, barite. Trace: native arsenic, As-, Tl-, and Hg-sulfosalts.	Quartz, calcite, pyrite, arsenopyrite, marcasite, realgar, orpiment, stibnite, cinnabar, fluorite, barite, chalcocopyrite. Trace: As-, Tl-, and Hg-sulfosalts.	Quartz, calcite, pyrite, realgar, orpiment, marcasite, stibnite, cinnabar, barite, fluorite, gold. Trace: Tl-, As-sulfosalts

of extensive studies done to date on "Carlin-type" deposits, many uncertainties still exist regarding their genesis. For example, stable isotope data from the same samples at Carlin have been interpreted by the same geologists to support different genetic models. At this time, the conditions of ore deposition and the nature of the ore fluids and sources of ore components at Alšar are unknown.

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REFERENCES

- ALVAREZ, A.A. & NOBLE, D.C. (1988): Sedimentary rock-hosted disseminated precious metal mineralization at Purísima Concepción, Yauricocha district, central Peru. *Econ. Geol.* **83**, 1368-1378.
- AREHART, G.B., CHRYSOULIS, S.L. & KESLER, S.E. (1993): Gold and arsenic in iron sulfides from sediment-hosted disseminated gold deposits: implications for depositional processes. *Econ. Geol.* **88**, 171-185.
- ARSOVSKI, M. & IVANOV, T. (1977a): Neotectonics, magmatism and metallogeny on the territory of Yugoslavia. In *Metallogeny and Plate Tectonics in the Northeast Mediterranean* (S. Janković, ed.). Univ. of Belgrade, Belgrade, Yugoslavia (471-482).
- & ——— (1977b): Geotectonic evolution of the Vardar Zone. In *Proc. 6th Colloquium on Geology of the Aegean Region* (G. Kallergis, ed.). Institute of Geological and Mining Research, Athens, Greece (569-577).
- ASHLEY, R.P., CUNNINGHAM, C.G., BOSTICK, N.H., DEAN, W.E. & CHOU, I-MING (1991): Geology and geochemistry of three sedimentary-rock-hosted gold deposits in Guizhou Province, People's Republic of China. *Ore Geol. Rev.* **6**, 133-151.
- BAGBY, W.C. & BERGER, B.R. (1985): Geologic characteristics of sediment-hosted disseminated precious-metal deposits in the western United States. In *Geology and Geochemistry of Epithermal Systems* (B.R. Berger & P.M. Bethke, eds.). *Rev. Econ. Geol.* **2**, 169-202.
- BAKKEN, B.M. (1990): *Gold Mineralization, Wall-Rock Alteration, and the Geochemical Evolution of the Hydrothermal System in the Main Orebody, Carlin Mine, Nevada*. Ph.D. thesis, Stanford Univ., Stanford, California.
- & EINAUDI, M.T. (1986): Spatial and temporal relations between wall rock alteration and gold mineralization, main pit, Carlin gold mine, Nevada, U.S.A. In *Gold '86* (A.J. Macdonald, ed.). Konsult International Inc., Willowdale, Ontario (488-496).
- & ——— (1989): Volume loss and mass transport during hydrothermal alteration and weathering, Carlin gold mine, Nevada. *Geol. Soc. Am., Abstr. Programs* **21**(6), A295.
- , FLEMING, R.H. & HOCHHELLA, M.F., JR. (1991): High-resolution microscopy of auriferous pyrite from the Post deposit, Carlin district, Nevada. In *Process Mineralogy. XI. Characterization of Metallurgical and Recyclable Products* (D.M. Hausen, W. Petruk, R.D. Hagni & A. Vassiliou, eds.). The Minerals, Metals & Materials Soc., Warrendale, Pennsylvania (13-23).
- , HOCHHELLA, M.F., JR., MARSHALL, A.F. & TURNER, A.M. (1989): High-resolution microscopy of gold in unoxidized ore from the Carlin mine, Nevada. *Econ. Geol.* **84**, 171-179.
- BERAN, A., GOTZINGER, M. & RIECK, B. (1990): Fluid inclusions in realgar from Allchar. In *Symp. on Thallium Neutrino Detection* (Dubrovnik, Yugoslavia), 42 (abstr.).
- BERGER, B.R. & BAGBY, W.C. (1991): The geology and origin of Carlin-type gold deposits. In *Gold Metallogeny and Exploration* (R.P. Foster, ed.). Blackie, Glasgow (210-248).
- BODNAR, R.J., REYNOLDS, T.J. & KUEHN, C.A. (1985): Fluid inclusion systematics in epithermal systems. In *Geology and Geochemistry of Epithermal Systems* (B.R. Berger & P.M. Bethke, eds.). *Rev. Econ. Geol.* **2**, 73-97.
- BOEV, B. (1990a): Microelements in the volcanic rocks of the Kozuf Mountains. In *Proc. XIIth Congress on Geology of Yugoslavia (Ohrid). II. Mineralogy & Petrology. Geol. Soc. Macedonia* (5-14).
- (1990b): The origin of melts from which the volcanic rocks of the Kozuf Mountains were formed. In *Proc. XIIth Congress on Geology of Yugoslavia (Ohrid). II. Mineralogy & Petrology. Geol. Soc. Macedonia* (181-187).
- CASTOR, S.B. & WEISS, S.I. (1992): Contrasting styles of epithermal precious-metal mineralization in the southwestern Nevada volcanic field, USA. *Ore Geol. Rev.* **7**, 193-223.
- CUNNINGHAM, C.G., ASHLEY, R.P., CHOU, I-MING, HUANG, ZUSHU, WAN, CHAOYUAN & LI, WENKANG (1988): Newly discovered sedimentary rock-hosted disseminated gold deposits in the People's Republic of China. *Econ. Geol.* **83**, 1462-1467.
- DICKSON, F.W., RADTKE, A.S., WEISSBERG, B.G. & HEROPOULOS, C. (1975): Solid solutions of antimony, arsenic, and gold in stibnite (Sb_2S_3), orpiment (As_2S_3), and realgar (As_2S_2). *Econ. Geol.* **70**, 591-594.

- , RYE, R.O. & RADTKE, A.S. (1979): The Carlin gold deposit as a product of rock-water interactions. In *Papers on Mineral Deposits of Western North America* (J.D. Ridge, ed.). *Nevada Bur. Mines & Geol., Rep.* **33**, 101-108.
- FALICK, A.E., ILICH, M. & RUSSELL, M.J. (1991): A stable isotope study of the magnesite deposits associated with the Alpine-type ultramafic rocks of Yugoslavia. *Econ. Geol.* **86**, 847-861.
- FLEET, M.E., CHRYSOULIS, S.L., MACLEAN, P.J., DAVIDSON, R. & WEISNER, C.G. (1993): Arsenian pyrite from gold deposits: Au and As distribution investigated by SIMS and EMP, and color staining and surface oxidation by XPS and LMS. *Can. Mineral.* **31**, 1-17.
- GRANT, J.A. (1986): The isocon diagram – a simple solution to Gresens' equation for metasomatic alteration. *Econ. Geol.* **81**, 1976-1982.
- ILICH, M. (1974): Hydrothermal-sedimentary dolomite: the missing link? *Am. Assoc. Petrol. Geol., Bull.* **58**, 1331-1347.
- IVANOV, T. (1965): Zonal distribution of elements and minerals in the deposit Alšar. In *Symp. on Problems of Postmagmatic Ore Deposition II* (Prague). Geol. Soc. Czechoslovakia (186-191).
- JANKOVIĆ, S. (1974): Metallogenic provinces of Yugoslavia in time and space (an overview). In *Metallogeny and Concepts of the Geotectonic Development of Yugoslavia* (S. Janković, ed.). Belgrade, Yugoslavia (37-63).
- (1977): Major Alpine ore deposits and metallogenic units in the northeastern Mediterranean and concepts of plate tectonics. In *Metallogeny and Plate Tectonics in the Northeastern Mediterranean* (S. Janković, ed.). Faculty Mining Geol., Univ. Belgrade, Yugoslavia (105-172).
- (1979): Antimony deposits in southeast Europe. Inst. of Research, Geol. and Geophys., Univ. of Belgrade, Belgrade, Yugoslavia (25-48).
- (1982): Yugoslavia. In *Mineral Deposits of Europe. II. Southeast Europe*. Inst. of Mining and Metallurgy, London, U.K. (143-202).
- & JELENKOVIĆ, R. (1990): General metallogenic features of thallium mineralization in the Alšar deposit (Yugoslavia). In *Symp. on Thallium Neutrino Detection* (Dubrovnik, Yugoslavia), 32-35 (abstr.).
- & PETKOVIĆ, M. (1974): Metallogeny and concepts of the development of Yugoslavia. In *Metallogeny and Concepts of the Geotectonic Development of Yugoslavia* (S. Janković, ed.). Faculty Mining Geol., Univ. Belgrade, Belgrade, Yugoslavia (443-477).
- JELENKOVIĆ, R. & PAVICEVIĆ, M.K. (1990): The erosion investigations of the Alšar district based on the applied geomorphological and structro-geological methods. In *Symp. on Thallium Neutrino Detection* (Dubrovnik, Yugoslavia), 30-31 (abstr.).
- JEWELL, P.W. & PARRY, W.T. (1988): Geochemistry of the Mercur gold deposit (Utah, U.S.A.). *Chem. Geol.* **69**, 245-265.
- KOLIOS, N., INNOCENTI, F., MANETTI, P., PECCERILLO, A. & GIULIANI, O. (1980): The Pliocene Volcanism of the Voras Mts. (central Macedonia, Greece). *Bull. Volcanol.* **43**, 553-568.
- KUEHN, C.A. (1989): *Studies of Disseminated Gold Deposits near Carlin, Nevada: Evidence for a Deep Geologic Setting of Ore Formation*. Ph.D. thesis, Pennsylvania State Univ., University Park, Pennsylvania.
- & ROSE, A.W. (1992): Geology and geochemistry of wall-rock alteration at the Carlin gold deposit, Nevada. *Econ. Geol.* **87**, 1697-1721.
- MACEDONIAN GEOLOGICAL SURVEY (1980): Preliminary geological map of the Vitoliste Quadrangle, State Federal Republic of Yugoslavia. (1:100,000 scale, color map), 1 sheet.
- MUROWCHICK, J.B. (1992): Marcasite inversion and the petrographic determination of pyrite ancestry. *Econ. Geol.* **87**, 1141-1152.
- & BARNES, H.L. (1986): Marcasite precipitation from hydrothermal solutions. *Geochim. Cosmochim. Acta* **50**, 2615-2629.
- MUTSCHLER, F.E., GRIFFIN, M.E., STEVENS, D.S. & SHANNON, S.S. (1985): Precious metal deposits related to alkaline rocks in the North American Cordillera – an interpretative review. *Geol. Soc. S. Afr., Trans.* **88**, 355-377.
- NOLAN, T.B. (1962): The Eureka mining district, Nevada. *U.S. Geol. Surv., Prof. Pap.* **406**.
- PAVICEVIĆ, M.K. (1988): Lorandite from Alšar – a low energy solar neutrino dosimeter. *Nuclear Instruments Methods Phys. Res.* **A271**, 287-296.
- PERCIVAL, T.J., BAGBY, W.C. & RADTKE, A.S. (1988): Physical and chemical features of precious-metals deposits hosted by sedimentary rocks in the western United States. In *Bulk Mineable Precious Metal Deposits of the Western United States* (R. Schafer, J. Cooper & P. Vikre, eds.). The Geological Society of Nevada, Reno, Nevada (11-34).
- & BOEV, B. (1990): As-Tl-Sb-Hg-Au-Ba mineralization Alšar district, Yugoslavia. A unique type of Yugoslavian ore deposit. In *Symp. on Thallium Neutrino Detection* (Dubrovnik, Yugoslavia), 36-37 (abstr.).
- & RADTKE, A.S. (1990): Carlin type gold mineralization in the Alšar district, Macedonia, Yugoslavia. *Eighth IAGOD Symp. (Ottawa)*, 108 (abstr.).
- & ——— (1993): Thallium in disseminated replacement gold deposits of the Carlin-type; a preliminary report. *Neues Jahrb. Mineral. Abh.* **166**, 65-75.

- _____, _____ & BAGBY, W.C. (1990): Relationships among carbonate-replacement gold deposits, gold skarns, and intrusive rocks, Bau mining district, Sarawak, Malaysia. *Mining Geol.* **40**, 1-16.
- RADTKE, A.S. (1985): Geology of the Carlin gold deposit, Nevada. *U.S. Geol. Surv., Prof. Pap.* **1267**.
- _____, & DICKSON, F.W. (1974): Genesis and vertical position of fine-grained disseminated replacement-type gold deposits in Nevada and Utah, USA. In *Problems of Ore Deposition. Fourth IAGOD Symp. (Varna)* **1**, 71-78.
- _____, RYE, R.O. & DICKSON, F.W. (1980): Geology and stable isotope studies of the Carlin gold deposit, Nevada. *Econ. Geol.* **75**, 641-672.
- _____, TAYLOR, C.M. & HEROPOULOS, C. (1973): Antimony-bearing orpiment, Carlin gold deposit, Nevada. *U.S. Geol. Surv. J. Res.* **1**, 85-87.
- RIECK, B. (1993): Famous mineral localities: Allchar, Macedonia. *Mineral. Rec.* **24**, 437-449.
- ROSE, A.W. & KUEHN, C.A. (1987): Ore deposition from highly acidic CO₂-rich solutions at the Carlin gold deposit, Eureka county, Nevada. *Geol. Soc. Am., Abstr. Programs* **19**, 824.
- RYTUBA, J.J. (1977): *Mutual Solubilities of Pyrite, Pyrrhotite, Quartz and Gold in Aqueous NaCl Solutions from 200° to 500°C, and 500 to 1,500 bars, and Genesis of the Cortez Gold Deposit, Nevada*. Ph.D. thesis, Stanford Univ., Stanford, California.
- SERAFTIMOVSKI, T., BOEV, B. & MUDRINIĆ, C. (1991): Isotopic composition of the sulphur in the sulphides from As-Sb deposit, Alšar. *Geol. Macedonica* **5**, 165-172.
- SILLITOE, R.H. (1990): Intrusion-related gold deposits. In *Gold Metallogeny and Exploration* (R.P. Foster, ed.). Blackie, Glasgow (165-209).
- _____, & BONHAM, H.F., Jr. (1990): Sediment-hosted gold deposits: distal products of magmatic-hydrothermal systems. *Geology* **18**, 157-161.
- SMITH, A.G. & SPRAY, J.G. (1984): A half-ridge transform model for the Hellenic-Dinaric ophiolites. In *The Geological Evolution of the Eastern Mediterranean* (J.E. Dixon & A.H.F. Robertson, eds.). *Geol. Soc., Spec. Publ.* **17**, 629-644.
- SPRAY, J.G., BÉBIEN, J., REX, D.C. & RODDICK, J.C. (1984): Age constraints on the igneous and metamorphic evolution of the Hellenic-Dinaric ophiolites. In *The Geologic Evolution of the Mediterranean* (J.E. Dixon & A.H.F. Robertson, eds.). *Geol. Soc., Spec. Publ.* **17**, 619-627.
- WELLS, J.D. & MULLENS, T.E. (1973): Gold-bearing arsenian pyrite determined by microprobe analysis, Cortez and Carlin gold mines, Nevada. *Econ. Geol.* **68**, 187-201.

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