UDC 55 **CODEN – GEOME 2** **ISSN 0352 – 1206**

GEOLOGICA MACEDONICA

Geologica Macedonica *Geologica Macedonica*	Год. Vol.	**24**	Број No	1	стр. pp.	1–74	Штип Štip	2010

Geologica Macedonica	Год.	**24**	Број	1	стр.	1–74	Штип	2010
Geologica Macedonica	Vol.		No		pp.		Štip	

GEOLOGICA MACEDONICA

Published by: – Издава:
The "Goce Delčev" University, Faculty of Natural and Technical Sciences, Štip, Republic of Macedonia
Универзитет „Гоце Делчев“, Факултет за природни и технички науки, Штип, Република Македонија

Language editor	Лектура
Marijana Kroteva	**Маријана Кротева**
(English)	(англиски)
Georgi Georgievski, Ph. D.	**д-р Георги Георгиевски**
(Macedonian)	(македонски)
Technical editor	Технички уредник
Blagoja Bogatinoski	**Благоја Богатиноски**
Proof-reader	Коректор
Alena Georgievska	**Алена Георгиевска**
Address	Адреса
GEOLOGICA MACEDONICA	**GEOLOGICA MACEDONICA**
EDITORIAL BOARD	**РЕДАКЦИЈА**
Faculty of Natural and Technical Sciences	**Факултет за природни и технички науки**
P. O. Box 96	**пошт. фах 96**
MK-2000 Štip, Republic of Macedonia	**МК-2000 Штип, Република Македонија**
Tel. ++ 389 032 550 575	**Тел. 032 550 575**

E-mail: todor.serafimovski@ugd.edu.mk

400 copies	Тираж: 400
Published yearly	Излегува еднаш годишно
Printed by:	Печати:
2ri Avgust – Štip	2ри Август – Штип
Price: 500 den	Цена: 500 ден.
The edition was published in December 2010	Бројот е отпечатен во декември 2010

Photo on the cover:	На корицата:
Argillitic alteration, Kadiica, Republic of Macedonia	Аргилитска алтерација, Кадиица, Република Мекедонија

Geologica Macedonica *Geologica Macedonica*	Год. Vol.	**24**	Број No	1	стр. pp.	1–74	Штип Štip	2010

СОДРЖИНА

Geologica Macedonica	Год.	**24**	Број	1	стр.	1–74	Штип	2010
Geologica Macedonica	Vol.		No		pp.		Štip	

TABLE OF CONTENTS

GEOME 2
Manuscript received: April 21, 2010
Accepted: October 10, 2010

Geologica Macedonica, Vol. **24**, No. 1, pp. 63–71 (2010)
ISSN 0352 – 1206
UDC: 550.84 : 553.3(497.715)

Original scientific paper

FLUID INCLUSIONS AND K/Ar DATING OF THE ALLŠAR Au-Sb-As-Tl MINERAL DEPOSIT, MACEDONIA

Sabina Strmić Palinkaš[1], Sibila Borojević Šoštarić[2], Ladislav Palinkaš[1], Zoltan Pecskay[3], Blažo Boev[4], Vladimir Bermanec[1]

[1]*Faculty of Science, University of Zagreb, Horvatovac 95, HR-10000 Zagreb, Croatia*
[2]*Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Pierottijeva 6. HR-10000 Zagreb, Croatia*
[3]*Institute of Nuclear Research, Hungarian Academy of Sciences, Bem tér. 18c, HU-4001 Debrecen, Hungary*
[4]*Faculty of Natural and Technical Sciences, "Goce Delčev" University, Goce Delčev 89, MK-2000, Štip, Republic of Macedonia*
blazo.boev@ugd.edu.mk

Abstract: The Allšar Au-Sb-As-Tl mineral deposit, Macedonia, occurs in the southern part of the Vardar zone. The deposit carries Carlin-type of mineralization hosted by calcareous sedimentary complex. Mineral assemblages and alterations display characteristic zonal distribution. According to the fluid inclusion data, mineral deposition occurred as a result of cooling, dilution and neutralization of the ore-bearing fluids. Neogene magmatism (4.6 to 5.8 Ma) served as the heat source responsible for driving convective hydrothermal circulation at the Allšar deposit.

Key words: carlin; gold; thallium; arsenic; antimony; fluid inclusions; K/Ar dating

INTRODUCTION

The Allšar Au-Sb-As-Tl mineral deposit is located at the north-western margins of Kožuf Mts. in the southern part of the Vardar zone, 110 km SE from Skopje, Macedonia (Fig. 1). The deposit is unique in the world because of the presence of the mineral lorandite ($TlAsS_2$), which is of particular interest for nuclear physicists and geochemists. Lorandite offers the possibility of geochemical detection of proton–proton-solar neutrinos which have very low detection limits and threshold energies (Pavićević et al., 2006).

Several studies have been carried out at the Allšar deposit, including ore-stage mineral paragenesis (Janković, 1988; Janković & Jelenović, 1994; Percival & Radtke, 1994), characterization of the petrological and geochemical features of the volcano-intrusive complex of the Kožuf Mts. (Boev, 1988; Karamata et al., 1994), age of volcanic and hydrothermal activity in the area (Jakupi et al., 1982; Lippolt & Fuhrmann, 1986; Kolios et al., 1988; Boev, 1988; Troesch & Franz, 1992), and others. However, the questions about the nature of mineralizing fluids (Beran et al., 1994), sources of metals and the role of magmatism (Frantz et al., 1994) are still open. Similar problems remain a contentious issue for the worldwide Carlin-type deposits as well (e.g., Hofstra & Cline, 2000; Su et al., 2010).

The deposit displays distinctive features of the Carlin-type of mineralization as (1) strong structural control of mineralization by faults and folds; (2) calcareous sedimentary host rocks of diverse facies ± igneous rocks; (3) decarbonation, silicification, argillization and sulfidation alterations; (4) submicron gold in association with pyrite, arsenian pyrite and arsenopyrite and (5) geochemical signature of Au, As, Hg, Sb and Tl (Radtke, 1985; Hofstra & Cline, 2000).

The mineralization occurs within the three, not sharply defined, zones (Fig. 1): (1) Southern, high temperature, zone characterized by dominance of Au mineralization accompanied with variable amount of Sb and As minerals; (2) Central part of the deposit beside Au, Sb and As mineralization contains significant amounts of Tl minerals, minor amount of Ba, Hg and traces of Pb and (3) Northern, low temperature, zone is represented by As and Tl mineralization, accompanied by minor Sb and traces of Hg and Au (Ivanov, 1986; Janković et al., 1997).

The aim of the present study is to elucidate the characteristics of fluid evolution by constraining the physico-chemical condition of Sb-As-Tl mineralization based on the analysis of fluid inclusions. Beside microthermometry, analyses of evaporate mound by scanning electron microscope with an attached X-ray energy dispersive system (SEM/EDX) is performed. Whereas the Au-Sb-As-Tl mineralization shows close spatial relationship to the volcanics, K/Ar dating of quartz latite is used for the refinement of the mineral deposition age.

GEOLOGICAL SETTING

The Allšar deposit is situated along a regional fault belt between the Vardar zone on the east and Pelagonian massif on the west. The deposit is related with a Neogene calc-alkaline volcano-intrusive complex intruded into Paleozoic-Mezozoic basement of the Vardar zone. The basement is composed of Precambrian gneisses, metamorphosed Triassic complex (marble, dolostones, minor schist) and Jurassic ophiolites followed by Cretaceous and Tertiary flysch, carbonate rocks and Neogene molasse deposits (Percival & Radtke, 1994; Janković & Jelenović, 1994). Volcanic activity in the area lasted between 7.0 and 1.8 Ma (Boev, 1988). Its products are extrusive rocks, ranging in composition from andesite, quartz-latite to dacite, occasionally trachyte and latite, generally enriched in K and Rb (Karamata et al., 1994), and pyroclastic equivalents.

The mineralization, represented by disseminated submicrometer-sized gold particles and Sb-As-Tl sulphides and sulfosalts and distributed over an area extending 2500 m WE and 200 m SN, shows a zonal pattern (Fig. 1). Zone I occupies the southernmost part of the deposit. It is characterized by extensive widespread replacement-induced silicification containing variable concentrations of gold, antimony and arsenic. The silicification varies in intensity from partial to total replacement (jasperoid). Central part of the deposit (Zone II) beside gold, antimony and arsenic contains significant amounts of thallium and minor amounts of barium, mercury and lead. The mineralization is hosted by argillized tuffs, Tertiary dolostones and rarely Triassic carbonate rocks. Thallium mineralization prevails within northern part of the deposit (Zone III). The principal host rocks are altered carbonate and tuffaceous rocks (Ivanov, 1986; Percival & Radtke, 1994, Janković et al., 1997).

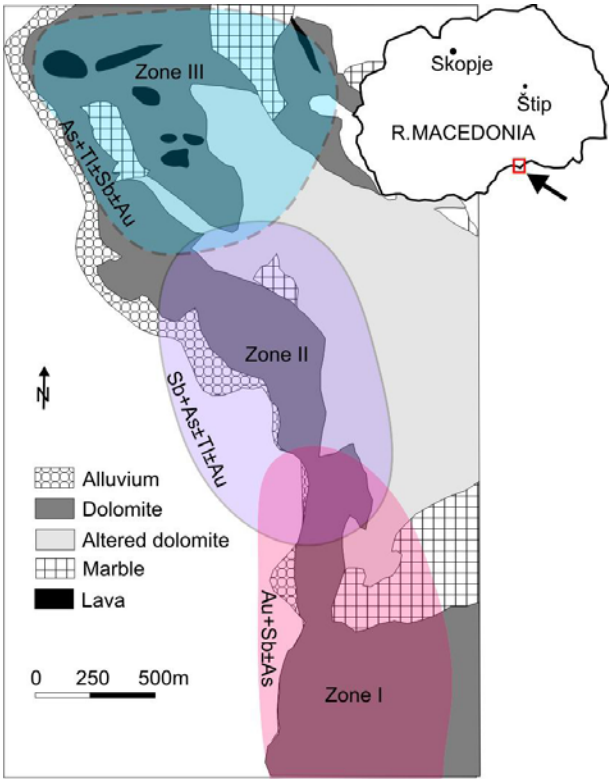

Fig. 1. Geographical and geological setting of the Allšar mineral deposit, Macedonia (after Janković et al., 1997)

SAMPLES AND METHODS

Fluid inclusion studies were carried out to estimate the P-T-X conditions during the mineralization. Microthermometric measurements were performed on primary fluid inclusions within doubly polished, ~0.3 mm thick, wafers of: (1) Quartz associated with high temperature sulfide mineralization (Zone I, Fig. 1); (2) Quartz and calcite from central part of deposit (Zone II, Fig. 1), (3) Realgar, orpiment, lorandite and dolomite associated with sulfide mineralization barren of Sb and enriched in As and Tl (Zone III, Fig. 1) and (4) Agate associated with an low temperature mineralization northernmost of Zone III (Fig. 1). Measurements were conducted at Linkam THMS 600 stage mounted on Olympus BX 51 microscope using 10x and 50x Olympus long-working distance objective lenses for visible light. Two synthetic fluid inclusion standards (SYN FLINC; pure H_2O, mixed H_2O-CO_2) were used to calibrate equipment. The precision of the system was ±2.0°C for homogenization temperature, and ±0.2°C in the temperature range between –60 and +10°C.

Ultraviolet (UV) fluorescence microscopy of hydrocarbons bearing inclusions was performed at Olympus BH 2 photomicroscope under magnification of 300×. The technique involves stimulation of a thin section by UV (ultraviolet light at 450–490 nm wavelength), which causes the specimen to fluoresce in the visible light spectrum. This visible light is captured in a specially adapted optical microscope. Organic materials, mostly hydrocarbons in the form of mobile oil, bitumen and "dead" oil, kerogen and other detrital organic components, are activate UV fluorescence. Therefore, mineral hosts with organic inclusions can be identified. Maturation degree of hydrocarbons is a function of colors displayed under UV and can be approximated using method described after Hagemann & Hollenbach (1986) and McLimans (1987).

Analyses of evaporate mounds were carried out to constrain the chemical composition of mineralizing fluid. Analyses were focused on realgar and orpiment used for microthermometry. Evaporate mounds were prepared according to the procedure described by Kontak (2004). The doubly polished wafers of realgar and orpiment were rapidly heated at heating-freezing stage described above. Massive decrepitation of fluid inclusions within realgar occurs in the range between 180 and 220°C. Although leaking of fluid inclusions within orpiment starts at temperature below 100°C, samples were heated at 160°C to produce enough evaporate mounds. Decrepitated wafers were removed on Cu tape attached to metal plate and transferred to the SEM, ready for chemical analysis. Evaporate mounds were located using backscattered (BSE) and secondary electron (SE) imagining. The analyses were done using the following operating conditions: 3–40 μm beam, accelerating voltage 15 kV, current 10 nA and counting time 40 seconds.

Measurements of K/Ar ages were performed at the Institute of Nuclear Reasearch of the Hungarian Academy of Science (ATOMKI), Debrecen. The samples were crashed to 0.063–0.315 mm size. Mineral separation was done by magnetic field and heavy liquids. One aliquot of samples (100 mg) was pulverized for potassium determination. Powders were digested in HF with the addition of some sulphuric and perhloric acids. The digested samples were dissolved in 100 ml 0.25 mol/1 HCl and diluted fivefold. Na and Li (100 ppm) were added as buffer and internal standard. Potassium concentration was measured with a digitalized flame photometer. Another aliquot of samples (500 mg) was used for Ar analyses. The samples were degassed by high-frequency induction heating, and the conventional getter materials were used for cleaning Ar. The ^{38}Ar spike was introduced to the system from a gas pipette before degassing. The cleaned Ar was directly introduced into the mass spectrometer, operated in the static mode. Recording and evolution of Ar spectra was controlled by a microcomputer. Details of the instruments, the applied methods and results of calibration have been described by Balogh (1985).

X-ray diffraction spectra were obtained on random oriented powders with a Phillips PW 3040/60 X'Pert PRO X-ray diffractometer with Cu Kα radiation at 45 kV and 40 mA (a counting time of 0.5 s per 0.5° step was used for 2θ in the 4–63° range). Samples powder was pressed on holder before measurements in order to minimize possible orientations effects.

RESULTS

Microthermometry of fluid inclusions

Microthermometric measurements were performed on primary, L+V, inclusions within quartz samples from the Zone I (Fig. 2.a). First melting (eutectic temperature, Te) obtained in interval between –44.0 and –58.0°C (Fig. 3.a) indicates the presence of bivalent cations, probably Ca^{2+} or Mg^{2+}, within the system (Crawford, 1981). Final melting of hydrate ($T_m$hyd1) was recorded in temperature range between –24.2 and –42.0°C (Fig. 3.b). Ice melting temperatures ($T_m$ice) in interval from –2.4 to –18.1°C (Fig. 3.c) point to salinity between 4 to 21.3 wt.% NaCl equ. Homogenization (T_h) by vapor disappearance occurred in temperature range from 131 to 200°C (Fig. 3.d). Only one fluid inclusion nucleate recognizable chlatrate phase melted at temperature of –0.5°C ($T_m$chl), suggesting presence of CO_2 and salinity of 16 wt.% NaCl equ. Homogenization temperature was recorded at 201°C.

Microthermometric measurements within quartz (Fig. 2.b) and calcite (Fig. 2.c) from Zone II were conducted on two-phase (L+V) inclusions of the primary origin. The initial melting temperature (T_e) in range between –50.0 and –56.0°C indicates presence of bivalent cations (Fig. 3.a). Final melting of hydrate ($T_m$hyd1) was noticed between –27.2 and –39.0°C (Fig. 3.b). Ice melting temperatures ($T_m$ice) in interval from –10.5 to –13.1°C (Fig. 3.c) is in concordance with salinity between 14.5 and 17.1 wt.% NaCl equ. Homogenization into liquid phase occurred in range from 120 to 165°C (Fig. 3.d).

Microthermometric measurements were carried out on the primary, L+V, inclusions hosted by realgar (Fig. 2.d), orpiment (Fig. 2.e), dolomite (Fig. 2.f) and lorandite (Fig. 2.g) from Zone III. The eutectic temperature (T_e) in an interval between –50.3 and –54.2°C indicates presence of bivalent cations (Fig. 3.a). Melting runs in the temperature range between –35 and 0°C determined existence of two hydrates. Melting of the first hydrate ($T_m$hyd1) was recorded in temperature interval between –22.0 and –24.5°C (Fig. 3.b). Temperature interval of the final melting of the second hydrate ($T_m$hyd2) is observed between –11.0 and –15.4°C (Fig. 3.b). The ice melting temperature ($T_m$ice) the interval between –1.5 and –4.1°C (Fig. 3.c) corresponds to salinity of 2.6 to 6.9 wt.% NaCl equ. Homogenization within quartz and dolomite into liquid phase (T_h) was recorded between 120 and 152°C (Fig. 3.d). Temperature of total homogenization within orpiment and lorandite was not recorded due to massive decrepitation of fluid inclusions at lower temperatures.

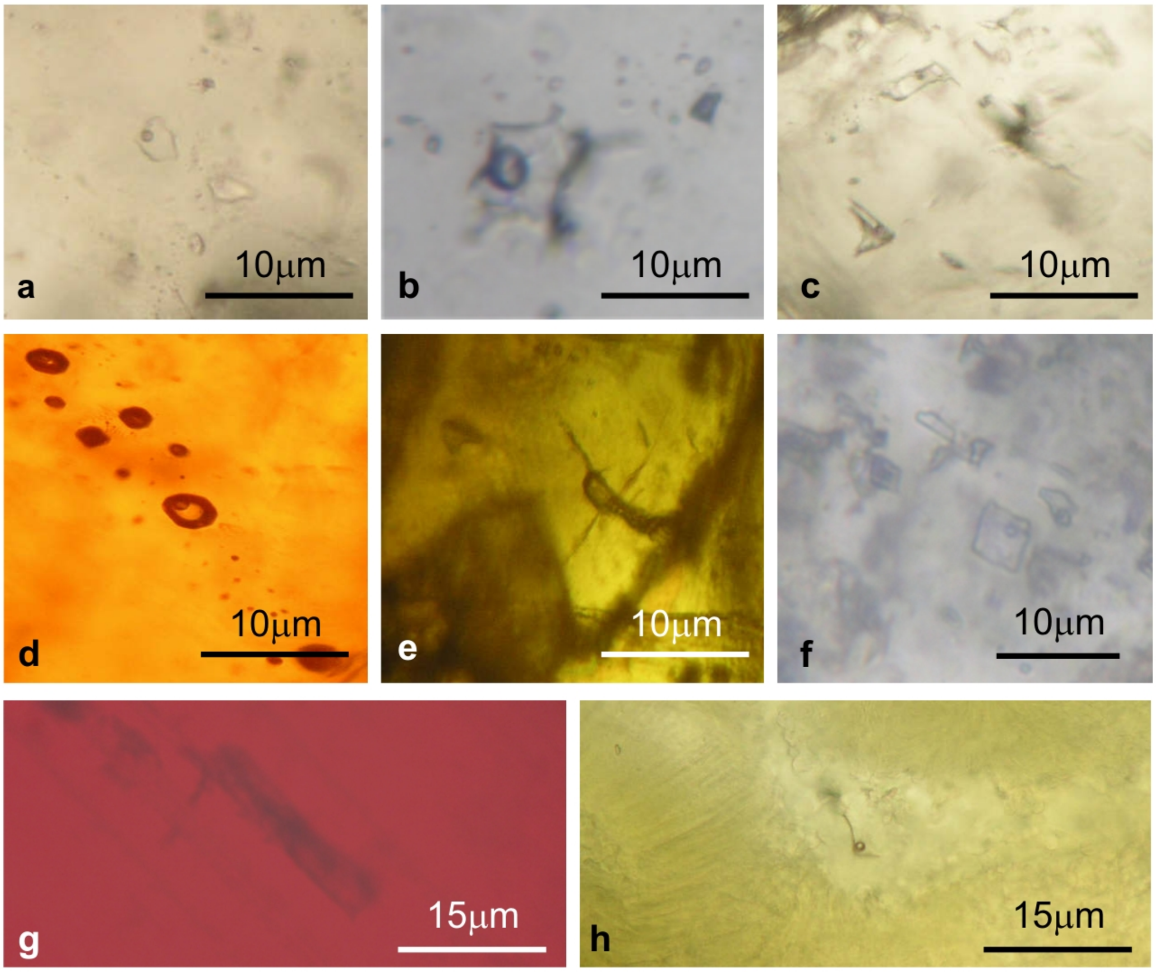

Fig. 2. Fluid inclusions within a) quartz (Zone I); b) quartz (Zone II); c) calcite (Zone II); d) realgar (Zone III); e) orpiment (Zone III), f) dolomite (Zone III); g) lorandite (Zone III); h) agate (north of Zone III).

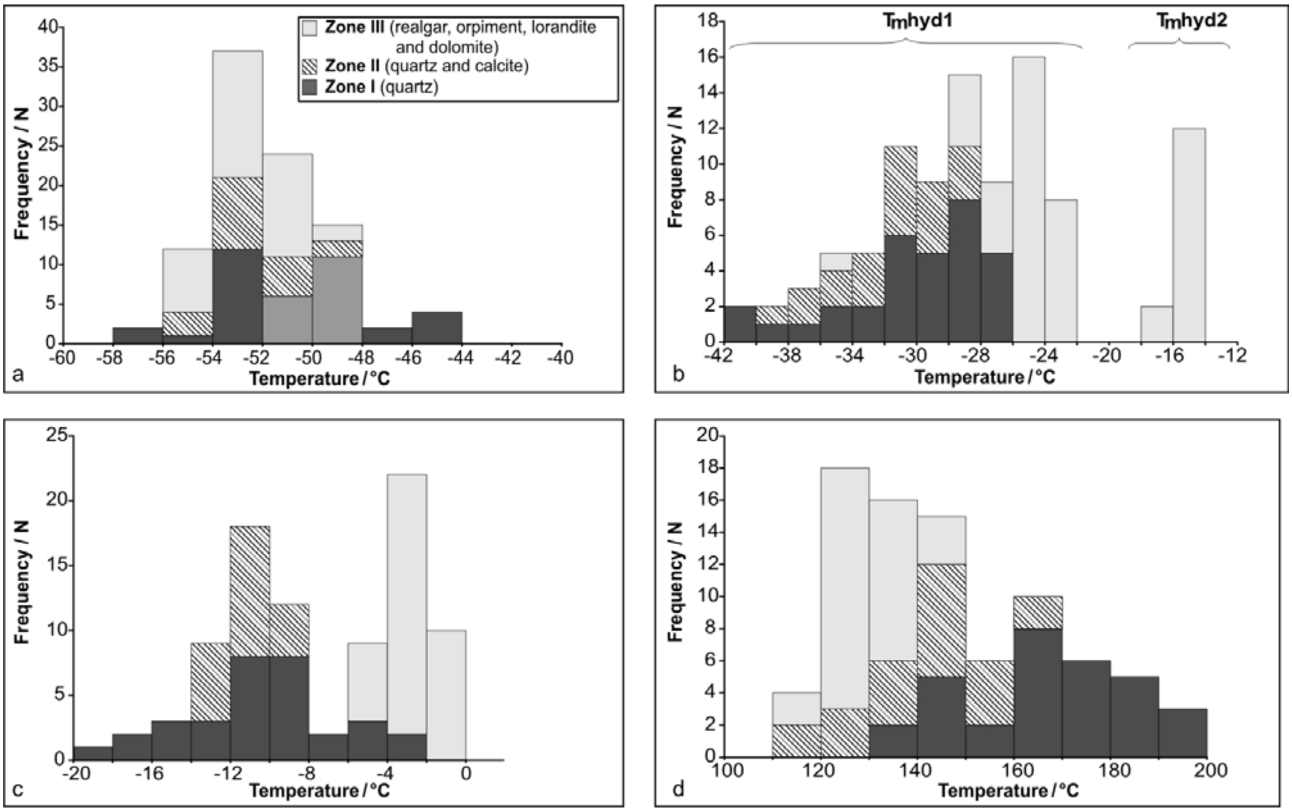

Fig. 3. Frequency distribution of a) the eutectic temperature; b) melting temperatures of hydrates; c) the last melting temperature of ice; d) homogenization temperature within vapor phase.

Microthermometric measurements were performed on aqueous inclusions containing CO_2 and hydrocarbons and multiphase hydrocarbon inclusions within agate (Fig. 2.h). During heating of aqueous inclusions containing CO_2 and hydrocarbons first homogenization in temperature range from +31.0 to +33.0°C occur within vapor bubble (liquid to vapor transition). Total homogenization to liquid state was recorded between 102 and 125°C (Fig. 3). Melting of chlatrates at temperature range from 2.4 to 7.0°C corresponds salinity from 6.0 to 13.5 wt.% NaCl equ.

Complex hydrocarbons bearing inclusions are remaining unfrozen at minimum stage temperature of –180°C. During subsequent heating, only observed changes within these inclusions were reduction in size or shape of some of the components, omitting the complete phase transitions. None of these inclusions were homogenized before decripitation, which occurred at temperatures range from 170 to 180°C.

Ultraviolet fluorescence microscopy

Ultraviolet (UV) fluorescence microscopy was performed on hydrocarbons bearing inclusions trapped within agate. This type of inclusion shows yellow and green fluorescence suggesting immature organic matter (e.g., Hagemann & Hollerbach 1986; McLimans 1987; Bodnar 1990). The intensity of fluorescence is increasing with the size of inclusions. Also, UV microphotographs show presence of various pieces of organic matter trapped within agate, with similar fluorescence colours to the described inclusions.

Composition of evaporate mounds

Analyses of realgar samples indicate Na and K chlorides composition of evaporate mounds. The presence of Al is also observed. A comparison of composition of evaporates mounds and microthermometric measurements points to composition of hydrates present within frozen inclusions. Hydrate with final melting temperature in the range between –22.0 and –24.5°C ($T_m$hyd1) is hydrohalite ($NaCl \times 2H_2O$). Hydrate with temperature interval of the final melting between –11.0 and –15.4°C ($T_m$hyd2) is $KCl \times 2H_2O$.

Analyses of orpiment samples point that evaporate mounds consist only of Na and K chlorides (Fig. 4).

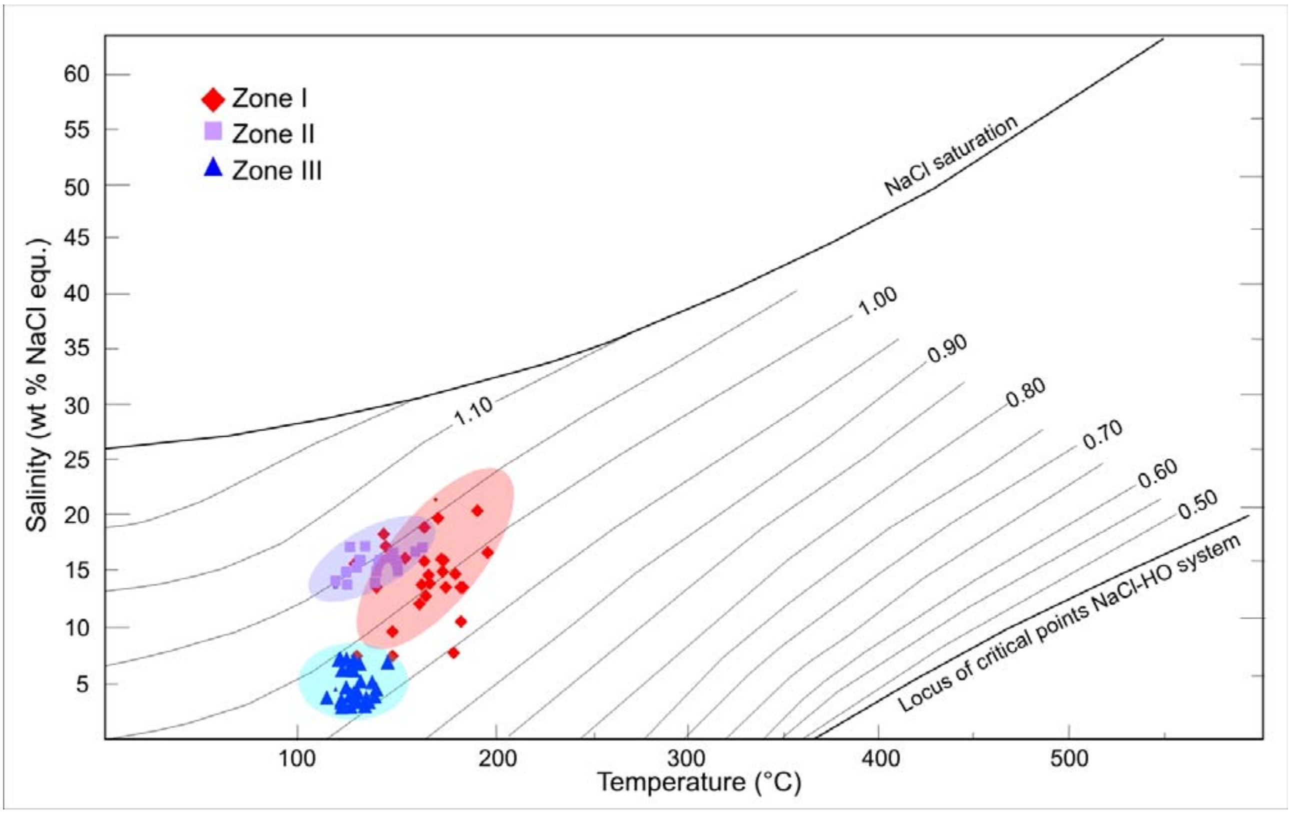

Fig. 4. Bivariate plot of homogenization temperature versus salinity

K/Ar dating

The K/Ar age dating was performed on quartz-latite sample collected on the Kožuf Mts., approximately 0.5 km N from the deposit. The whole rock and separated concentrate of hornblende, feldspar and biotite obtained K/Ar ages range from 4.6 to 5.8 Ma. The analytical data and ages of whole rock sample and separated minerals are shown in Table 1.

Table 1

The K/Ar data obtain on quartz-latite from the Kožuf Mts., Macedonia.

Sample	Dated fraction	K %	^{40}Ar* cm^3/g	^{40}Ar* %	K/Ar age (Ma)
MK-1.	Whole rock	3.05	5.486×10^{-7}	40.6	4.62 ± 0.19
MK-1.	hornblende	1.90	4.399×10^{-7}	33.1	5.79 ± 0.21
MK-1.	Biotite	4.45	9.719×10^{-7}	36.2	5.61 ± 0.20
MK-1.	feldspar	2.14	4.291×10^{-7}	38.9	5.15 ± 0.21

DISCUSSION

The Allšar deposit shares several common features with the Carlin-type deposits worldwide: (1) structural controls of mineralization; (2) calcareous sedimentary host rocks mostly accompanied with igneous rocks; (3) alterations including decarbonization, silicification, argillization and sulfidation; (4) submicron-sized gold in association with Fe-sulfides and (5) enrichment in Au, As, Hg, Sb and Tl.

The deposit is characterized by a zonal distribution of mineral assemblages and alterations. The fluid inclusions study reveals a change in temperature and composition of the mineralizing fluid across the different zones of the deposit (Fig. 4). Homogenization temperatures and salinities decrease from the southern toward the northern part of the deposit interpreted as a result of cooling and dilution. The main dissolved salts in the southern zone are Ca-Na-chlorides with a Na/Ca molar ratio between 0.2 and 19.3. In the central part of the deposit, the Na/Ca molar ratio varies in a narrow range between 0.3 and 1.3. In the northern part of the deposit, fluids are enriched in potassium. The presence of CO_2 is related to Sb-bearing jasperoids (Zone I) and to the opal precipitated north of the Zone III.

The ore fluids transported gold, arsenic, antimony, thallium, mercury and iron. The dominance of marcasite over pyrite in Zone I suggests a pH below 5. The mineralization consisting mainly of sulfides suggests that the ore forming fluids were enriched in reducing sulfur. Under such condition thallium is a very mobile element (Vink, 1993). Chemical analyses of country rocks within the Allšar deposit suggest volcanic and tuffaceous rocks as a possible source of thallium (Percival & Radtke, 1994; Frantz et al., 1994). Reaction of the ore fluids with the host carbonates resulted in an increase of pH in the northern part of the deposit. Whereas thallium sulfides show a small stability field under alkaline and reducing conditions (Vink, 1993) an increase in pH would optimize the thallium precipitation.

Although the Carlin-type deposits worldwide are spatially affiliated to organic rich carbonate rocks the role of organic matter in this type of mineralization is still unknown. Early observations on the Carlin deposit, Nevada, USA (e.g. Joralemon, 1951) suggested that metals were precipitated by reactions between mineralizing fluids and organic matter from the wall rocks which had served as a reductant or that metals were transported by organometallic complexes. Furthermore, the metal sources of the world's largest mercury deposits, Almadén (Spain: Saupé & Arnold, 1992) and Idrija (Slovenia: Palinkaš et al., 2004), are inferred to be in organic rich volcano-sedimentary complex. Contrary, some of recent works have suggested that the organic matter did not play an important role during the formation of Carlin-type mineralization (e.g. Kuehn & Rose, 1995; Gize et al., 2000).

However, it is important to notice that Beran et al. (1990) reported hydrocarbon bearing fluid inclusions within realgar from the Allšar deposit (Zone III) and that fluid inclusions hosted by opal show involvement of organic matter as well.

According to the fluid inclusion data Neogene magmatism (4.6 to 5.8 Ma) was the heat source responsible for driving convective hydrothermal circulation at the Allšar deposit, similar to that proposed for other Carlin-type deposits worldwide (e.g., Sillitoe & Bonham, 1990; Henry & Ressel, 2006; Johnston et al., 2008).

CONCLUSION

The Allšar mineral deposit occurs within sedimentary complex of the southern Vardar zone. Structurally controlled mineralization comprises mostly disseminated submicrometer-sized gold particles and Sb-As-Tl sulphides and sulfosalts. The mineralization and alterations display zonal pattern which coincides with fluid inclusion data. The southern zone (Zone I) hosts Au mineralization together with variable amount of Sb and As minerals. Alteration consists primarily of moderate to strong silicification (jasperoids). Fluid inclusion data accompanied with mineralogical features (predominance of marcasite, strong silicification) suggest participation of high temperature (T_h = 131 – 200°C), saline (up to 21.3 wt.% NaCl equ.) and low pH fluids. The central zone (Zone II), beside Au, Sb and As, carries significant amounts of Tl minerals, minor amount of Ba, Hg and traces of Pb. The mineralization is hosted by argillized tuffs, Tertiary dolostones and Triassic carbonate rocks. Decrease in both, homogenization temperature (T_h = 120 – 165°C) and salinity (14.5 and 17.1 wt.% NaCl equ.) points to the cooling and the dilution of ore-forming fluids. The northern zone (Zone III) represents the most important source of Tl mineralization. The deposition of thallium sulfides required reducing conditions. Fluid inclusion data suggest precipitation from relatively cooled (T_h = 120 – 152°C) and diluted (2.6 to 6.9 wt.% NaCl equ.) solutions. An involvement of organic matter within ore-bearing fluids was recorded by its contribution in ore-forming processes is still obscure. The authors suggest that Neogene magmatism (4.6 to 5.8 Ma) represented the heat source responsible for driving convective hydrothermal circulation at the Allšar deposit.

REFERENCES

Balogh K., 1985: K/Ar dating of Neogene volcanic activity in Hungary: experimental technique, experiences and methods of chronological studies, *ATOMKI report, Debrecen*, **D/1**, 277–288.

Beran A., Götzinger M.A., Rieck B., 1994: A fluid inclusion study of realgar from the Allšar deposit, FYR Macedonia, *N. Jahrb. Mineral. Abh.*, **167**, 345–348.

Bodnar R. J., 1990: Petroleum migration in Miocene Monterey Formation. California. USA: constraints from fluid-inclusion studies. *Mineral. Mag.*, **54**, 295–304.

Boev, B., 1988: Petrologic, Geochemical and Volcanologic Characteristics of the Volcanic Rocks of Mt. Kožuf. Ph.D. Thesis, Rudarsko-Geol. Fak., Štip, 195 pp. (in Macedonian).

Crawford M. L., 1981: Phase equilibria in aqueous fluid inclusions. Fluid inclusions: applications to petrology. In: Hollister L.S., Crawford M.L. (Eds.): *Fluid Inclusions: Applications to Petrology, Mineralogical Association of Canada Short Course Handbook*, **6**, 75–100.

Frantz E., Palme H., Todt W., El Goresy A., Pavičević M. K., 1994: Geochemistry of Tl–As minerals and host rocks at Allšar (FYR Macedonia). Solar neutrino detection with TI-205 the "LOREX" Project; geology, mineralogy and geochemistry of the Allšar deposit locality Crven Dol, *N. Jb. Miner. Abh.*, **167**, 359–399.

Gize A. P., Kuehn C. A., Furlong K. P., Gaunt J. M., 2000: Organic maturation modeling applied to ore genesis and exploration. In: Giordano T. H., Kettler R. M., Wood S. A. (Eds.) *Ore genesis and exploration: the roles of organic matter, Reviews in Economic Geology*, **9**, 87–104.

Hagemann H. W., Hollerbach A., 1986: The fluorescence behavior of crude oils with respect to their thermal maturation and degradation, *Org. Geochem.*, **10**, 473–480.

Hofstra, A. H., Cline, J. S., 2000: Characteristics and models for Carlin-type gold deposits. In: Hagemann S. G., Brown P. E. (Eds.): *Gold 2000, SEG Reviews in Economic Geology*, **13**, 163–220.

Ivanov T., 1986: Allšar the richest ore deposit of Tl in the world. *GSI-report 86–9*, Darmstadt, 6 pp.

Jakupi B., Kostić A., Anatanasijević R., Jovanović L., Torović Z., Pereygin V. P., Stetsenko S. G., 1982: On the geological age determination of orpiments from Alshar (Macedonia) by fission fragment track method, *S. G. Bull. du Mus. d'Histoir. Natur. Ser. A.*, 37.

Janković S., 1988: The Allšar Tl–As–Sb Deposit, Yugoslavia and its specific metallogenic features, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **271**, 286.

Janković S., Boev B., Serafimovski T., 1997: Magmatism and Tertiary mineralization of the Kožuf metalogenetic district, the Republic of Macedonia, with particular reference to the Alšar deposit. Univerzitet "Sv. Kiril i Metodij" – Skopje, Rudarsko-geološki fakultet, Štip, Special issue, **5**, 262 pp.

Janković S., Jelenković R., 1994: Thallium mineralization in the Allšar Sb-As-Tl-Au deposit, *N. Jb. Miner. Abh.*, **167**, 283–297.

Johnston M. K., Thompson T. B., Emmons D. L., Jones K., 2008: Geology of the Cove Mine, Lander County, Nevada, and a genetic model for the McCoy-Cove hydrothermal system, *Econ. Geol.*, **103**, 759–782.

Joralemon P., 1951: The occurrence of gold at the Getchell Mine, Nevada, *Econ. Geol.,* **46**, 267–310.

Karamata S., Pavičević M. K., Korikovkij S. K., Boronikhin V. A., Amthauer G., 1994: Petrology and mineralogy of Neogene volcanic rocks from the Allšar area, the FY Republic of Macedonia, *N Jahrb Mineral Abh*, **167**, 317–328.

Kolios N., Innocenti F., Maneti P., Peccerillo A., Giuliani O., 1988: The Pliocene volcanism of the Voras Mts. (Central Macedonia, Greece), *Bull. Volcanol.*, **1**, 3–43.

Kontak D. J., 2004: Analysis of evaporate mounds as a complement to fluid-inclusion thermometric data: case studies from granitic environments in Nova Scotia and Peru. *Can. Mineral.*, **42**, 1315–1329.

Kuehn C. A., Rose, A. W., 1995: Carlin Gold Deposits, Nevada: Origin in a Deep Zone of Mixing between Normally Pressured and Overpressured Fluids, *Econ. Geol.*, **90**, 17–36.

Lippolt H. J., Fuhrmann U., 1986: K–Ar Age deteminations on volcanics of Alshar Mine, Yugoslavia*. GSI-report 86–9*, Darmstadt, 2 pp.

McLimans R. K., 1987: The application of fluid inclusions to migration of oil and diagenesis in petroleum reservoirs, *Appl. Geochem.*, **2**, 585–603.

Palinkaš L., Strmić S., Spangenberg S., Prochaska W., Herlec U., 2004: Ore-forming fluids in the Grübler orebody, Idrija mercury deposit, Slovenia, *Schweiz. Miner. Petrog.*, **84**, 173–188.

Pavičević M. K., Cvetković V., Amthauer G., Bieniok A., Boev B., Brandstatter F., Gotzinger M., Jelenković R., Prelević D., Prohaska T., 2006: Quartz from Allšar as monitor for cosmogenic ^{26}Al: Geochemical and petrogenetic constraints, *Mineral. Petrol.*, **88**, 527–550.

Percival T. J., Radtke A. S., 1994: Sedimentary-rock-hosted disseminated gold mineralization in the Alšar district, Macedonia, *Can. Mineral.*, **32**, 649–665.

Radtke A. S., 1985: Geology of the Carlin gold deposit, Nevada. *U.S. Geological. Survey Professional Paper*, **1267**, 124 p.

Ressel M. W., Henry C. D., 2006: Igneous geology of the Carlin trend, Nevada: Development of the Eocene plutonic complex and significance for Carlin-type gold deposits, *Econ. Geol.*, **101**, 347–383.

Saupé A. F., Arnold M., 1992: Sulphur isotope geochemistry of the ores and country rocks at the Almadén mercury deposit, Ciudad Real, Spain, *Geochim. Cosmochim. Acta*, **56**, 3765–3780.

Sillitoe R. H., Bonham H. F., 1990: Sediment-hosted gold deposits: Distal products of magmatic-hydrothermal systems, *Geology*, **18**, 157–161.

Su W., Heinrich C. A., Pettke T., Zhang X., Hu R., Xia B., 2010: Sediment-Hosted Gold Deposits in Guizhou, China: Products of Wall-Rock Sulfidation by Deep Crustal Fluids, *Econ. Geol.*, **104**, 73–93.

Troesch M., Frantz E., 1992: ^{40}Ar/^{39}Ar Alter der Tl-As Mine von Crven Dol, Allšar (Macedonia), *Eur. J. Mineral.*, **4**, 276.

Vink B. W., 1993: The behavior of thallium in the (sub) surface environment in terms of Eh and pH, *Chem. Geol.*, **109**, 119–123.

Резиме

ГАСНО-ТЕ×НИ ИНКЛУЗИИ И ОДРЕДУВАЊЕ НА СТАРОСТА СПОРЕД МЕТОДОТ K/Ar НА Au-Sb-As-Tl НАОЃАЛИШТЕТО АЛШАР, МАКЕДОНИЈА

Сабина Стрмиќ Палинкаш [1], Сибила Боројевиќ Шоштариќ [2], Ладислав Палинкаш[1],
Золтан Печкај[3], Блажо Боев[4], Владимир Берманец[1]

[1]*Природно-математички факултет, Универзитет во Загреб,*
Хорватовац 95, 10000 Загреб, Хрватска
[2]*Факултет за рударство, геологија и нафтно инженерство, Универзитет во Загреб,*
Пиеротиева 6, 10000 Загреб, Хрватска
[3]*Институт за нуклеарни истражувања, Унгарска Академија на науките,*
БемТер 18ц, 4001 Дебрецен, Унгарија
[4]*Факултет за природни и технички науки, Универзитет "Гоце Делчев",*
Гоце Делчев 89, 2000 Штип, Република Македонија
blazo.boev@ugd.edu.mk

Клучни зборови: карлин; злато; талиум; арсен; антимон; гасно-течни инклузии; одредување на старост според методот К/Ар

Au-Sb-As-Tl наоѓалиштето Алшар, Македонија, се јавува во јужниот дел на Вардарската зона. Наоѓалиштето е носител на Карлински тип на минерализација сместено во карбонатен седиментен комплекс. Минералните асоцијации и алтерации пројавуваат карактеристична зонална дистрибуција. Во согласност со податоците од гасно-течните инклузии, формирањето на минерализацијата е резултат на ладењето, разблажувањето и неутрализацијата на рудоносните флуиди. Неогениот магматизам (4.6 до 5.8 Ма) служел како извор на топлина одговорен за одржување на конвектината хидротермална циркулација во наоѓалиштето Алшар.