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## TABLE OF CONTENTS

<b>332. Blažo Boev, Vladica Cvetković, Rade Jelenković, Ivan Boev</b> IMPLICATIONS OF THE GEOLOGICAL CHARACTERISTICS AND GENESIS OF THE ALLCHAR DEPOSIT FOR THE LOREX PROJECT .....	5–20
<b>333. Afrodita Zendelska, Mirjana Golomeova, Šaban Jakupi, Kiril Lisičkov, Stefan Kuvendžiev, Mirko Marinkovski</b> CHARACTERIZATION AND APPLICATION OF CLINOPTILOLITE FOR REMOVAL OF HEAVY METAL IONS FROM WATER RESOURCES.....	21–32
<b>334. Katerina Bačeva Andonovska, Trajče Stafilov, Vlado Matevski</b> BIOACCUMULATION OF SOME TOXIC ELEMENTS BY ENDEMIC PLANT SPECIES <i>ONOBRYCHIS DEGENII</i> DÖRFLER, <i>KNAUTIA CAROLI-RECHINGERI</i> MICEV. AND <i>CENTAUREA KAVADARENSIS</i> MICEV. FROM ALLCHAR LOCALITY, REPUBLIC OF MACEDONIA .....	33–44
<b>335. Violeta Stojanova, Goše Petrov</b> PALEOECOLOGICAL SIGNIFICANCE OF BENTHIC FORAMINIFERAL FAUNA FROM THE OVČE POLE BASIN, REPUBLIC OF MACEDONIA .....	45–57
<b>336. Violeta Stefanova, Todor Serafimovski, Goran Tasev</b> NATIVE GOLD COMPOSITION AND MORPHOLOGY THROUGH THE MINERAL PROCESSING STAGES AT THE BUČIM COPPER MINE, REPUBLIC OF MACEDONIA .....	59–74
<b>337. Tena Šijakova-Ivanova, Lidija Robeva-Čukovska, Filip Jovanovski, Stefan Kareski</b> MINERALOGICAL CHARACTERIZATION OF RIEBECKITE FROM ALINCI, REPUBLIC OF MACEDONIA .....	75–87
<b>Instructions to authors .....</b>	89–90

<i>Geologica Macedonica</i>	Vol.	<b>32</b>	No	<b>1</b>	pp.	<b>1–90</b>	Štip	<b>2018</b>
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## СОДРЖИНА

- 332. Блажо Боев, Владица Цветковиќ, Раде Јеленковиќ, Иван Боев**  
ВЛИЈАНИЕ НА ГЕОЛОШКИТЕ КАРАКТЕРИСТИКИ И ГЕНЕЗАТА  
НА НАОЃАЛИШТЕТО АЛШАР ВРЗ ПРОЕКТОТ ЛОРЕКС ..... 5–20
- 333. Афродита Зенделска, Мирјана Голомеова, Шабан Јакупи, Кирил Лисичков,  
Стефан Кувенциев, Мирко Маринковски**  
КАРАКТЕРИЗАЦИЈА НА КЛИНОПТИЛОЛИТ И НЕГОВА ПРИМЕНА  
ЗА ОТСТРАНУВАЊЕ НА ЈОНИ НА ТЕШКИ МЕТАЛИ ОД ВОДНИ РЕСУРСИ ..... 21–32
- 334. Катерина Бачева Андоновска, Трајче Стафилов, Владо Матевски**  
БИОАКУМУЛАЦИЈА НА НЕКОИ ТОКСИЧНИ ЕЛЕМЕНТИ ОД ЕНДЕМСКИТЕ  
ВИДОВИ РАСТЕНИЈА *ONOBRYCHIS DEGENII* DÖRFLER, *KNAUTIA*  
*CAROLI-RECHINGERI* MICEV. И *CENTAUREA KAVADARENSIS* MICEV.  
ОД ЛОКАЛИТЕТОТ АЛШАР, РЕПУБЛИКА МАКЕДОНИЈА ..... 33–44
- 335. Виолета Стојанова, Гоше Петров**  
ПАЛЕОЕКОЛОШКО ЗНАЧЕЊЕ НА БЕНТОСНАТА ФОРАМИНИФЕРНА  
ФАУНА ОД ОВЧЕПОЛСКИОТ БАСЕН, Р. МАКЕДОНИЈА ..... 45–57
- 336. Виолета Стефанова, Тодор Серафимовски, Горан Тасев**  
СОСТАВ И МОРФОЛОГИЈА НА САМОРОДНОТО ЗЛАТО  
НИЗ ФАЗИТЕ НА МИНЕРАЛНОТО ПРОЦЕСИРАЊЕ ВО РУДНИКОТ ЗА БАКАР  
БУЧИМ, РЕПУБЛИКА МАКЕДОНИЈА ..... 59–74
- 337. Тена Шијакова-Иванова, Лидија Робева-Чуковска, Филип Јовановски,  
Стефан Карески**  
МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА РИБЕКИТОТ ОД АЛИНЦИ,  
РЕПУБЛИКА МАКЕДОНИЈА ..... 75–87
- Упатство за авторите** ..... 89–90

## IMPLICATIONS OF THE GEOLOGICAL CHARACTERISTICS AND GENESIS OF THE ALLCHAR DEPOSIT FOR THE LOREX PROJECT

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**A b s t r a c t:** The polychronous and polygenetic Sb-As-Tl-Au Allchar deposit was formed in complex physico-chemical processes occurring in a heterogeneous geological environment, in interaction of polyphase hydrothermal fluids with the surrounding magmatic, sediment and metamorphic rocks. The genesis of ore mineralization is related to the products of polyphase magmatic activity of Pliocene age (~6.5 to ~1.8 My), whereas its spatial location was controlled by magmatic, structural and lithological factors. The Allchar deposit comprises several orebodies of various shapes, textural-structural characteristics and element associations. Thallium mineralization, which is of significance for the LOREX project, has been proved in the northern (Crven Dol) and the central parts of the Allchar deposit. The present depth of ore mineralization from the present soil surface is 40–120 m, whereas the paleodepth of its formation is considerably bigger. Using the method of quantitative geomorphological analysis, the erosion rate has been established to be 30–35 m/My at the broader area of the Crven Dol locality and 27–50 m/My in the central part of the deposit. Using the AMS-measurement of <sup>26</sup>Al in quartz from the southeastern part of the Allchar deposit, the erosion rate was established to be 50 to 70 m/My. Geological and mineralogical investigations to date, regarding lorandite, its trace elements – Pb, U and Th being the first and foremost, the quantities of lorandite in orebodies, and the geological age of Tl-mineralization, have provided positive results and indicate the feasibility of the LOREX project.

**Key words:** Allchar deposit; LOREX; thallium; age of mineralization; erosion

### INTRODUCTION

The Allchar Sb-As-Tl-Au volcanogenic hydrothermal deposit is situated at the northwestern margins of Kožuf Mts. (Republic of Macedonia), close to the border between Republic of Macedonia and Greece. From the geotectonic point of view, ore mineralization is related to a Pliocene volcano-intrusive complex located between the rigid Pelagonian block in the west, and the labile Vardar zone in the east (Janković and Jelenković, 1994). From the metallogenic point of view, the Allchar deposit belongs to the Kožuf ore district as part of the SerboMacedonian metallogenic province.

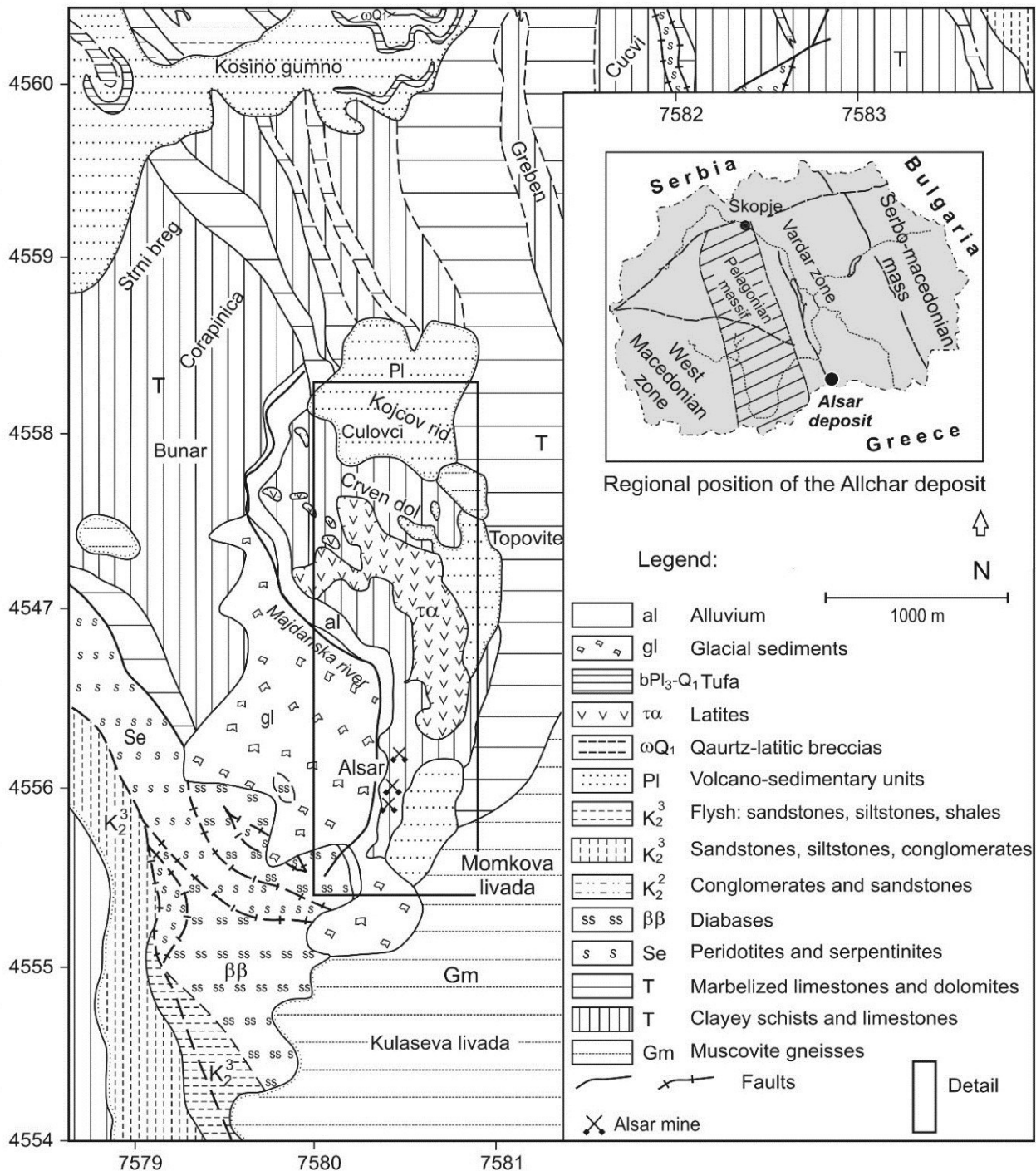
The dominant lithological members comprising the Kožuf ore district are the following: a complex of metamorphic rocks of Pre-Cambrian and Paleozoic age; the sediment rocks of the Triassic, Jurassic and Upper Cretaceous; a complex of sediments of upper Eocene age; the sediments and pyroclastic rocks of Pliocene age; the Quarternary sediments; as well as the magmatic rocks of various

composition and age (metamorphosed rhyolites and pyroclastic rocks; serpentized ultrabasic rocks; basic magmatic rocks; and the complex of volcanic rocks). Magmatic and structural control factors, that is the complex of volcanic rocks with extensively developed extrusive facies, formed in the period between 6 and 1.8 My (Lippolt and Fuhrmann, 1986; Kolios et al., 1988; Boev, 1988; Yanev et al., 2008), as well as numerous faults and cracks of various genesis and spatial orientation, are of special interest for the formation of Sb-As-Tl-Au ore mineralization.

The geological setting of the Allchar deposit is dominated by the formations of the Middle and Upper Triassic age and by the calc-alkali volcanogenic-intrusive complex of the Neogene age (Jelenković and Boev, 2011). The prevalent lithological members in the central part of the deposit are carbonate rocks (limestones, dolomites and marbles), partly sandstones and claystones, whereas quartz-

sericite-feldspar schists are prevalent in the eastern part of the deposit. Calc-alkali volcanism manifested in the occurrence of tuffs, lava flows, volcanogenic-sediment series and subvolcanic-hypabyssal intrusions with a genetic, and partly spatial relation to ore mineralization, is present in all parts of the deposit. The youngest rocks of Tertiary age are tuffaceous dolomites overlaying Mesozoic rocks in

the central, northern and southwestern parts of the deposit. This unit is of volcanogenic-sedimentary origin and is frequently mineralized. In addition to those units, in the broader deposit area, there are also formations of Jurassic age (mafic-ultramafic complexes transformed into serpentinites), Neogene molasse sediments deposited in small lacustrine basins and Quaternary sediments (Figure 1).



**Fig. 1.** Geographic and geotectonic location of the Allchar deposit (a) and a schematic geological map of the broader deposit area with the vertical projection of underground mining workings onto the terrain surface and with prevalence zones of various associations of ore elements (b)

A characteristic feature of ore mineralization in the region of the Allchar deposit is the presence of zones in the spatial distribution of chief ore components (Sb, As, Tl, Au) and the accompanying associations of elements. In the northern part of the deposit (Crven Dol), there is a prevalence of As-Tl mineralization accompanied with Sb, locally and

traces of Hg and Au. In the central part of the deposit, the basic ore components are Sb and Au, accompanied with As, Tl, minor Ba, Hg and traces of Pb (the central part); whereas the southern part of the deposit is characterized with mineralization of gold accompanied with varying concentrations of Sb and As.

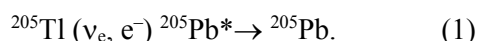
## DETERMINATION OF SOLAR NEUTRINO FLUX BY MEANS OF LORANDITE – LOREX

In addition to its having a great significance as a world thallium deposit unique by its quantity of thallium reserves and by the number of thallium minerals discovered Allchar also contains lorandite (TlAs<sub>2</sub>) in sufficient quantities to have captured the interest of a wider circle of astrophysicists, nuclear physicists, and geochemists in terms of its possible use as a geochemical detector of pp-solar neutrinos as early in 1970s (Freedman et al., 1976).

Namely, the Sun is a powerful source of neutrinos, resultant from thermonuclear reactions occurring in its center, the flux of which is

$$\Phi = 6.5 \cdot 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}.$$

The dominant component in the solar neutrino spectrum consists of so-called pp-neutrinos whose flux is determined by means of radiochemical and geochemical detectors (Kirsten, 1999). Among a larger number of possible detectors (Rowley et al., 1980), lorandite, that is <sup>205</sup>Tl, is certainly one of the very important geochemical detectors due to its having the lowest detection thresholds ( $Q_{ec} = \text{keV}$ ) as well as the longest temporal exposure ( $T = 4.3 \text{ My}$ ). The detection principle is based on the following reaction of the neutrino capture ( $\nu_e$ ) by the <sup>205</sup>Tl isotope:



The reaction, after the electron emission ( $e^-$ ), results in radionuclide <sup>205</sup>Pb with half-life of  $T_{1/2} = 14.8 \text{ My}$ .

For the time being, the use of <sup>205</sup>Tl as a solar neutrino detector is possible only by means of the mineral lorandite (TlAs<sub>2</sub>) from the Allchar deposit in Macedonia (Freedman et al., 1976). Ever since, 1986, a large number of institutions from Europe and USA have been cooperating in this very complex, multidisciplinary international project, whose acronym is LOREX, from: LORandite EXperiment (Pavičević, 1988).

All the aspects of research in the LOREX (astrophysical, nuclear, geological, mineralogical, etc.) have chiefly been covered by the proceedings of three international conferences (Nolte, 1986; Nolte and Pavičević, 1988, and Pavičević and Amthauer, 1994).

The main goal of this project is to determine the average flux of pp-neutrinos  $\Phi_\nu$  for the age period of lorandite in Allchar:

$$\Phi_\nu \sigma_\nu = C \frac{(N^{205}\text{Pb})_{\text{exp}} - (N^{205}\text{Pb})_B}{m(1 - e^{-\lambda T})} \quad (2)$$

for the value of constant  $C$ ,

$$C = 3.79 \cdot 10^{-19} \text{ mol a}^{-1}, \quad (3)$$

where  $\sigma_\nu$  is the cross-section of the neutrino capture in <sup>205</sup>Tl,  $(N^{205}\text{Pb})_{\text{exp}}$  is experimentally determined concentration of <sup>205</sup>Pb in lorandite of mass  $m$ ,  $(N^{205}\text{Pb})_B$  is concentration of <sup>205</sup>Pb in lorandite resultant from background reactions,  $\lambda$  is radioactive constant for <sup>205</sup>Pb, and  $T$  is the age of thallium mineralization in Allchar of  $4.31 \pm 0.02 \text{ My}$  (Neubauer et al., 2009b). In other words, determination of the solar neutrino flux is measurement of the concentration of <sup>205</sup>Pb in lorandite  $(N^{205}\text{Pb})_{\text{exp}}$  deducted by the content of <sup>205</sup>Pb resultant from background reactions  $(N^{205}\text{Pb})_B$  for the period of  $T$ .

To achieve success in the LOREX project, several crucial problems need to be solved. They are the following: experimental determination of the cross-section of the neutrino capture in <sup>205</sup>Tl, background reactions or the contribution in <sup>205</sup>Pb in lorandite resultant from the cosmic radiation and natural radioactivity, and detection of ultra-low concentrations in <sup>205</sup>Pb, which is  $10^{-19} \text{ g/g}$  (Pavičević, 1994; Pavičević et al., 2009). However, LOREX is a “natural detector of solar neutrinos” in contrast to radiochemical detectors. Hence, all relevant geological and genetic aspects of the Allchar deposit, as well as the mineralogical characteristics of lorandite and co-



genetic minerals must be investigated in great detail in order to grasp the impacts of the interaction of neutrinos and cosmic radiation with lorandite as a detector. Successful completion of the project depends on the accuracy and precision of the measurement of certain geological, mineralogical and geochemical values and characteristics, as well as on the extent of those investigations (Amthauer et al., 2012). They include:

– *Thallium orebodies in the Allchar area.* Orebodies investigated to date of potential interest for the LOREX project are the following: Crven Dol (Figure 2) and the so-called central part (Figure 3). This implies: orebody type, present depth, presence of thallium minerals, i.e. lorandite. In the case of Crven Dol orebody, the orebody profile, the size of

lorandite crystal, type of contact with other minerals and the possibility of lorandite separation.

– *The content of Pb in lorandite.* The content of Pb in lorandite directly affects the sensitivity and accuracy of  $^{205}\text{Pb}$  determination, which constitutes the “project detection signal”. The higher the Pb content, the lower the  $^{205}\text{Pb}$  determination method sensitivity and  $^{205}\text{Pb}$  measurement accuracy.

– *Concentration of U and Th in lorandite.* The contribution of  $^{205}\text{Pb}$  from natural radioactivity, i.e. the contribution to so-called background reactions (Equation 2. value for  $(N^{205}\text{Pb})_B$ ) depends on the concentration of those elements. The higher the concentrations of these elements than 1 ppm, the lower the accuracy of determination of  $^{205}\text{Pb}$  in lorandite coming from neutrinos.

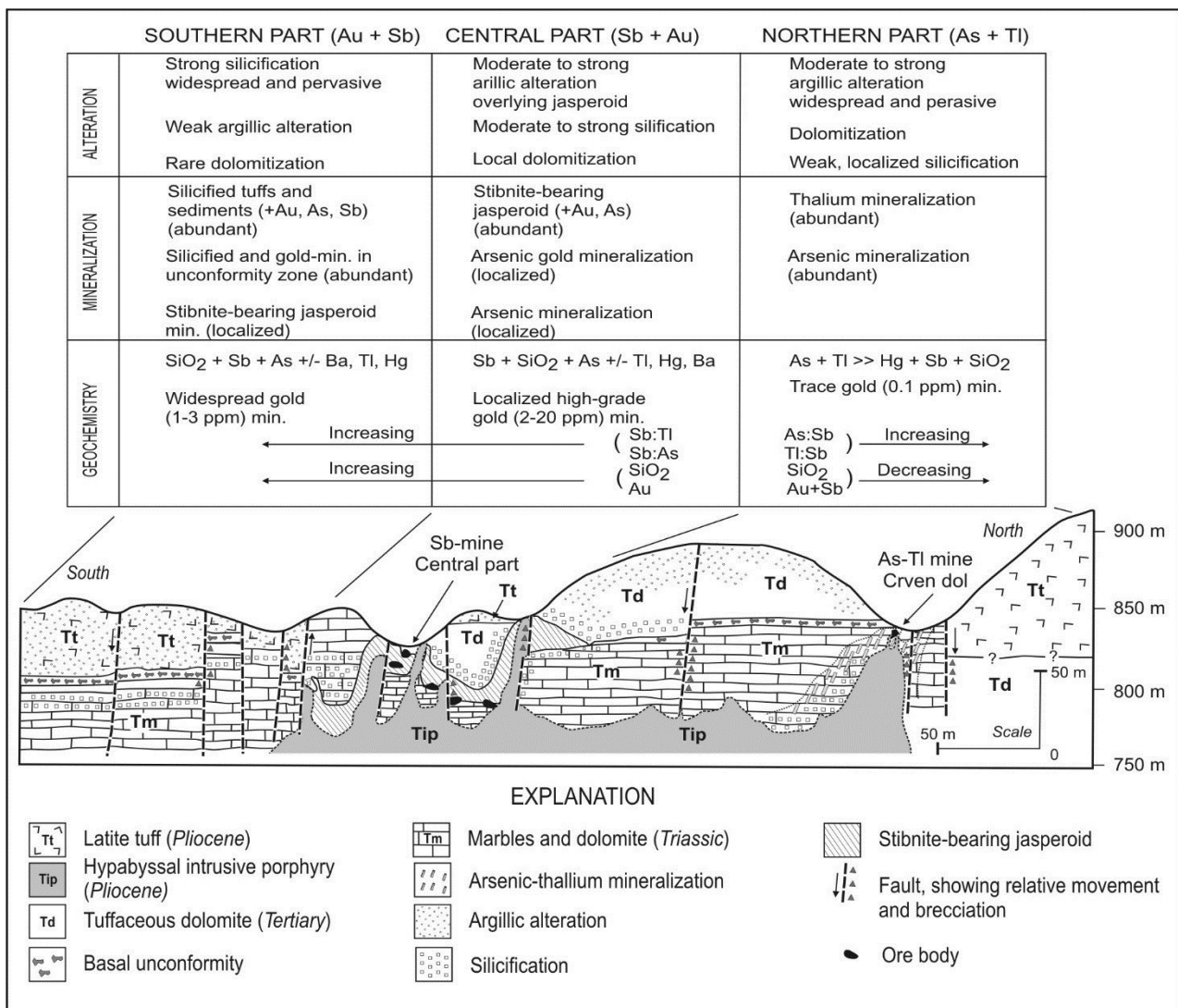
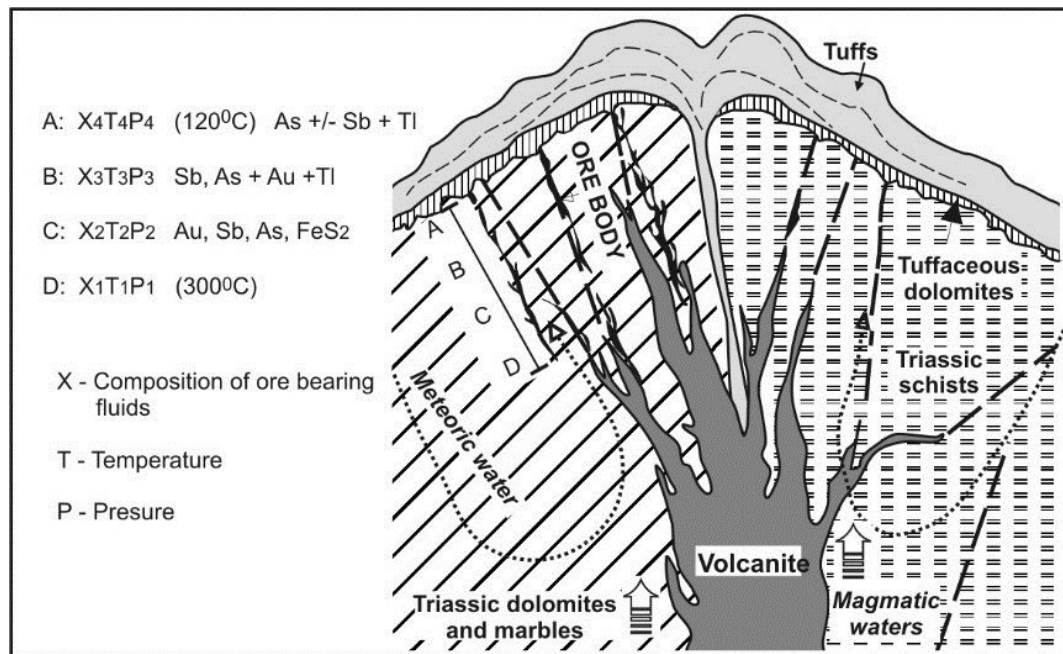


Fig. 2. A schematic geological cross-section of the Allchar deposit, with marked position of the southern, central, and northern parts of the deposit, characteristic facies of hydrothermal alteration, types of mineralization, and geochemical characteristics of mineralization (Percival and Radtke, 1994, modified)



**Fig. 3.** A schematic model of formation of the volcano-intrusive complex of Allchar, with the marked positions of the dominant types of ore mineralization on the example of the central part of the deposit (Janković, 1993, modified)

– *Geological age of Tl mineralization, i.e. lorandite.* The accuracy of determination of the average neutrino flux (Equation 2) is dependent on the geological age of lorandite as one of the four most important values in the project (in addition to  $(N^{205}\text{Pb})_{\text{exp}}$ ,  $(N^{205}\text{Pb})_B$  and  $m$ ) and is the “geological clock” of the detector, i.e. lorandite.

– *The paleodepth of lorandite in the Allchar deposit.* That is one of the most difficult and the most complex problem of the project, on which the success of LOREX project, the accuracy of determining the average solar neutrino flux, first of all, depends to a high degree. Namely, the existing lorandite depth has changed throughout the geological age of the Allchar deposit depending on the soil erosion, i.e. overlaying. The change in mineralization depth affects the contribution of  $^{205}\text{Pb}$  resultant from cosmic radiation, as the dominant component of background reactions.

– *Determination of the soil erosion in the Allchar district.* In investigations to date, two methods have been used to determine soil erosion: a) geomorphological analysis (Jelenković and Pavićević, 1994) and b) application of cosmogenic radioactive nuclides (Lal, 1991).  $^{26}\text{Al}$  and  $^{10}\text{Be}$  in quartz as monitor, that is,  $^{53}\text{Mn}$  in pyrite or marcasite may be applied as possible cosmogenic radioactive nuclides (in the case of LOREX) (Pavićević, 1994; Pavićević et al., 2004 and 2009). There are investigations underway into the application of cosmogenic stable nuclides  $^3\text{He}$  and  $^{21}\text{Ne}$  in quartz (Kounov et al., 2007).

From the standpoint of the importance of above investigations for LOREX, attention will be paid to those geological and genetic characteristics of Allchar that are directly correlated to them.

#### GEOLOGICAL SETTING OF THE ALLCHAR DEPOSIT, GENETIC MODEL AND AGE OF ORE MINERALIZATION

Geological setting of the Allchar deposit is complex. It is located in the basement composed predominantly of the Triassic rocks including dolomite, marble and siliceous dolomite in the west, and Triassic schists in the east, the Jurassic ophiolites (gabbro-peridotites) and the Cretaceous sediments (Ivanov, 1986; Janković, 1993).

Volcano-intrusive rocks of Allchar district include latite, quartz-latite, trachyte, sporadically andesite and dacite. Tuffs and related volcanoclastic rocks predominate. Intrusive facies of subvolcanic and hypabyssal latite porphyry intrusion occur at several places, predominantly in the old underground workings (Jankovic and Jelenković, 1994;

Volkov et al., 2006). The volcanic rocks are in general enriched in K and Rb (Boev, 1988; Karamata et al., 1994).

Volcanic rocks of the Kožuf Mts. were investigated in detail by Frantz et al. (1994) and Lepitkova (1995), and by Kolios et al. (1980, 1988), Eleftheriadis (1988, 1989, 1991) and Eleftheriadis et al. (2003) from its southern extension in Almopias and Voras Mountains in Greece. The volcanism is contemporaneous with widespread Plio/Pleistocene extensional tectonics as recently proposed both in Greece and Macedonia (Mercier and Sauvage, 1965; Dimanatos, 2006; Dumurdžanov et al., 2004, 2005; Burchfiel et al., 2008). The well investigated Macedonian part (Kožuf Mountains) exposes shoshonites to rhyolites, which was classified as low-Mg-K group by Yanev and coworkers (Yanev et al., 2008).

#### *Main geological characteristics of the Allchar deposit*

The Allchar deposit is polychronous and polygenetic. It has formed as a result of complex physicochemical processes occurring in a heterogeneous geological environment, in the interaction of multi-stage hydrothermal fluids with the products of poly-phase magmatic activity and surrounding sedimentary and metamorphic rocks. Mobilization, transportation and depositing of ore mineralization, as well as the supergene transformations of primary ore minerals, were determined by, and partly accompanied with, intensive pre-, sin-, and post-ore structural-tectonic terrain shaping. In those processes, there formed in the deposit several orebodies of varying ore shapes, textural-structural varieties and associations of minerals and elements, localized in various, tectonically predisposed geological environments.

The Allchar deposit is a NNW-SSE oriented antiform. It comprises several orebodies within a zone 2 km long and around 300–500 m wide. The localization of mineralization is spatially associated with an environment characterized by increased porosity and permeability, typically related to fractures and fractured zones in the vicinity of subvolcanic intrusive bodies. Such steeply dipping orebearing structures resulted from sliptype shearing movements represented by brecciated rocks often in a fine-grained gougy matrix. The increased porosity and composition of the tuffs are favorable environment for hydrothermal fluid migration and introduction of ore elements. Another favorable environment is a porous and permeable

basal zone developed as a strata-bound body along the Triassic erosion surface (Percival, 1990; Percival and Radtke, 1994).

Mineralization is associated with hydrothermally altered wallrocks including the Triassic carbonates (dolomites and marbles), the Tertiary magmatic rocks and volcano-sedimentary sequence (tuffaceous dolomite). Silicification and argillitization are the most predominant alteration products, and quartz is very abundant in hydrothermally altered volcanoclastites (Percival and Radtke, 1994; Pavičević et al., 2006). The alteration is generally believed to be associated with Plio-/Pleistocene andesite volcanism and latite intrusion, which extends from Kožuf Mts. in FYR Macedonia to Voras Mts. in Greece (Janković, 1993; Pe-Piper and Piper, 2002; Yanev et al., 2008).

The major elemental components of the Allchar deposit are Sb, As, Tl, Fe and Au, accompanied by minor Hg and Ba, and traces of Pb, Zn, Cu. Enrichment of Tl in the Allchar deposit is closely associated with increased concentrations of volatiles, such as As, Sb, Hg (Amthauer et al., 2012).

The distribution of ore metals and their concentration rates display a lateral zoning. These zones are not sharply defined and typically a gradual transition exists between zones (Figure 2).

- (i) In the northern part of deposit As and Tl prevail, accompanied by minor Sb, locally traces of Hg and Au.
- (ii) The central part of deposit is dominated by Sb and Au, but also contains significant amounts of As, Tl, minor Ba, Hg and traces of Pb.
- (iii) The southern part of the deposit is characterized by dominance of gold mineralization accompanied by variable amounts of antimony.

The most important ore minerals of the Allchar deposit are Fe-sulphides, As- and Tl-minerals, cinnabarite, and Pb- and Sb-sulphosalts, accompanied by native gold or sometimes sulphur (Janković, 1960, 1993; Ivanov 1960; 1986; Janković and Jelenković 1994; Percival and Radtke 1994).

The Allchar deposit represents the largest and richest Tl resource known in the world (Ivanov, 1986; Janković and Jelenković, 1994). The biggest part of Tl mineral resources is located in the Crven Dol orebody, situated in the northwestern part of the Allchar deposit. Mineralization was identified in various levels (823 m, 790 m and 763 m) and it is situated at greater depth in the central than in the northern part of the deposit. In addition to lorandite, there also appear realgar and more rarely orpiment.

Probable ore reserves are estimated at 4000 tons with 0.3 % Tl and 6 % As. Today, it is an abandoned underground mine.

#### *Forms of orebodies, textural varieties and ore mineral composition*

The Allchar deposit consists of several orebodies of various morphological characteristics, varying degrees of ore mineral concentrations (textural-structural varieties of ore), mineral compositions and element associations. From the standpoint of environment of their localization, that is the control factors of spatial position of orebodies and conditions for formation, there are two dominant environments of their formation: a) "Central part and southern part" of the Allchar deposit, and b) "Northern part" of the Allchar deposit (Janković S., Jelenković R., 1994; Janković S., Boev B., Serafimovski T., 1997).

In the central and southern parts of the deposit, hydrothermal mineralization of antimony, accompanied with As, Tl, and Au minerals, is dominant (Amthauer et al., 2012). It consists of:

(1) sheet-form, prevalently stibnite orebodies (ore veins and elongated lenses), localized in the zones of contact between subvolcanic magmatic bodies and dolomites and tuffaceous dolomites, as well as bodies in the tectonized zones in carbonaceous rocks and silicified tuffs (dominated by orebodies of massive, brecciated and stockwork texture);

(2) orebodies in the shape of lenses localized in carbonaceous rocks accompanied with morphologically complex, stockwork-type of ore mineralization (realgar bodies);

(3) structurally controlled elongated-lenticular to vein-like, primarily massive pyrite-marcasite bodies and bodies of complex, predominantly stibnite composition;

(4) veinlet- or vein-type stibnite orebodies spatially controlled by the systems of cracks and fault zones in tuffaceous dolomites and dolomites of the Triassic age, and lenticular, predominantly compact stibnite bodies in silicified dolomites (jasperoids);

(5) morphologically complex, irregularly lenticular and columnar stibnite impregnation-type orebodies accompanied with pyrite, marcasite and gold (contact of basalt tuffaceous dolomites and/or Triassic carbonaceous rocks and in silicified, to various degrees argillitized volcanites); pyrite-marcasite and stibnite bodies, accompanied with arsenic and thallium sulfides (zones of silicified dolomites – jasperoids), and

(6) veinlet-vein-type orpiment type of ore mineralization formed in the zone of dolomite-volcanite contact.

In the northern part of the deposit, which also encompasses the Crven Dol site, the predominant mineralization is that of As-Tl-Fe-S, rarely of Sb with traces of Au and Hg. It consists of:

(1) morphologically complex, massive realgar orebodies, localized in dolomites in the zone of contact with subvolcanic intrusions, as well as in brecciation zones;

(2) stratiform, band-type and vein-like orebodies of orpiment in tuffs and tuffaceous dolomites, localized in the lower levels of massive realgar orebodies;

(3) morphologically complex, impregnation type Tl-As mineralization in carbonaceous rocks, mostly dolomites, and

(4) morphologically complex ore mineralization with supergene (secondary) arsenic minerals.

From the standpoint of the LOREX project realization, orebodies in the "Central part" of the Allchar deposit (types 2, 3 and 5 localized at the hypsometric level of ~850–775 m), as well as the types of orebodies in the northern part of the deposit, at the Crven Dol location (types 1 and 3 localized at the level of ~800–750 m), are of special significance. Investigatory works conducted to date indicate the presence of the most significant thallium resources in this area, from which lorandite and cogenetic minerals can be extracted. Further, the research conducted to date has yielded calculation of the paleodepth of ore mineralization formation and of the erosion degree for those sites.

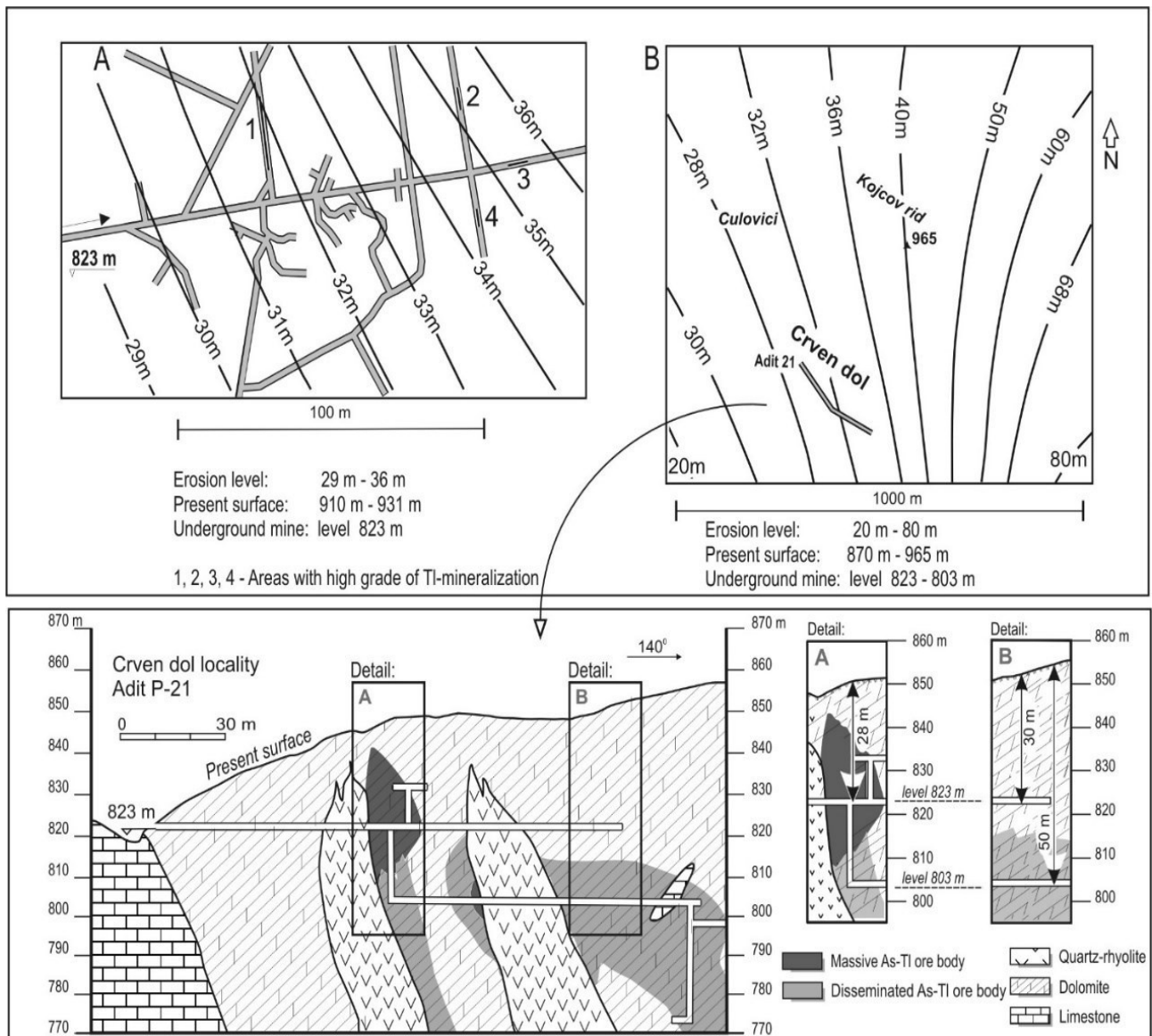
#### *General model of ore mineralization formation*

The numerousness of separate morphological, textural-structural and mineral types of orebodies in the Allchar deposit, together with the vertical and lateral zoning in the distribution of ore elements in the deposit (southern, central, and northern parts of the deposit), points to the complexity of metallogenic development of the broader area of the analyzed site, that is, to the existence of a complex volcanic apparatus in the domain of a mineralization system of Pliocene age and to a synchronous pulsative hydrothermal activity of various geochemical features in the spatially separate parts of the hydrothermal system (Jelenković and Boev, 2011). Although the process of ore mineralization process is a complex one, two complementary genetic systems may generally be pinpointed: (1) the system of the "central and southern part" of the Allchar deposit

and (2) the system of the “northern part” of the Allchar deposit. Those systems differ not only in terms of the characteristics of spatial localization environment and of the control factors of the spatial location of orebodies and types or ore formation, but also in terms of the conditions of their formation. In certain segments of the model, however, including the primary sources of ore elements, sulfur, origin of hydrothermal fluids, etc., the models have a series of similarities.

The common characteristics of the ore mineralization are the following: 1 – relation to the com-

plex vulcano-intrusive Allchar complex of Pliocene age, 2 – structural and lithologically controlled position of orebodies, 3 – relation of ore mineralization with hydrothermally altered rocks, 4 – presence of various morphological and textural-structural types of orebodies, 5 – formation of ore mineralization in relatively small depths from paleosurface in various lithological units, 6 – depositing of ore mineralization from low-temperature hydrothermal fluids, 7 – complex mineral composition of orebodies with a dominant presence of minerals from the group of sulfides (Figure 4).



**Fig. 4. A)** Maps of the erosion degree in the Allchar area obtained using the method of quantitative geomorphological analysis (erosion isohypses refer to the period of 1 My). Fig. on the left: A schematic of the erosion degree in the central part of the Allchar deposit with the marked position of mining works and zones of higher thallium contents. Fig. on the right: A schematic of the erosion degree in the broader area of the Crven Dol locality with the marked position of the adit P-21. **B)** Geological profile through orebodies of arsenic and thallium in the Crven Dol locality (Adit-21) with the marked position of mining works, their depth relative to the land surface and the textural varieties of ore.

In the case of the central and southern parts of the Allchar deposit, the following model of ore mineralization formation may be accepted:

*Primary sources of sulfur and useful components:* According to the results obtained from investigations into  $\delta^{34}\text{S}$  isotope to date (Serafimovski and Boev, 1990/91), it is maintained that the sulfur from ore minerals of the Allchar deposit has volcanic origin. The sulfur isotopic composition of several samples of different parageneses and location was analyzed by Franz and coworkers (Frantz et al., 1994). Large variations are found in  $\delta^{34}\text{S}$  values of crustal and mantle rocks. These differences of  $\delta^{34}\text{S}$  values are the result of the chemical behaviour of sulfur within the Earth's crust. All obtained  $\delta^{34}\text{S}$  values are close to zero. Therefore, only magmatic origin can account for isotopic sulfur composition and associated minerals. The basic and accessory ore elements (Sb, As, Tl, Au) come from the surrounding Pliocene volcanites, and negligibly from the surrounding ore-formation rocks. On the basis of Pb-isotopic data, the ultimate origin of this element was in the continental crust.

*Origin and composition of hydrothermal solutions, mobilization of ore elements:* Hydrothermal solutions are mixtures of waters of different, prevalently magmatic and meteoritic origin. In the initial phases of activity, in the course of lateral-secretional leaching of ore elements from the primary sources, the solutions were acidic in character, with high sulphur fugacity. The ore-bearing fluids had taken over the thermic energy for movement from volcanites.

*Environments and conditions of transportation of ore elements:* The transportation of ore components (Sb, As, Tl, Au) to the site of deposition was enabled by the tectonic predisposition of the environment, that is by the presence of numerous fracture-fissure and fault systems, zones of contact between volcanites and surrounding rocks, as well as by stratification planes in the surrounding rocks. The transportation of ore components had been done by low-salinity solutions, most probably in the form of complex ions (bisulfide complexes), partly in the form of colloids, in poorly reductive conditions.

*Depositing of ore minerals:* The most significant part of ore mineralization had been deposited in the form of minerals of the sulfide and sulfosalt groups as a result of various processes: solution cooling, secondary boiling at 120 – 160 °C, at the depths of up to 500 m, and in complex fluid-surrounding rock reactions. Depending on the lithological and geochemical characteristics of the environment, that is on the extent of their tectonization, orebodies of

various shapes and vertical distribution had been formed in the deposit. In the conditions of a reactive environment (dolomites, dolomite-volcanite contact), the vertical mineralization interval was small, whereas in the conditions of a poorly reactive environment (silicified dolomites, tuffaceous dolomites, felsitic tuffs, argillization zones), it was up to 150 – 200 m. Other processes (mixing of fluids, etc.), although possible, were of no great significance.

Ore minerals had been deposited successively. In the first phase, pyrite was deposited, followed by arsenopyrite, then Sb-Pb sulfosalts, realgar, orpiment, and, finally, Tl-sulfosalts.

The generic model of the northern part of the deposit encompasses the following elements:

*Primary sources of sulphur and useful components:* According to the investigations conducted to date, the sulfur is of magmatic origin. Ore minerals (As, Tl and so on) originated from volcanites (quartzlatite/latite) from which they were mobilized by hydrothermal solutions (Frantz et al., 1994).

*Origin and composition of hydrothermal solutions, mobilization of ore elements:* Hydrothermal fluids, mixtures of waters of magmatic and meteor origin, whose temperature was in the range of 280–250–120 °C, took over the thermic energy from volcanites. Solution salinity was in the range of 7.9 and 12.9 equiv.% NaCl (Beran et al., 1990). Transportation of ore elements was done in the form of complex ions by means of acid to weakly alkaline systems of low salinity, in oxidizing environment.

*Environments and conditions of transportation of ore elements:* Ore mineralization, most probably of Pliocene age (Troesh and Frantz, 1992- Neubauer et al. 2009b), was deposited at small depths from the terrain surface, in conditions of strongly oxidizing environment and high As and Tl fugacity.

*Depositing of ore elements:* Complex, poly-phase processes of deposition of ore minerals from hydrothermal solutions have occurred as a result of a change in geochemical equilibrium of hydrothermal fluids due to their interaction with carbonaceous rocks (prevalently dolomites) and in the processes of metasomatic replacement of parent rocks. Depositing of ore minerals was preceded by a process of dolomite ankeritization and argillization of silicate rocks (400 °C, low pH values), followed by precipitation of massive small-grain mixture of siderite, pyrite, and marcasite with minor Tl. In the next stage in oxidation conditions, there occurred precipitation of pyrite with low As contents, followed by depositing of small quantities of orpiment and realgar with minor antimony at the temperature of

some 180 °C (Balić-Žunić et al., 1993). There followed depositing of thallium mineral. After the depositing of the main mineralization phase, there occurred supergene transformation of primarily formed ore mineralization and formation of numerous supergene minerals.

From the standpoint of the LOREX project, two segments of the model of formation of the Allchar deposit are of special interest: 1) the age of surrounding host rocks and ore mineralization, and 2) the primary depth of ore mineralization formation and its position relative to the present land surface.

#### *The age of mineralization and of volcanic rocks*

No determination of age of ore minerals from the Allchar deposit using modern methods of laboratory testing has been ever conducted. Hence, the exact time of formation of orebodies from this deposit cannot be spoken of with any high degree of certainty. Based on the analysis of the geological setting of the Allchar deposit and its immediate surroundings, especially on the analysis of the control factors of the spatial position of the orebodies (magmatic, structural, and lithological control factors), as well as on other relevant geological parameters or ore mineralization (morphostructural and genetic types of orebodies, relation of orebodies to hydrothermal alterations, and so on), however, the formation of the deposit may be linked to the formation of the complex volcano-intrusive complex in the broader Allchar area.

Based on the contemporary degree of knowledge of the sequence of volcanic stages in the broader Allchar area (Neubauer et al., 2009a), as well as the knowledge of the time of formation of various volcanic rocks and particular minerals formed in the course of hydrothermal alteration of the surrounding rocks of the orebodies, it is possible to draw preliminary conclusions on the ore mineralization age. It may be inferred that the depositing of ore minerals, that is the formation of various morphogenetic types of ore bodies, is in direct relation to the volcanic and post-volcanic structural-geological shaping of the terrain, i.e. with hydrothermal ore-bearing fluids that had been active in the final stages of the geological evolution of the volcanic apparatus. Deposit of ore minerals was most probably concurrent with hydrothermal alteration of surrounding host rocks and, partly, subsequent to it.

The age of volcanism in the broader Allchar deposit area was determined on several occasions in

the 1986–2009 period, using radiometric methods (K/Ar and Ar/Ar) on samples from various localities (Crven Dol, Kojčev Rid, Rudina, ADR and Vitačevo) (Table 1).

Determination of age using the K/Ar method was done on the following minerals, i.e. rocks from the Crven Dol locality: biotite and feldspars from tuffs (Lippolt and Furman, 1986); biotite, feldspars and pyroxenes from andesite (Lippolt and Furman, 1986), tuffs and volcanites (Boev, 1988), volcanites (Kolios et al., 1988), biotite from latite (Karamata et al., 1994).

Determination of age using the Ar/Ar method was done on minerals and rocks from the localities of Crven Dol, Kojčev Rid, ADR, Rudina and Vitačevo. The following were analyzed: sanidines from andesite from the Crven Dol locality (Troesh and Franc, 1992), biotites, feldspars and amphiboles from latite from the Kojčev Rid locality (Neubauer et al., 2009a), feldspars from the zones of intensively altered volcanites from the ADR and Rudina localities (Neubauer et al., 2009a), biotites from tuffs (Neubauer et al., 2009a) from the Vitačevo locality, and feldspars from tuffs from the Rudina locality (Neubauer et al., 2009a). The data on the petrologic and geochemical characteristics of the analyzed rocks may be found in the papers of Boev (1988), Yanev et al. (2008) and Neubauer et al. (2009a and 2009b), whereas the results of the conducted investigations are shown in Table 1.

Based on the above, it is possible to infer that two basic stages of volcanogenic-intrusive activity occurred in the broader Allchar deposit area: 1) the older, Miocene stage of volcanic activity, comprising the dikes of calc-alkali rocks fully hydrothermally altered during Pliocene, and 2) a younger stage of volcanism of Pliocene age, which developed in the broader Allchar deposit area.

Judging by the results of investigations to date, the younger stage of volcanic activity occurred in several sub-stages in the period of ~6.5 to ~1.8 My (Boev, 1988). Andesites and tuffs from the Crven Dol area formed in the period of 6.5 to 3.9 My, tuffs from the Vitačevo and Rudina localities in the period of  $5.1 \pm 0.1$  to  $4.31 \pm 0.2$  My, according to Neubauer and coworkers (Neubauer et al., 2009a), the biotite ages of  $5.0 \pm 0.1$  and  $5.1 \pm 0.1$  My from blocks of the Vitačevo tuff are geologically significant and interpreted to date the age of initial Pliocene volcanism in the Allchar region, whereas the latites from the Kojčev Rid locality formed in the period of  $4.8 \pm 0.2$  to 3.3 My. Experiments with amphibole from a subvolcanic latite body result in

disturbed  $^{40}\text{Ar}/^{39}\text{Ar}$  release patterns and an age of  $4.8 \pm 0.2$  My. Biotites yield slightly varying ages ranging between  $4.6 \pm 0.2$  and  $4.8 \pm 0.2$  My. K-feldspar disturbed, staircase patterns with ages increasing from  $3.3 \pm 0.2$  to  $4.0$  My. The mineral

ages of the subvolcanic latite body are interpreted, therefore, to monitor rapid cooling from ca.  $550 - 500$  °C (amphibole) through ca.  $300$ °C (biotite) to ca.  $250$  to  $160$  C (K-feldspar) between  $4.8 \pm 0.2$  and  $3.3 \pm 0.2$  My.

Table 1

*Geological age of Allchar*

Location	Rock	Mineral	Sample No.	Method	Age My	Error $\pm$ My	Reference
Crven Dol	Tuff	Biotite	1	K/Ar	4.1	0.7	Lippolt and Fuhrman, 1986
	Tuff	Biotite	2	K/Ar	4.4	0.4	
	Tuff	Feldspar	1	K/Ar	4.6	0.4	
	Tuff	Feldspar	2	K/Ar	4.4	0.5	
	Andesite	Biotite	1	K/Ar	5.1	1.9	
	Andesite	Feldspar	1	K/Ar	4.8	2.0	
	Andesite	Pyroxen	1	K/Ar	6.5	4.3	
	Andesite	Ground	1	K/Ar	3.9	0.2	
Crven Dol	Tuff	Ground	3	K/Ar	4.5 – 5.0	0.2	Boev, 1988
	Volcanite	Ground	2	K/Ar	6.5 – 1.8	0.2	
Crven Dol	Volcanite	Ground	10	K/Ar	4.5 – 1.8	0.2	Kolios et al., 1988
Crven Dol	Andesite	Sanidine	1	Ar/Ar	4.22	0.07	Troesch & Franz, 1992
Crven Dol	Latite	Biotite	1	K/Ar	5.78	0.12	Karamata et al., 1994
Kojčov Rid	Sub volcanic latite	Biotite	1	Ar/Ar	4.6 – 4.8	0.2	Neubauer et al., 2009
		K-feldspar	1	Ar/Ar	3.3 – 4.0	0.2	
		Amphibole	1	Ar/Ar	4.8	0.2	
Rudina	Altered zone	K-feldspar	1	Ar/Ar	4.31	0.02	
Vitačevo	Latite block	Biotite	1	Ar/Ar	5.0 – 5.1	0.1	
Vitačevo	Leucocratic block	Amphibole	1	Ar/Ar	1.7 – 2.6	0.1	

In the final stages of volcanic activity in the Allchar area, there was hydrothermal alteration of surrounding rocks that may conditionally be marked as the period of initial depositing of ore minerals in this area. Judging by the investigations of the age of K-feldspars from the Rudina locality, the beginning of intensive alteration of surrounding ore formation rocks, and we also infer the initial depositing of ore minerals is related to the period of  $4.31 \pm 0.02$  My (Neubauer et al., 2009b). It needs to be mentioned, however, that the above alteration age values differ from the established age of the sericite concentrate from the Rudina and Vitačevo localities ( $119.8 \pm 1.2$  to  $125.1 \pm 1.8$  My; Neubauer et al., 2009b). Since

they correspond to the age of metamorphic rocks in the basement of the Vardar zone (white mica and biotite age values ranging from  $144.4$  to  $64.0$  My; Most, 2003), one of the possible explanations is that the analyzed sericites were remobilized from the basement rocks, which needs to be either confirmed or refuted by future investigations.

*Paleodepth of ore mineralization formation and the erosion degree*

Based on the present knowledge of the characteristics of the geological setting of the Allchar deposit and of its immediate surroundings,



it may be inferred that the primary depth of ore mineralization formation varied in the range between 250–1000 m. The depth of individual orebodies varies, although mineralization formed deeper in the central part relative to the northern part of deposit. The vertical interval of mineralization for individual orebodies and/or small mineralized faults-mineral showings, ranges from 5 to 30 m to 100 m. Following ore deposition, large amounts of volcanic material covered the deposit. The volcanic cover is locally over a few hundred meters thick and protected the ore deposit from erosion. Volcanic activity, with intermittent eruptions of tuffs, lasted until 1.8 My ago and was followed by erosion of material lying above the Allchar ore deposit. Thus, the depth of mineralization was not constant, but a function of time and erosional rate. Rate of erosion was locally accelerated by uplifting.

The present depth of ore mineralization is considerably smaller than the paleodepth and is in the function of the erosion degree. In the previous period, its degree was determined using the following methods: 1 – Quantitative geomorphological analyses (Jelenković and Pavičević, 1994) and 2 – AMS determination of  $^{26}\text{Al}$  in quartz (Pavičević et al., 2004).

Quantitative geomorphological analyses: A special attention was paid to the method of terrain's slope analysis, to the theoretical development of the relief mode in time and to the analysis of the relief energy. The structural-geological investigations referred to the analysis of the terrain's geological structure and were used as an addition to the geomorphological structure and to the geomorphologic

research. In this way, the terrain degree erosion, corrected by the appropriate numerical values, reflected the influence of the tectonic and geological structure. Research into the erosion degree at the Allchar region was done at the area of 56 km<sup>2</sup>; a detailed research at the Crven Dol locality was conducted at the area of 6 km<sup>2</sup> (Figure 4).

Taking into consideration the results obtained by working out the terrain slanting line map, by the energy map and by the maps of their trends, a map of erosion degree at the Allchar area was constructed. It fully includes the factor of the regional structural-tectonic evolution and shows the real erosion state. It could be concluded that the most intensive erosion had happened in the W and SW regional part where the most intensive terrain elevating was present. Taking into consideration the size of the analyzed area and the degree of knowledge about its structural-geological setting, the data obtained about the erosion degree can be considered as relatively correct. Even notwithstanding some mistakes which surely exist, the applied calculation method, with some corrections on the basis of structural-geological research, could be reliable.

Based on preliminary geological studies, it has been concluded that the average depth of erosion is approximately 200 m, and locally deeper. The mineralized interval at Crven Dol, where lorandite used in the "LOREX" project occurs, lies, at present, at a depth of between 40 and 120 m beneath the present land surface. The depth of the Crven Dol mineralization 1.8 My. ago is thought to have been at least 250 m.

## CONCLUSION

Complex geological investigation of the Allchar deposit for the needs of LOREX project, began in September 1985, after "The Feasibility of the Solar Neutrino Detection with  $^{205}\text{Pb}$  by Geochemical and Accelerator Mass Spectroscopic Measurements" Workshop (TU – Munich, September 23 and 24, 1985). Results achieved to date, as well as the expected results of future investigations, may be divided into three groups:

- a) *Evident results that need no further improvement, since they meet the project requirements*

Orebodies of antimony, arsenic, and thallium in Crven Dol (As-Tl) and Central part (Sb-As-Tl)

localities, may provide sufficient quantities of ore for separation of "pure crystals" of lorandite in quantities of up to several kg (from at least three different depths from the soil surface) (Janković and Jelenković, 1994).

Stoichiometric composition of lorandite and trace elements in ore minerals from orebodies from the Crven Dol locality are well investigated (Pavičević, 1988; Pavičević and El Goresy, 1988; Palme et al., 1988; Pavičević, 1994; Franz et al., 1994).

Average concentrations of Pb, U and Th in lorandite, are respectable: 3.6 ppm Pb, 0.12 ppm U and 0.02 ppm Th, respectively (Pavičević, 1994; Franz et al., 1994).

Average concentrations of Pb, U and Th in realgar are: 0.02 ppm Pb, 0.03 ppm U and 0.004 ppm Th, respectively (Pavičević, 1994; Franz et al., 1994).

Average concentrations of Pb, U and Th in orpiment are: 0.77 ppm Pb, 0.04 ppm U and 0.004 ppm Th, respectively (Pavičević, 1994; Franz et al., 1994).

The geological age of hydrothermally altered andesites from the Crven Dol localities determined on sanidines is  $4.22 \pm 0.07$  My (Troesch and Franz, 1992).

The geological age of hydrothermal alteration in the Rudina locality (which is connected to the orebody in the central part of the Allchar deposit) determined on sericites is  $4.31 \pm 0.02$  My (Neubauer et al., 2009b).

Quantitative geomorphological analysis of the Allchar area where the orebodies with thallium mineralization are situated (Crven Dol and Central part), has enabled a map of erosional isohipses to be designed. The established erosion rate values are: 30 to 35 m/My for the Crven Dol locality and 27 to 50 m/My for the central part locality (Jelenković and Pavičević, 1994).

#### b) Investigations underway

Preliminary investigations of the soil erosion rate using AMS-measurement of  $^{26}\text{Al}$  in quartz from the site in the southeastern part of Allchar gives results of 50 to 70 m/My (Pavičević et al., 2004). However, the "Model of erosion determination by means of a single radionuclide" has to be corrected by the calculation model (in case of quartz) with both radionuclides, i.e.  $^{26}\text{Al}$  and  $^{10}\text{Be}$ .

Eighteen quartz samples have been investigated in the meantime, in which AMS-measurements determined the concentrations of  $^{10}\text{Be}$  and  $^{26}\text{Al}$ . Calculation of the erosion rate based on two cosmogenic nuclides in the same monitor – quartz is underway using CosmoCalc calculus (Vermeesch, 2007).

AMS-measurements of  $^{53}\text{Mn}$  in pyrite-marcasite samples from the Crven Dol location and from two locations belonging to the central part have been scheduled for November 2009. After those measurements, the erosion rate will be calculated using three cosmogenic radionuclides in two different monitors – quartz and pyrite-marcasite.

Measurement of stable cosmogenic nuclides  $^3\text{He}$  and  $^{21}\text{Ne}$  in quartz samples (Kounov et al., 2007) from three locations belonging to the Central part, ought to be completed by the beginning of November 2009.

Lorandite and realgar from the Crven Dol orebody are potential monitors for determination of the geological age using *in situ* Re/Os method.

#### c) Investigations planned for the near future:

Geological investigations of pyroxene from a location near Crven Dol, so as to determine soil erosion using stable cosmogenic nuclides  $^3\text{He}$  and  $^{21}\text{Ne}$  (Goethals et al., 2009).

In the next stage of investigation, revitalization of the underground mining workings (tunnels and adits) from the Crven Dol and Central part localities to extract sufficient quantities of loranditebearing ore.

The following stage is mineralogical enrichment and separation of lorandite and cogenetic minerals (realgar, orpiment, pyrite). This is also the last stage of geological investigations of Allchar that fall within the context of LOREX.

From the standpoint of results obtained to date from geological, mineralogical and geochemical investigations into the Sb-As-Tl mineralization in the Allchar deposit area, as well as from the standpoint of investigations scheduled for the near future (three years at most), we maintain, with high reliability, that successful completion of LOREX will be achieved.

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## Резиме

### ВЛИЈАНИЕ НА ГЕОЛОШКИТЕ КАРАКТЕРИСТИКИ И ГЕНЕЗАТА НА НАОЃАЛИШТЕТО АЛШАР ВРЗ ПРОЕКТОТ ЛОРЕКС

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**Клучни зборови:** Алшар; ЛОРЕКС; талиум; старост на минерализација; ерозија

Полигенетското и полихроно Sb–As–Tl–Au наоѓалиште Алшар е формирано во комплексни физичко-хемиски процеси кои се појавуваат во хетерогена геолошка средина, со интеракција на полифазните хидротермални флуиди и околните магматски седименти и метаморфни карпи. Генезата на рудната минерализација е поврзана со продуктите на полифазната магматска активност со плиоценска старост

(~6,5 до ~1,8 милиони години), каде што поединечните локации се управувани од магматскиот, структурниот и литолошкиот фактор. Наоѓалиштето Алшар се состои од неколку рудни тела со разновиден изглед, текстурно-структурни карактеристики и асоцијација на елементи. Талиумската минерализација која е од значење за проектот ЛОРЕКС е присутна во северниот дел (Црвен Дол) и

централниот дел од наоѓалиштето Алшар. Сегашната длабочина на рудната минерализација, сметано од сегашната површина, изнесува од 40 до 120 метри, при што палеодлабочината на формирањето е секако поголема. Користејќи го методот на квантитативната геоморфолошка анализа, степенот на ерозија е одреден на 30–35 метри/милион години во делот на Црвен Дол, а 27–50 метри/милион години во централниот дел од наоѓалиштето. Користејќи ги

АМС-мерењата на  $^{26}\text{Al}$  во кварцот од југоисточниот дел од наоѓалиштето Алшар, степенот на ерозијата е одреден на 50 до 70 метри/милион години. До денес направените геолошки и минералошки испитувања на лорандитот и ретките елементи (како прво Pb, U и Th), на количината на лорандитот во рудното тело, како и на староста на рудната П-минерализација дадоа позитивни резултати и ја индицираат можноста за реализација на проектот ЛОРЕКС.