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Allchar Deposit in Republic of Macedonia – Petrology and Age Determination

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1. 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 (Fig.1). From the geotectonic point of view, ore mineralization is related to a Pliocene volcano-intrusive complex located between the rigid Pellagonian block in the west, and the labile Vardar zone in the east. From the metallogenic point of view, the Allchar deposit belongs to the Kožuf ore district as part of the Serbo-Macedonian metallogenetic province.

2. Geology of the Kozuf district

Geologically viewed the Kozuf district is built of several geologic formations distributed in several stratigraphic complexes: complex of Precambrian metamorphic rocks; complex of Paleozoic metamorphic rocks; complex of Triassic-Jurassic sedimentary rocks; complex of Upper-Cretaceous sedimentary rocks; complex of Upper-Eocene rocks; complex of Pliocene sediments and pyroclasts and complex of Quaternary sediments.

The geologic structure also includes magmatic rocks represented by: complex of metamorphosed rhyolites and pyroclasts; complex of serpentinized ultramafic rocks; complex of basic igneous rocks, and complex of volcanic of calc-alkaline suites.

The complex of Precambrian metamorphic rocks is built of albitic gneisses and marbles situated in the vicinity of the Mala Rupa metamorphic block on the east. On the west (Mount Kozuf) the complex is built of gneisses and micaschists located in the Elen Supe tectonic block.

Gneisses and marbles have been found in the tectonically emersion block at Mala Rupa, west of the village of Konsko. Rakicevic et.al, (1970) determined a Precambrian age.

Besides the metamorphic rocks in the Mala Rupa block in the western flank of the Vardar zone and the Pelagon (Kozjak Mt), a block of metamorphic rocks-Elen Supe containing rocks of different composition, but similar degree of metamorphism, was also determined. The

Elen Supe block is built of gneisses and micaschists and its composition is similar to that determined for the lower parts of the Pelagonian metamorphic complex.

The complex of Paleozoic metamorphic rocks, unlike the Precambrian gneisses and marbles, is of lower metamorphic degree. It conformably overlies marbles of Precambrian age.

Paleozoic metamorfic rocks are most common in Adzibarica, between Keci Kaj and Gladnica, Jelovarnik and Porta as a phyllite horizon, a horizon of phyllitic schists and cipolines, quartzporphyry, phyllites, argilloschists and metasandstones with marble interlations and finally a horizon of quartzites, quartz schists and metadiabases.

The phyllite horizon also contains sericitic and epidotic schists, cipolines and marbles and metamorphosed quartzporphyry intruded by quartz veins (Adzibarica, between Keci Kaj and Gladnica). Graphitic schists have also been noticed in the series of sericitic schists. The horizon is approximately 750 m thick. It was also revealed in Adzibarica, Jelovarnik and Porta as well as in the vicinity of the Dusnica River source.

Fig. 1. Geographical position of the Alsar deposit

Cipolines and marbles alternate phyllitic schists in the horizon of cipolines and phyllitic schists west of Flora, Alcak, Ursa and Jelovranik along the River Dosnica course. They are overlain by schistose quartz porphyry distinguished as a separate horizon.

A horizon of quartzites and metasandstones was determined in Boulska Reka near Dina, Kalugjerica and Usevica. It also contains meta diabases with sporadic sulphide mineralization.

Rakicevic and Pendzerkovski (1970) determined these metamorphic rocks as early Paleozoic. Mersier (1973) determined the age of this series and that of Porta as Jurassic based on the degree of metamoprhism and because it concordantly overlies the Mala Rupa-Tsena series which he determined as Triassic.

Upper Cretaceous limestones overlie the horizon of phyllites, argilloschists and metasandstones with intercalations of marbles in the upper course of the River Dosnica.

The complex of Triassic-Jurassic sedimentary rocks is subdivided into two facies near the village of Uma (Rakicevic and Pendzerkovski, 1970):

- A facies of poly coloured shales with intercalations of limestones
- A facies of limestones and dolomite limestones of Triassic age.

*The Jurassic*is present as a facies of slab-like stratified limestones and a facies of limestones and clayey schists, quartzites and cherts in the Dve Usi, Flora and Jelovarnik localities. The rocks in the River Boula valley are covered by a thick series of pyroclastic rocks and tuffs.

The complex of Upper Cretaceous rocks is present as a series of limestones and conglomerates that corresponds to the Barremian and Albian, as well as a series of limestones of Turronian age.

The series of limestones is present in the Cardak, Dudica and Gladnica localities and in the Rzanovo and Studena Voda where these sediments comprise the top part of the nickeliferous-iron ores. The stratified limestones in the lower parts consist of marls with residues of *Nerinea olisoponensis cf. optuca, O. Turonica* fauna. Temkova (1962) considers them to be of Turronian age. According to Maksimovic (1981) the top stratigraphic border is outlined by the transgression of Alb-Cennomanian and Cennomanian when the weathering crust was mostly destroyed and re-deposited as oolitic sedimentary iron and bauxite ores.

Large portion of the Kozuf district is occupied by massive limestones, particularly in the Cardak, Dudica and Gladnica areas where they transgressively overlie Paleozoic rocks. Limestones are rather broken and karstified and 400 to 600 m thick. This is the largest thickness determined for the Sennonian limestones found in the Republic of Macedonia. Poorly preserved rudists are discovered in them and based on that data the age of these limestones was determined as Sennonian. Because of the large fissure density and karsification they represent water collectors for the rich sources of the Rivers Stara and Zarnica. The limestones of the Dudica district are intensively hydrothermally altered and intruded by young subvolcanic rocks.

The complex of Upper Eocene sediments is present as basal conglomerates overlain by flysch sediments. The basal conglomerates near the villages of Kumanicevo, Dragozel, Gornikovo and Barovo are mainly built of marly and limestone pebbles. Gabbro pebbles, diabases and limestones predominate in the conglomerates between Krnjevo and Barovo. Conglomerates alternate limestones and marly limestones or marls. The Upper Eocene sediments near the Barovo and Krnjevo villages are 800 m thick.

The complex of Pliocene sediments and pyroclasts is widespread in the Kozuf district. Essentially lacustrine sediments are built of coarse-clastic sediments that overlie the basement of various geologic formations. They overlie Upper Eocenic sediments between Barovo and Krnjevo. They are present as large-grained conglomerates and clayey sandstone sediments (between the villages of Dolna Bosava and Krnjevo).

Gravel sediments have been determined in the basement of the tuffs near the village of Gorna Bosava in the valley of the River Nistaica above the village of Cemersko. There are sands and clayey sands with intercalations of sand-clays or clayey sediments over the series of conglomerates near Krnjevo which itself is overlain by clayey carbonate rocks.

Marls overlain by clayey sand and clayey carbonate sediments with large amounts of fossil residues, bones and fauna (of mammals) occur near the village of Barovo. The last skeletons of this fauna were found in the topmost level of these clastic lacustrine sediments in diatomaceous earth beneath volcanic sediments-tuffs near Stukovi Orai in the vicinity of the village of Barovo (Garevski, 1960). The age of the sediments was determined as lower part of the Upper Pliocene based on the fauna (Izmailov, 1960). Radovanovic (1930) determined the age of these sediments as Pontian.

The Pliocene clastic sediments in the southern parts of the basin end with a travertine and lie immediately beneath the pyroclastic sediments (above the village of Boula).

Pyroclastic sedimentary rocks cover Pliocene lacustrine sediments in the south parts of the basin near Vitacevo and Gatenovo. In the southmost part they overlie the rocks of the northern slopes of Mount Kozuf and extend along the Macedonian-Greek border, south of the village of Mrezicko. In the north they extend close to the town of Kavardci and Dolni Disan (south of Negotino). The final tuffs and conglomerates can be seen in the vicinity of the village of Radnja. The volcanic sediments are from several meters up to several hundred meters thick.

A horizon of aglomerative tuffs overlain by a horizon of fine-grained volcanic ashes and glass occurs in close proximity to the Mokliski Monastery in the valley of the River Luda Mara over the clastic lacustrine sediments present as carbonate clayey material. The latest horizon of volcanic sediments consists of brecciated well banded volcanic tuffs-pyroclasts. The largest blocks of volcanic rocks were found in the north slopes of Mount Kozuf, beneath the volcanic craters and domes (above the village of Radnja and Bara, in the vicinity of Gladnica, Ametkova Glava and Konopiste).

The complex of Quaternary sediments: Large amounts of significant Quaternary terraces are found right of the River Konska. The layers are 20 to 30 m thick. They are large-grained sediments consisting of rounded fragments, built mainly of gneisses, marbles and quartz that formed from crystalline rocks from the vicinity of Mala Rupa and Keci Kaj. These terrace sediments were completely worked out - washed for gold during ancient period that is noticeable in the terrain.

Larger terrace sediments are not noticed along the valley of the River Dosnica because of the steep river sides. However, today's terrace layers can be found in the river bed. Traces of washed out river terraces can be seen in individual parts, particularly in the lower river course at the end of the cliff below the village of Dren.

Quaternary tuff sediments (20 meters thick) can be seen near the village of Sermenin in an area of approximately 200 to 300 meters in size.They are located in the mouth of the River Belica and the River Sermeninska. Similar tuffs can be seen in the River Boulska near Dina.

The River Bosava with its tributaries brings mainly volcanic material, because it passes through volcanic sedimentary series in its upper and middle courses.

Deluvial coarse-grained clastic sediments overlie the volcanic sediments near Vitacevo. Redeposited volcanic glass and ashes, known as pemza and pumice, as well as redeposited aglomerative tuffs can be noticed along the Mrezicko-Kavadarci road.

The complex of metamorphosed rhyolites and quartzporhyry is located in Paleozoic schists or Jurassic metasediments in Adzibarica and Gladnica (Mersier 1973). It is known that they are interstratified in phyllite horizon conditionally determined as Paleozoic without any stratigrafic data. Quartzporphyry near Bel Kamen and Dve Usi in the vicinity of the villages Konsko and Dudica have also been identified.

Quartzporphyries are greyish-white to green rocks and represent metamorphosed magmatic rocks, or rhyolites and pyroclasts developed, most probably, at the same time period as the sedimentary rocks that formed the phyllites. Such rocks have also been established in the terrains of neighbouring Greece in Kastaneri, south of the village of Uma.

Based on data reported by Mersier (1973) they are of Upper Jurassic age. Rakicevic and Pendzerkovski (1970) determined these rocks as early Paleozoic.

The complex of serpentinized ultramafic rocks is situated in the Studena Voda-Rzanovo-Kumanicevo zone. It represents a tectonic structure on which serpentinites along with Jurassic and Upper Cretaceous metasediments cover Paleozoic and Triassic metamorphic rocks.

Lateritic deposits of nickeliferous iron ore developed over the Rzanovo-Studena Voda zone and along with sediments of the top parts were dynamometamorphosed in conditions of prehnite pumpelite up to greenschist facies (Boev, 1982).

A large mass of serpentinized ultramafic rocks is located in the River Mrezicka above the village of Mrezicko. Serpentinized masses are also found near Alsar. The serpentinites near Mrezicko and wider are highly tectonized grading, in some parts, into serpentine and talcshists. Smaal chromite pods are known in the ultramaphic rocks.

Large masses of serpentinized ultramafic rocks are also located along the Rzanovo-Studena Voda tectonic zone. Detailed petrologic investigations determined these rocks as dunites and harzburgites. They are almost completely altered to serpentinites and only in some places relicts of fresh ultramafic rocks can be seen. Gabbro pegmatites and rodingites have also been found in the zone.

The complex of mafic igneous rocks is present as gabbro diabase complex that occupies the eastern and north-eastern parts of Kozuf district. Gabbros, diabases and spilites predominate in the complex. Minor intrusions of leucocratic granitic rocks quartzmonzonitic in composition like those in Gornicet were determined in the bordering parts between intrusive mafic rocks-gabbros and effusive rocks-spilites. Granite-porphyry dikes were also determined in the mafic rocks near Smokvica, Davidovo and Dren.

Quartzdiorites and granodiorites were identified in the north-west part of the gabbro diabase complex, near the village of Boula and Radnja as well as near Milovan and along the valley of the River Dosnica. Smaller pegmatitic lodes intersecting quartzdiorites or granodiorites were also found near Radnja Tajder (1939) carried out detailed petrologic investigations of the gabbros of this complex and determined the following major types: wehrlite, troctolite, olivine gabbro, gabbro-eucrite, uralite-gabbro, diorite and quartzdiorite, basalts and diabases.

The easternmost parts of the gabbro diabase complex on both sides of the River Vardar (from Demir Kapija to Udovo) and even further to Gevgelija are represented by diabases, spilites and keratophyre. Spilites are the most abundant among them.

Karamata (1973) gave the basic genetic assumptions related to this gabbro diabase complex. He reports that Dren-Boula gabbro diabase complex is a product of multi stage extrusions of large amounts of basaltic magma forming, first, the diabase spilite parties. Later, the prompted new masses intruded beneath the diabase crust (rarely intersecting it) forming new diabase spilite extrusions. The intruded igneous masses partiallly differentiated, but the tectonic processes and magma pulasations precluded magma differentiation.

3. Structural and volcanic characteristics of the Kozuf district

The Kozuf district is a large volcanic complex situated in the south of the Republic of Macedonia. It spreads in the area of Mount Kozuf.

According to the regional geologic setting of the Balkans, it is part of the Vardar zone. In the east the Kozuf district is limited by a fault zone which is the west border of the Demir Kapija

- Gevgelija gabbro diabase ophiolite massif. In the west it is bordered by a fault zone that separates the Pelagonian massif and the Vardar zone.
The location of this volcanic complex in the Kozuf-Kilkis transverse zone (Arsovski, 1962) and the intersection with the Vardar zone indicates a central type volcanism, activated on the tectonic intersection formed by the reactivated regional fault structures of Vardar strike (NW - SE to N - S) and the Kozuf - Kilkis (E - W) fault structure formed during the neotectonic period. This type of volcanism is characterized by ring-radial structures.
A schematic morphostructural map of the Kozuf district, was made using the anlaysis of satellite scanograms, aerophotos and geologic data obtained by field investigations (Fig.2). The neotectonic fault structures grouped into three systems.
A fault system of Vardar strike are reactivated fault structures, the oldest being those of NW - SE and the youngest of N - S orientation. Products of both incipient and major phases of volcanic activity are located along these faults. Intensive hydrothermal activity (in the area of Dudica and Alsar) of N - S strike took place affecting the products of incipient volcanic activity.
A system of faults of NE - SW to E - W strike. This system is relatively younger than the Vardar system manifesting recent seismic activity. The intersection between this fault system and faults of Vardar strike points to the younger and final volcanic activity in the Kozuf district.
Ring structures are represented by several morphologically negative shapes (that can be seen in scanograms) and a positive structure in the area of Dudica. The area of the most striking negative ring structure (Vasov Grad-Mrezicko-Topli Dol-Rozden-Alsar) is built mainly of volcanic material but it also includes Pliocene as well as Triassic and Cretaceous sedimentary material. This composition, the concentric shape and radial pattern of internal rupture structures, the type of drainage indicate that this large ring structure is a collaps caldera.
The Dudica positive ring structure can not be seen in scanograms, but it can clearly be defined by field investigations and analyses such as drainage system. Most probably the volcanic activity started in the area of this positive structure (Stara Mircevica). The products of initial volcanic activity are hydrothermally altered and covered by the products of later and final volcanic activity. The volcanic activity in the Kozuf district started in the Miocene and the isotopic age of rocks was determined as 12.1 m.y. (Troesch and Frantz, 1992)
The volcanic characteristics of the Kozuf district were determined by field investigations and analyses of plane photographs. The volcanic activities produced volcanic necks, frozen supply channels, large quantities of pyroclastitic material. Lava flows and development of typical volcanic domes have not been identified. This results from the nature of the magmatic activity and the composition of magma that gave the material for the rocks during the final phases of differentiation.
The magmatic activity included intermediary, occasionaly acidic, magma which was immobile and fairly rich in volatile components. This led to a rapid closure of supply channels resulting in a large explosive phase during volcanic activities. This is proved by the large presence of pyroclastic and epiclastic material such as lacustrine tuffs, conglomerates, volcanic glass and ashes. The large amounts of borone and fluorine in the volcanic rocks from Kozuf points to the existence of a long duration of emanation phase in the evolution of this volcanism.

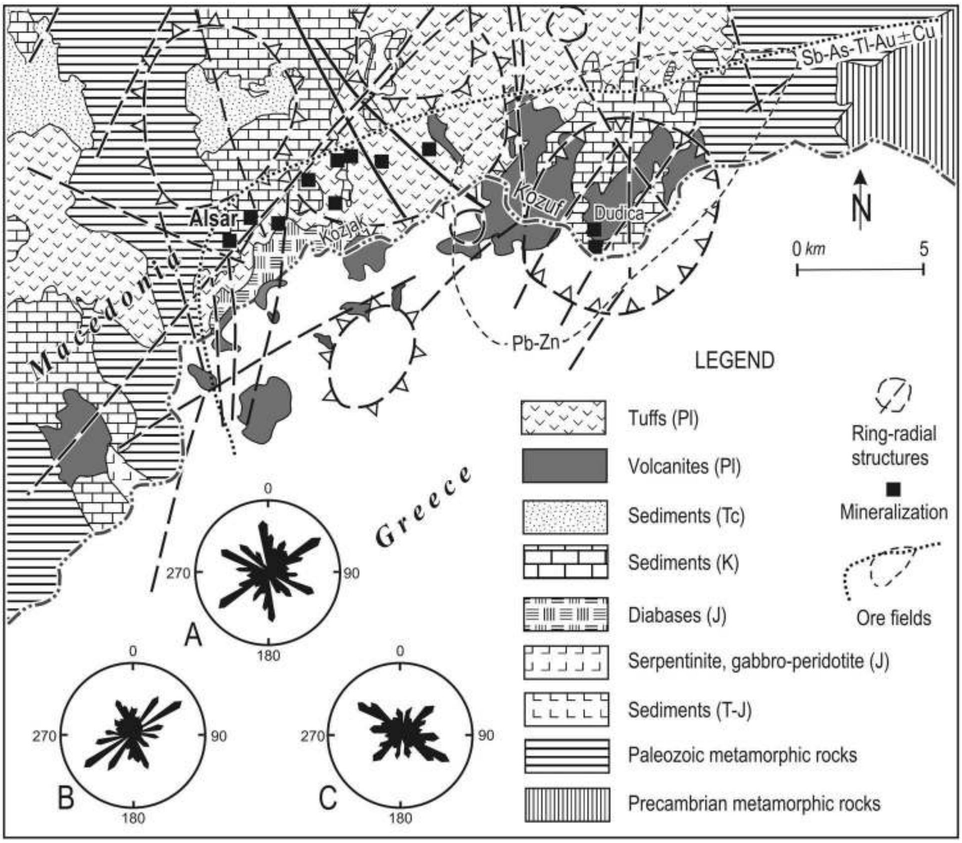


Fig. 2. Schematic morphostructural map of the Kozuf district (Boev, 1985)

4. Magmatism of the Kozuf district

The magmatic complex of the Kozuf district is a segment of the widespread magmatic activity in the petrographic province formed in the Vardar zone and the Serbo-Macedonian Mass.

General features of the petrographic province. - During the Tertiary, from the Eocene to the Pliocene, granodioritic magmas in this terrain intruded and extruded to the surface in individual tectonic zones. The evolution of this magmatism was first reported by Ilic (1962), and later shown in detail by Karamata (1962), and Karamata and Djordjevic (1980). The principal geochemical features of this magmatism were given by Karamata (1984) and Antonovic and Filipovic (1987), and individual areas were investigated in detail by Boev (1988) and Serafimovski (1990).

The Tertiary magmatism in the the Vardar zone and the Serbo-Macedonian Mass took place after closure of the Mesozoic oceanic basin (Karamata, 1983). This closure is due to the approach of the Dinaride slab and the Carpatho-Balkan block to the Serbo-Macedonian mass and the successive collison of the continental segments (Dimitrievic, 1974, Karamata, 1975, 1981). The process related to subduction during Dogger and Upper Jurassic was accompanied by calc-alkaline magmatism during the Middle and Upper Createaceous in the Carpatho-Balkanides.

Following-up continental collison resulted in thickening of the continental crust and its intrusion into the upper envelop and isostatic upliftings. Discontinuous compression caused temporary melting of the basal parts of the continental crust and mixing with larger or smaller amounts of material from the envelop (Knezevic et al., 1989). These pulsations and tactonomagmatic activities took place in the Oligocene, Miocene and Pliocene for several times (Thompson et al., 1982).

Magmas were distributed in individual areas, most commonly, in the middle parts of arch-dome structures and formed volcano-plutonic belts. Rocks formed from granodiorite, quartzdiorite to quartzmonzonite magmas and built intrusive bodies of various sizes and very large and small volcanic complexes. Rocks occur at and / or near the surface due to upliftings of individual tectonic blocks and the intensity of erosion. However, these complexes can be interpreted as volcano-plutonic complexes in which deep intrusive parts are sometimes revealed by deep erosion processes.

Generally viewed, these rocks occur in two belts that join in their middle parts (the area of Kopaonik) and separate to the north and northwest and southeast and south- southeast. These belts are not connected to one geologic unit, and are located on both sides of the ophioloite belt and intersect the geotectonic units of the Balkan Peninsula - the Dinarides, the Vardar zone and the Serbo-Macedonian mass under a slight angle.

5. Volcanic rocks of the Kozuf district

The volcanic rocks formed during the Pliocene along transverse tectonic structures of Vardar strike are revealed on Kozuf and Kozjak Mts. in the southern marginal parts of the Tikves - Mariovo Tertiary basin. Volcanic activity is manifested by the occurrence of numerous volcanic heaps which basically represent frozen supply channel, and large masses of pyroclastiic materials.Generally, the volcanic domes are distributed in a zone of east-northeast extension, most commonly on tectonic structures, in the places where they intersect older structures of northwest orientation (the Vardar strike). The transverse tectonic structures are of neotectonic age, formed in the Pliocene and lie parallel to the north margin of the Aegean valley between Thessaloniki and Kavala.

Volcanic activity in Mts. Kozuf and Kozjak is represented as various types of volcanic rocks and volcanoclasts (volcanic breccias, conglomerates and tuffs). Volcanoclasts occur as sedimentary layers in the southern parts of the Tikves-Mariovo Tertiary basin where they comprise the topmost parts of the sediments. In some places the volcanoclasts are 200 to 300 meters thick.

Volcanic rocks are present as alkali basalt (small bodies), quartzlatites (delenites), andesite-latites (trachyandesites), transitional latite-quartzlatite and quartzlatite-latite (delenite-latite), as well as latite, trachyte, trachyrhyolites and rhyolites.

The volcanic rocks of Kozuf and Kozjak Mts display greatest similarity to the series of volcanic rocks of the Buchim-Borov Dol ore district, both in their mineralogy and chemical compositions the only difference being in the time period of their formation. Namely, the rocks of Kozuf and Kozjak Mts. formed in the Pliocene, whereas those from Buchim- Borov Dol formed in the Upper Oligocene. The former are extrusive (and explosive), the latter are subvolcanic and subvolcanic to hypoabyssal facies which means that their individual upper parts are eroded deeper.

Petrology. *Alkali basalts* (trachybasalts) are the least abundant rocks in Kozuf district. They are established in the Bara locality near the source of the River Nisava. Similar rocks are found in the wider Tikves basin such as the marginal parts of the valley near the village of Koresnica, near Demir Kapija, Karaudzule on the Negotino-Stip road, near the villages of Debriste, Mrzen, Oraovec and Gaber north of Bojanciste (Tajder, 1940, Boev, 1988, Jankovic et, al,1977).

The basalt of Bara is a dark to black rock of porphyrytic texture. It is composed of andesine (with 42% An), amphibole, biotite and augite as phenocrysts and cryptocrystalline groundmass. Chemical analyses (Table 1) show that it is a basic rocks that contains $Si0_2$ ranging from 50.12 up to 51.20%, containing fairly large amount of Mg0 - the largest magnesium content among the volcanic rocks of Kozuf. It also contains some alkalis which classifies it as alkali basalt.

	1	2	3
SiO_2	50.12	50.75	51.20
TiO_2	0.65	0.58	0.60
Al_2O_3	16.70	15.86	17.80
Fe_2O_3	1.66	1.58	2.01
FeO	2.39	2.12	2.42
MnO	0.07	0.07	0.06
MgO	10.80	10.50	11.20
CaO	4.42	4.70	4.60
Na_2O	3.05	3.12	3.25
K_2O	3.51	3.45	3.65
P_2O_5	0.33	0.25	0.45
H_2O	6.37	6.50	5.72

Table 1. Chemical composition of alkali basalts of the Kozuf area (%)

Andesite porphyry volcanic rocks are established near Studena Voda, Tresten Kamen and Sreden Rid (Boev, 1988). They have pronounced porphyritic texture in which phenocrysts are represented by plagioclase that is consistent with basic andesine to acid labrador (about 50% An), amphibole, biotite and augite. The groundmass of the rock is microcrystalline, with vitrophyre base.

Chemical composition (Table 2) shows that they are intermediary rocks with 59.20 to 59.94% $Si0_2$ and that they have fairly large amount of Na_20 relative to K_20, whereas the Al_20_3 content ranges from 16.25 to 16.80%.

Latites and andesite-latites of Kozuf and Kozjak Mts. are porphyry volcanic rocks (calc-alkaline) composed of idiomoprhous phenocrysts of andesine (40 - 47% An), sanidine, amphibole, biotite and pyroxene. The groundmass is microcrystalline composed of microliths and plagioclases, sandinie, biotite and pyroxene. Apatite, ilmenite, rutile, pyrite and magnetite occur as accessory minerals. Chemical and geochemical analyses show that latites are intermediary rocks in which the $Si0_2$ content ranges from 58.67 to 60.86%, and that of Al_20_3 from 17.38 to 18.20%. It should be mentioned that they have relatively uniform amounts of major oxides such as Ca0, Na_20, and K_20 that classifies these rocks as monzonites. The Mg0 content ranges from 1.11 to 2.43% which is a characteristic of calc-alkaline rocks (Table 3).

	1	2	3
SiO_2	59.94	59.75	59.20
TiO_2	0.54	0.56	0.60
Al_2O_3	16.30	16.25	16.80
Fe_2O_3	3.97	3.88	3.71
FeO	1.52	1.48	1.50
MnO	0.05	0.06	0.06
MgO	2.00	1.95	2.12
CaO	7.33	5.52	5.60
Na_2O	2.11	2.70	3.10
K_2O	0.83	0.85	0.92
P_2O_5	0.45	0.46	0.45
H_2O	3.60	6.35	5.75

Table 2. Chemical composition of andesites of Kozuf (%)

The distribution of microelements and rare earth elements is given in Fig. 8. The diagrams and data about the content of microelements and rare earths (Table 3) display that latites possess increased concentrations of incompatible LIL elements such as Rb, Ba, and Sr. The digrams (Fig.3) also indicate a pronounced minimum of europium that gives information about fractionation processes of primary magmas or the character of partial meltings. It is obvious that the rocks are fairly rich in light rare earths with respect to heavy rare earths, with amount of rare earths of 280 ppm.

Quartzlatites (delenites) are transition varieties to latites. They are the most widespread volcanic rocks in Kozuf. They have been discovered in Blatec, Golubec, Miajlovo, in the vicinity of Dudica (Cardak, Sarena a.a.), Porta, Bela Voda, up to typical quartzlatites (delenites) near Momina Cuka. This group of volcanic rocks contains all transition varieties from latites to quartzlatites and has leucocratic nature. Quartzlatites are rocks with porphyritic structure composed mainly of andesine phenocrysts (38 to 45% An) and sanidine. They also contain low amounts of femic minerals such as amphibole, biotite and augite. Individual types of quartzlatites such as those at Bela Voda, Cardak, Golubec etc. contain large-grained idiomorphic amphibole as well as more glass in the groundmass that gives the rocks dark-grey to black colour. Quartzlatites contain higher silicium dioxide content, almost equal content of alkali oxides and lower potassium oxide content than that in latites which gives the volcanic rocks (quartzlatite of Momina Cuka) more acidic nature (Table 4).

	1	2	3	4	5	6
SiO_2	60.86	58.67	59.97	59.68	60.37	60.04
TiO_2	0.52	0.71	0.62	0.65	0.62	0.62
Al_2O_3	18.20	17.81	17.65	17.38	17.53	17.61
Fe_2O_3	4.64	5.51	4.87	4.97	4.88	4.24
MnO	0.11	0.11	0.09	0.12	0.10	0.07
MgO	1.11	1.50	1.25	2.07	1.18	2.43
CaO	4.10	5.48	4.45	4.58	4.71	5.32
Na_2O	4.35	4.05	4.44	4.35	3.83	3.87
K_2O	4.75	4.71	4.99	4.76	4.94	4.18
P_2O_5	0.56	0.68	0.73	0.73	0.56	0.16
H_2O	0.80	0.78	0.92	0.72	1.28	1.17
Zn	100	80	100	100	90	90
Mo	1	2	1	2	1	1
Ni	20	30	30	20	20	30
Co	20	20	20	20	20	20
Cd	1	1	1	1	1	1
As	13	12	11	10	10	11
Sb	0.9	0.8	0.8	0.9	1	0.9
Se	0.2	0.2	0.1	0.3	0.2	0.1
Sc	10	15	11	12	10	11
Hf	5	6	5	5	5	5
Ta	0.8	0.8	0.7	0.6	0.8	0.9
Th	31	28	29	30	31	31
U	9	8	7	8	9	9
Rb	180	174	154	181	180	174
Zr	210	200	210	210	190	200
Sr	1170	1100	1110	1050	1120	1100
Ba	1760	1800	1850	1750	1850	1800
Cr	25	26	25	26	26	25
W	4	3	4	4	4	3
Cs	41	42	41	42	42	41
La	85	85	95	78	80	81
Ce	157	145	200	210	170	175
Sm	9.1	8.13	11.2	11.1	14.1	13.2
Eu	1.9	2.0	2.1	2.3	2.5	1.9
Tb	0.78	0.75	0.74	0.68	1.11	1.10
Yb	1.85	2.01	2.20	2.50	2.70	2.82
Lu	0.28	0.30	0.31	0.32	0.30	0.29

Table 3. Chemical composition (in %) and microelements (in ppm) of the latite and andesite-latite

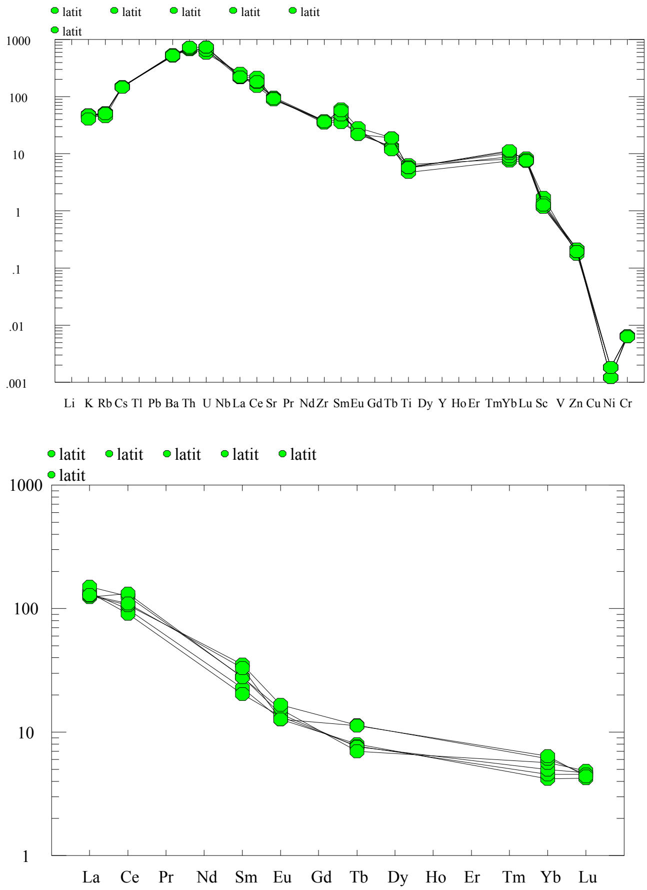
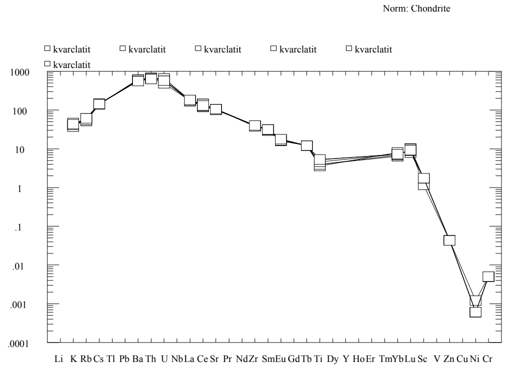


Fig. 3. Distributinot pattern of trace elements and rare earth elements in the latie and andesite-latiteof the Kozuf district (Jankovic et al, 1977)

The composition determined for quartzlatites classifies them in the alkali calcium group of rocks. Because of the large calcium and silica contents they are transitions between intermediary to acidic type of rocks. Their chemical composition is in agreement with their mineralogical composition since they are basically composed of plagioclases, potassium feldspars, amphibole and accessory minerals. It should be mentioned that taking in consideration the chemical composition of the rocks alone, would classify them as trachy-andesites or latites. However, from the aspect of their chemical composition, the presence of 14% of normative quartz in particular, the plagioclase and potassium feldspar ratio of 60:40, it is clear that they are quartzlatites.
Data related to the presence of microelements and REE indicates that the quartzlatites are enriched in LIL elements or the incompatible elements (Fig.4). They possess high contents of light elements, while total rare earths amount to 240 ppm. The rocks also contain fairly high arsenic and antimony amounts along with nickel and cobalt concentrations which is an indication of character of the deep fundament in the area.

	1	2	3	4	5	6
SiO_2	64.06	65.81	65.08	63.16	62.72	61.97
TiO_2	0.39	0.43	0.43	0.57	0.50	0.58
Al_2O_3	17.86	16.72	17.04	16.62	17.84	18.54
Fe_2O_3	3.02	2.90	3.39	4.44	4.12	3.82
MnO	0.03	0.05	0.08	0.09	0.08	0.07
MgO	1.44	0.61	0.47	1.32	0.79	0.52
CaO	3.69	3.12	5.04	4.20	3.64	2.40
Na_2O	4.21	4.56	4.34	3.92	4.09	4.74
K_2O	4.38	4.12	3.84	4.26	4.77	4.44
P_2O_5	0.19	0.39	0.54	0.50	0.54	0.19
H_2O	0.98	1.47	0.47	0.92	0.90	1.28
Zn	20	20	20	20	20	20
Mo	1	1	1	1	1	1
Ni	10	10	20	10	10	10
Co	10	10	10	10	10	10
Cd	1	1	1	1	1	1
As	10	10	10	10	10	10
Sb	0.8	0.7	0.8	0.7	0.8	0.8
Se	0.1	0.2	0.1	0.2	0.1	0.1
Sc	15	15	10	15	15	15
Hf	5	5	4	5	5	4
Ta	0.8	0.9	0.6	0.7	0.7	0.7
Th	27	28	28	29	28	27
U	7	8	8	7	6	7
Rb	190	210	200	180	190	210
Zr	220	210	220	220	210	220
Sr	1200	1250	1250	1200	1250	1250
Ba	1950	2000	2100	2100	1950	1900
Cr	20	20	20	20	20	20
W	3	4	4	3	4	5
Cs	40	41	39	39	40	40
La	62	65	66	63	63	67
Ce	140	138	115	120	125	125
Sm	7.3	7.4	6.8	7.1	7.2	7.2
Eu	1.52	1.50	1.38	1.47	1.42	1.54
Tb	0.7	0.7	0.7	0.7	0.7	0.7
Yb	2.0	1.6	1.7	1.8	1.8	1.8
Lu	0.30	0.39	0.38	0.34	0.34	0.35

Table 4. Chemical composition (in %) of quartzlatites and content of microelements (in ppm)



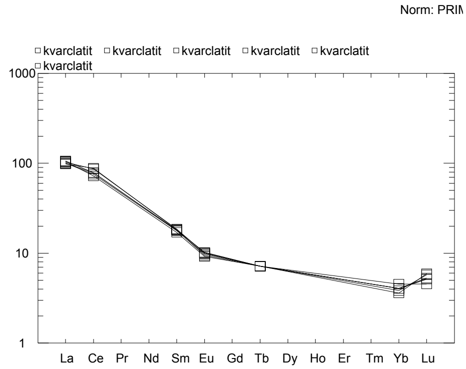


Fig. 4. Distributinot pattern of trace elements and rare earth elements in the qurtzlatites of the Kozuf district (Jankovic, et all, 1977)

Trachytes and trachyrhyolites are located in the westernmost parts of Kravica near the Sokol watch-house. The Kravica trachyte (an arsoite according to Tajder, 1940), occurs as a neck close to the Macedonian-Greek border in the territory of Greece. It is a well crystallized porphyry rock different in mineral composition from the rocks already described. It is composed of andesine, alkali feldspars such as sanidine and orthoclase and augite as femic mineral. The trachytes of the wider vicinity of Kravica are calc-alkaline in composition with large amounts of alkali oxides and higher potassium than sodium amounts that gives them pronounced potassic nature (Table 5). Chemical analyses indicate the presence of transition varieties called trachyrhyolites.

	1	2	3	4	5	6
SiO_2	55.82	55.81	55.52	58.39	56.16	60.12
TiO_2	0.95	0.86	0.92	0.93	0.93	0.55
Al_2O_3	18.41	18.06	18.88	19.17	17.76	17.84
Fe_2O_3	5.11	5.26	5.14	3.95	5.06	3.86
MnO	0.15	0.13	0.16	0.12	0.19	0.09
MgO	1.81	1.61	2.01	0.88	1.70	1.51
CaO	5.81	4.76	4.76	4.37	5.07	4.62
Na_2O	4.80	3.53	4.39	5.31	4.38	3.86
K_2O	5.74	6.50	6.37	6.10	6.26	5.05
P_2O_5	0.75	0.73	0.57	0.50	0.71	0.36
H_2O	1.09	2.26	2.22	1.15	1.38	1.27

Table 5. Chemical composition of trachytes (in %)

The Gradesnica Rhyolites are represented by lava extrusions of perlitic composition. Chemical analyses (Table 6) show that they are the most acid rocks occurring in the vicinity of Gradesnica west of Kozjak Mt. They are the last volcanic rocks formed in Kozuf and Kozjak Mts. They are of the Pleistocene (the Lower Quaternary) age and possess rhyolitic or vitrophyre composition. They are composed of glass with microliths of feldspars as small needles that have lava flow orientation. Large sanidine and plagioclase phenocrysts in their composition in some places make them typically porphyrytic. The rocks are fairly rich in silicium dioxide that gives them acidic nature. They are rich in alkalis, particularly potassium, but poor in calcium and magnesium oxides (Table 6).

	1	2	3	4	5	6
SiO_2	72.49	71.32	71.89	73.39	72.89	71.09
TiO_2	0.30	0.30	0.26	0.25	0.28	0.32
Al_2O_3	11.22	12.85	10.20	9.46	9.78	13.30
Fe_2O_3	6.19	4.95	6.61	8.04	8.04	4.13
MnO	0.12	0.12	0.12	0.11	0.15	0.26
MgO	0.14	0.22	0.93	0.37	0.25	0.18
CaO	0.78	0.75	0.55	0.40	0.60	0.71
Na_2O	2.87	3.21	2.15	2.32	2.46	3.24
K_2O	4.83	4.85	3.95	3.84	4.31	4.79
P_2O_5	0.06	0.60	0.08	0.03	0.07	0.03
H_2O	1.08	0.60	3.23	2.18	1.52	1.95

Table 6. Chemical composition of rhyolites of Kozuf (%)

6. Summary of the mineral composition of the volcanic rocks of Kozuf

The common feature of the volcanic rocks of Kozuf is the fairly high feldspar and almost equal amounts of plagioclases and potassium feldspar present as high potassium, calcium and sodium oxide in their mineral composition. Sporadically potassium content is higher than that of sodium oxides.

The disequilibrium in plagioclase and potassium contents results in the occurrence of transitional rocks types - from alkali to calc-alkaline series.

The silicium dioxide content results in the occurrence of transitional basic (from intermediary to acid) rocks that coincide with rhyolites. The $Si0_2$ content, including the basalt type of Bara (50.12%) ranges from 55.52% up to about 69%, only in exceptional cases to 73.39% $Si0_2$.

Locality	Rock type	SiO_2 content	Norm. quartz
Bara	basalt	50.12	-
Kravica	arsoit	56.12	-
Crna Tumba	trachyte	58.67	-
Dobro Pole	latite	60.86	5.73
Bela Voda	andesite-latite	60.04	8.50
Blatec	latite-Q latite	61.77	11.50
Dudica	quartz-latite	61.97	11.90
Momina Cuka	quartz-latite	63.68	12.00
Momina Cuka	quartz-latite	64.06	13.05
Mavra Petka	trachyte-riolite	66.44	16.74
Gradesnica	rhyolite	69.06	24.87
Gradesnica	rhiolite	73.39	41.26

Table 7. Correlation between $Si0_2$ content and normative quartz in the volcanic rocks of Kozuf

Quartz within phenocrysts can rarely be noticed in samples of volcanic rocks from Kozuf. It is mostly drawn into the groundmass and can not be seen under a microscope. Its content is shown as normative quartz calculated based on its chemical composition.
Another feature of the volcanic rocks from Kozuf is that they are characterized by the high feldspar abundances and the low amount of femic minerals such as pyroxene, biotite and amphibole in particular. It can be inferred that they are of salic nature because of 70% normative feldspars present in the rock. The total salic components amount to 95% (feldspars along with quartz). Table 7 gives the correlation between the $Si0_2$ and normative quartz in individual rock types from some localities.
Table 7 shows that the amount of normative quartz increases in rocks with higher $Si0_2$ content (the acidic igneous rocks).
An interesting analysis of the correlation between feldspars in individual rock types was also carried out (Table 8).

Locality	Rock	nor.fel.	nor.plag.	nor.K-fel	Pl / K f
Kravica	Arsoite	84.5	27.5	57	32 : 67
Dudica	Q latite	80.0	28	52	35 : 65
Tumba	Latite	81.0	43	38	53 : 47
M. Cuka	Q latite	80.5	46	34	57 : 43
B.Voda	and. Latite	75.5	44.5	31	59 : 41
Blatec	Latite	72.5	46	26.5	63 : 37
Bara	Basalt	67	49	18	73 : 27

Table 8. Correlations between normative feldspars in volcanic rocks of Kozuf

Data shown in Table 8 indicates that the amount of potassium feldspar increases with the increase of the amount of feldspar, but decreases with the decrease of the amount of feldspar. And vice versa, the amount of plagioclases decreases with the increase of the amount of feldspars, but increases with the decrease of the amount of feldspars. This behaviour is due either to the genesis of the rocks or the evolution of the primary isotopes.

7. Classification of the volcanic rocks of Kozuf

The diagram (Fig. 5) shows that only a small number of volcanic rocks analyzed belong to the field of andesites of subalkali nature. Most of the data related to the chemistry of the rocks plot in the field of latites and quartz latites (calc-alkaline rocks) with transition to trachytes (alkali rocks). The most acidic volcanic rocks plot in the field of rhyolites.
Fig. 6 shows classification of the volcanic rocks of Kozuf based on $Si0_2$ and K_20 contents. It shows that they contain high potassium contents. Only andesites plot in the field of rocks of low potassium.
The diagrams in Fig 7 and 8show that the volcanic rocks of Kozuf belong to the calc-alkaline series and that they are transitions between subalkali and alkali rocks.

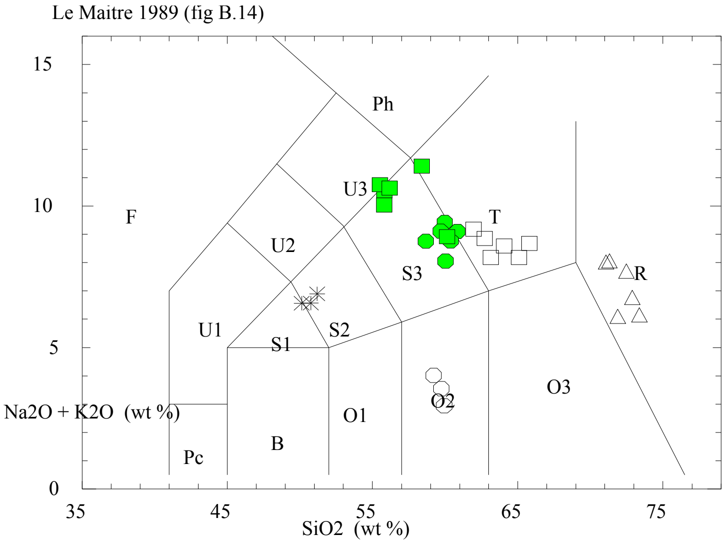


Fig. 5. Clasification of the Kozuf volcanic rocks based on the Le Maitre (1989) diagram (from Boev, 1988)

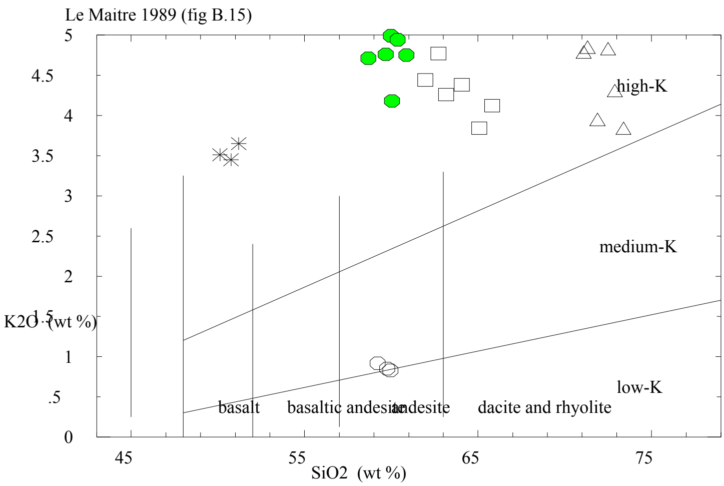


Fig. 6. Clasification of the Kozuf volcanic rocks based on SiO_2 / K_2O contents (Le Maitre, 1989) (from Boev, 1988)

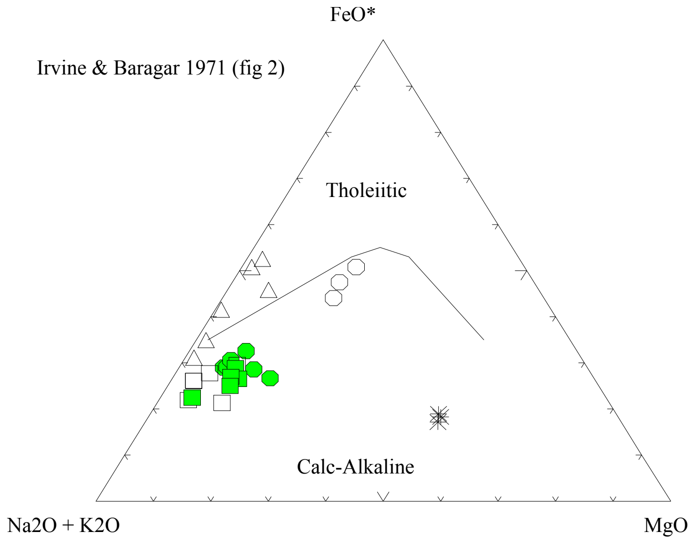


Fig. 7. Chemical composition of the Kozuf volcanic rocks (Irvine and Baragar, 1971) (from Boev, 1988)

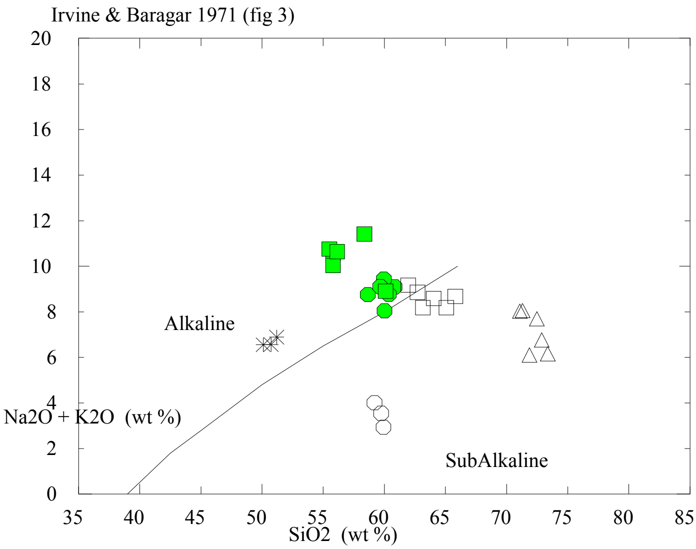


Fig. 8. Chemical composition of the Kozuf volcanic rocks (Irvine and Baragar, 1971) (from Boev, 1988)

8. Isotopic age of igneous rocks

Determination of isotopic age of Tertiary magmatism in the Republic of Macedonia was carried out by K/Ar method. Data obtained along with $^{87}Sr/^{86}Sr$ ratio are shown in Table 9.

Data indicate that the isotopic age in Tertiary volcanic and intrusive rocks ranges from 1.8 up to 29.0 m.y. depending on the locality. The youngest magmatic activity was determined for the Kozuf district (the south of Macedonia) where magmatic activity began in the period between the Miocene and Pliocene and terminated in the Quaternary. The highest isotopic value was determined for the rocks of Buchim-Borov Dol where the magmatic activity took place in the Oligocene.
The isotopic values for $^{87}Sr/^{86}Sr$ ratio indicate that they range from 0.706318 up to 0.710641.

Locality	Type of rock	Age in Ma	^{87}Sr / ^{86}Sr
Kozuf	Latite	1.8 ± 0.1	
Kozuf	Latite	5.o ± 0.2	0.708546
Kozuf	Qurtzlatite	6.5 ± 0.2	0.709019
Kozuf	Andesite	4.8 ± 0.2	
Bucim	Latite	24.6 ± 2.0	0.706928
Borov Dol	Andesite	29.0 ± 3.0	0.706897
Damjan	Andesite	28.6 ± 0.6	0.706633
Zletovo	Quarzlatite	26.5 ± 2.0	0.706318
Zletovo	Latite	24.7 ± 0.4	
Zletovo	Monconite	21.9 ± 0.4	0.707770
Sasa	Andesite-latite	14.0 ± 3.0	0.710641
Sasa	Quartzlatite	24.0 ± 3.0	0.710244

Table 9. Isotopic age of Tertiary magmatic rock from Teritory of the Republic of Macedonia (Boev et al., 1991)

The first data related to the age of volcanic rocks from Kozuf were reported by Cvijic (1906). He discovered round pebbles of extrusive rocks in Neogene lacustrine sediments. He came to the conclusion that andesite in the area of Kozuf intruded Cretaceous limestones and that they are post Cretaceous in age, even older than the Tikves Neogene.
From investigations carried out on volcanic rocks of Kozuf, Radovanovic (1930) concluded that the products of the volcanic activity are lacustrine and coeval with the Neogene sediments.
Based on investigations carried out in the terrains of Greece, Kosmat (1924) reports of possible Pliocene age for the volcanic rocks of Kozuf.
Based on superposition relationships between the volcanic agglomerative tuffs and the Neogene lacustrine sediments in which pikermi fauna was discovered in the top parts Ivanov (1960) infers that, most probably, the rocks are of the Pontian age.
Based on investigations carried out on pollens Mersier and Sauvage (1965) infer that these rocks are of Pliocene age.
Measurements of the isotopic composition of the volcanic rocks on Voras Mt. (Kozuf) in Greece gave the following data (1.8 to 5.0 m.y)(Kolios et all, 1980).

Boev (1988) carried out measurements on the isotopic composition of volcanic rocks of Kozuf in the Republic of Macedonia. Results obtained are shown in Table 10.

Rock type and locality	K%	K^{40}g/g x 10^{-6}	Ar %	$Ar^{40}cm^3$ x10^{-6}	Ar^{40}g/g x10^{-9}	Ar^{40} /K^{40} g/g x10^{-3}	m.y.
Latite of Baltova Cuka	4.36	5.08	3.0 3.0	0.84 0.76	1.50 1.36	0.29 0.27	5.0 4.7
Latite-Quartzlatite of Vasov Grad	2.55	3.04	2.0 3.0	0.64 0.64	1.14 1.16	0.38 0.38	6.5 6.5

Table 10. Isotopic age of volcanic rocks of theKozuf district (Boev, 1988)

Lipolt and Fuhrman (1986) measured some volcanic materials as products of the hydrothermal zone of Alsar and obtained results as follow (Table 11):

Rock	mineral	K%	^{40}Ar (ccm/g) x 10^{-6}	^{40}Ar atm %	m.y.
Tuff	biotite	5.19	0.83	80.4	4.1±0.7
	feldspar	1.55	0.28	63.0	4.6±0.4
Tuff	biotite	7.04	1.21	52.2	4.4±0.4
	feldspar	5.90	1.01	51.7	4.4±0.5
	biotite	4.07	0.80	78.5	5.1±1.9
Andesite	feldspar	1.18	0.22	78.7	4.8±1.9
	ground mass	5.62	0.86	25.2	3.9±0.2

Table 11. Age of volcanics of the hydrothermal zone of Alshar (Lippolt and Fuhrman, 1986)

The following conclusions can be drawn based on data of isotopic investigations: the age of the rocks is in the span of 6.5 to 1.8 m.y. that determines a Pliocenic age. Individual differentiates are of Lower Pliocene age. Troesch, Frantz and Lepitkova (1995) report of data about the subvolcanic phase in Alsar that is in accord with the Miocene (12.1 m.y.).

9. Genesis of the volcanic rocks of the Kozuf district

Boev (1988) reports of some conclusions related to the origin of magmas that formed the volcanic rocks of the Kozuf district. He considered that magma sources were located in the marginal parts between the continental crust and the envelope. He gives data about isotopic $^{87}Sr/^{86}Sr$ ratio that supports this assumption.

Further investigations carried out by Lepitkova (1991) confirmed the earlier assumptions about origin of the magma that gave the material for the formation of the volcanic rocks. Namely, values determined for the isotopic $^{87}Sr/^{86}Sr$ ratio are within 0.708568 and are very close to those that Boev (1988) determined for the volcanic rocks of Kozuf.

Fig. 9.shows the relationship between the volcanic rocks of Kozuf and individual geotectonic areas in which magmatic processes took place. The diagram indicates that data on the volcanic rocks of Kozuf plot in the field of continental slab- like basalts or the so called within plate basalts.

This confirmation can be applied to explain the processes that contributed to the formation of the volcanic rocks in Kozuf.

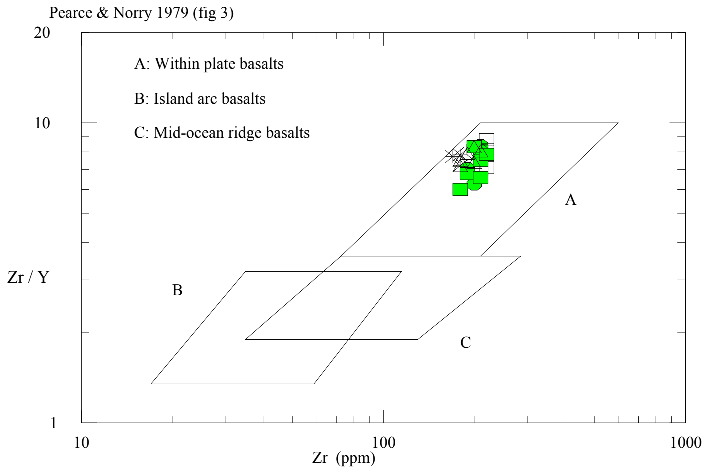


Fig. 9. Relations between the volcanic rocks of Kozuf and individual tectonic zones (based on Pearce and Norry, 1979) (From Boev, 1988)

It should be mentioned that CFB is related to the evolution of continental rift areas. The explanation about the genesis of magmas that gave the material for the formation of the volcanic rocks during the consolidation processes should be searched in the development of these structures present in the continental areas.

Chemistry of magmas related to continental rift zones is conditioned by heterogeneity of mineral and chemical compositions of the source in the envelop, the degree of partial melting and depth of its occurrence, the amount of magma that comes out on the surface etc.

There is poor geophysical data related to the presence of magmatic sources in the upper parts of the petrographic provinces. This is important for the fractionation crystallization along with the evolution of the chemistry in magmas.

The genesis of the volcanic rocks of Kozuf can be explained best within the evolution of the Vardar zone as a rift zone, recurred several times during its evolution.

Based on available data related to the magmatic activity that took place in the Vardar zone from Oligocene to the Pleistocene it can be assumed that the processes of this geotectonic unit can be related to processes that took place in continental rift zones.

Favourable conditions for the formation of magmatic sources in areas of increased thermal activity is due to partial meltings that took place in the upper parts of the envelop which supplied more materials from the lower parts of the crust.

Primary magmas formed in this mode penetrated the surface along individual structures that formed as a result of the evolution of the area changing their composition by contamination and assimilation processes.

In addition, normalized values of distribution of rare earths (Fig. 10) are applied to explain the genesis of the volcanic rocks.

Fig. 10.displays that there is no pronounced anomaly of Eu or predominance in fractionation processes of primary magma materials. The content of rare earth elements, enrichment in

light rare earths as well as the high content of LIL elements indicate that primary melt consisted of crystallized garnet that was conformable with residual plagioclase melt. Pressure in such systems amounts to some 15 Kb or 45 to 50 km depth.
From geophysical data of continental crust beneath Kozuf it can be inferred that the crust is about 40 km thick.
Based on the aforementioned data a conclusion can be drawn that magma sources were located in the marginal parts of the upper envelope and the lower crust taking in consideration, of course, erosional processes of several million years.

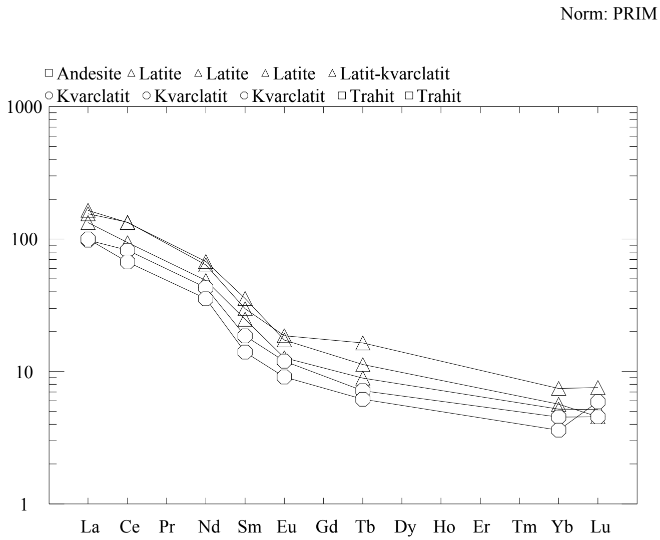


Fig. 10. The REE contents of the Kozuf volcanic rocks (From Boev, 1988)

The change in chemical composition of the extrusive magma yielding the series of volcanic rocks can be explained by assimilation processes that magma performed passing through different lithologic environments assimilating them but altering its composition as well. According to their mode of occurrence and spatial distribution the volcanic rocks of Kozuf are riftogenic, formed by magmatic activation in the marginal parts of the earth's crust and the upper envelop. This can be inferred from isotopic $^{87}Sr/^{86}Sr$ ratio that amounts from 0.7088 to 0.7090 (Boev, 1988).
Consolidation time, and the occurrence of volcanic rocks in the area were determined as 6 to 1.8 m.y. by K/Ar method (Boev, 1988) which is consistent with their stratigraphic age.

10. Principal ore seposits of the Kozuf distrct

The Kozuf metallogenic district is defined by its ore mineralization and controlling factors of its spatial distribution.
Based on available knowledge and the degree of investigations carried out several mineralization styles and metal associations such as copper, antimony, arsenic, thallium and gold were identified in the domain of the district. The Sb-As-Tl-Au is the predominating mineralization.

The following morphogenetic types are distinguished:

- Volcanogenic epithermal replacement mineralization of Sb-As-Tl association,
- Carlin-type gold mineralization,
- High sulphidation enargite vein-type mineralization accompanied, most probably, by gold mineralization as well
- Porphyry copper mineralization
- Epithermal Sb-As-Fe mineralization of vein-lense type related with fractures in the crystalline schists,
- Solfataric products are represented by native sulphur and marcasite, sporadically associated with galena.

The mineralization is of Pliocene age.

Magmatism of calc-alkaline suites and structures, both volcanic ring-radial and regional fractures are the principal factors controlling distribution of mineralization in time and space. Magmatic complexes are the principle source of ore metals and/or the source of heat energy for the formation of hydrothermal ore-bearing solutions that mobilized ore minerals from ultimate sources and transported them to the site of precipitation of mineral parageneses.

Fig. 2. shows the sites of mineralization of the Kozuf metallogenic district. The distribution pattern of mineralization is characterized by both lateral and vertical zoning. The central part of the district contains copper mineralization, surrounded by Sb-As ± Tl±Au deposit and occurrences (e.g. Alsar and Smrdliva Voda).

The Kozuf district is poorly explored, except of the Alsar deposit, and to some extent, the Dudica mineralization.

11. Alsar Sb-As-Tl-Au deposit

The Alsar complex Sb-As-Tl-Au deposit is one of the unique deposits in the world not because of its size, but mineral composition. It contains significant thallium concentrations that classify it as a unique deposit containing that metal. Besides economically significant antimony and arsenic concentrations, the Alsar deposit is the first Carlin- type gold deposit found in the Balkan Peninsula during the mid 1980s.

The latest mining activities started in 1881, and with some interruptions, lasted till 1913. During that period mainly arsenic ore was excavated and exported to Thessaloniki, Greece and Germany. Small amounts were mined out in the outcrops of the deposit. There is no data about the amount of arsenic ore mined out at that time.

The mineral potential of arsenic in the deposit is estimated at some 15.000 tons. According to today's criteria arsenic is a harmful component that results from antimony processing.

During the final years of the last century the first thallium minerals were discovered (lorandite, vrbaite a.a.) as constituents of arsenic-antimony ore.

Exploration for antimony carried out from 1953 to 1957 and from 1962 to 1965 resulted in the discovery of significant reserves of low grade ore. However, high arsenic contents in Sb-concentrations has precluded economic exploitation. The latest exploration for antimony was carried out in 1970-1973.

Mineral potential of the Alsar deposit, both mined out and available ore, exceeds 20.000 tons of antimony with 0.5% Sb as cut-off grade.

The name of the deposit pronounces as Alsar (Alshar), deriving the name of former Allchar mine (abbreviation of Allatini - a bank institution, owner of the concession, and Charteau - a mining engineer who worked in the mine).

Special interest for thallium as possible solar neutrino detector gave a new impulse for systematical investigations of thallium mineralization in the north part of the Alsar deposit (i.e. the Crven Dol ore body). This was an international LOREX Project aiming to establish reliability of the mineral lorandite from this deposit as thallium solar neutrino detector (Pavicevic, 1986, 1994). Some adits as no. 21 have been re- opened to enable taking the samples. This activity lasted from 1987 through 1993. Later it was restricted to laboratory investigations.

The mineral potential of thallium in the Alshar deposit has been estimated at 500 tons (order of magnitude).

The possible presence of gold in the Sb-As-Tl association at Alsar was initially suggested by Radtke and Dickinson (1984). During the 1986-1989 period gold mineralization was systematically explored. The results of both field and laboratory studies showed that the geological, geochemical, mineralogical and hydrothermal alteration features are strikingly similar to those which characterize Carlin-type mineralization of the Western United States (Percival and Radtke, 1990; Percival et al.,1992).

Unlike the Carlin-type gold deposits in the Western USA, the Alsar mineralization is hosted not only by sediments, but volcanics as well.

For the results of previous studies of the Alsar deposit, the reader is referred to Ivanov (1965, 1968), Jankovic (1960, 1979, 1982, 1988, 1993), Percival and Boev (1990), Percival et al. (1992), Percival and Radtke (1994), Boev and Serafimovski (1996) and for investigation of minerals to Krenner (1894), Locka (1904), Jezek (1912), Caye et al. (1967), Laurent et al. (1969), Johan et al. (1970, 1975), Terzic (1982), Balic-Zunic et al. (1986a,b, 1993), El Goresy and Pavicevic (1988), Palme et al. (1988), Jankovic and Jelenkovic (1994), Pasava et al. (1989, Frantz (1994), Frantz et al. (1994), Cvetkovic et al.(1994), Litbowitzky et al. 1995).

12. Main geological characteristics of the Allchar deposit

The Allchar deposit is polychronous and polygenetic. It has formed as a result of complex physico-chemical processes occurring in a heterogeneous geological environment, in the interaction of multi-stage hydrothermal fluids with the products of polyphase 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 environments characterized by increased porosity and permeability, typically related to fractures and fractured zones in the vicinity of subvolcanic intrusive bodies. Such steeply dipping ore-bearing 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 volcaniclastites (Percival and Radtke 1994; Pavićević 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.

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.

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, T1, 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 1965; 1986; Janković and Jelenković 1994; Percival and Radtke 1994).

13. Local geologic setting

Deposition of sandstone and claystone, followed by bedded and massive carbonate rocks (limestone, dolomite, marble) took place in the Middle and Upper Triassic. These rocks are the basement of the Alsar deposit (Fig. 11).

The quartz-sericite-feldspar schists are developed along the eastern flank of the deposit, while the central part is built of dolomite, marble, and sporadically limestone.

The dolomite series underlies marbel. Based on fission traces the age of dolomite was determined as 250 m.y. (Lepitkova, 1995).

The Mesozoic rocks are unconformably overlain by Pliocene cover and glacial till. The earliest Tertiary rocks are very likely tuffaceous dolomite. It unconformable overlies the Mesozoic basement rock, particularly in the central, northern and southwest parts of the deposit. This unit is of volcano- sedimentary provenance and commonly mineralized.

The massive tuffaceous dolomite contains sporadically intercalated sequences of fine-grained tuff, water lain ash or volcanic glass. This volcano-sedimentary unit is 100-130 m thick (Percival, 1990). The basal contact of the tuff and underlying Tertiary tuffaceous dolomite and pre-Tertiary rocks is often marked by an unconformity zone, 2 to 12 m thick. It consists of a mixture of unsorted and ungraded detrital material. This basal unconformity of the tuff unit indicates a discontinuity in the Tertiary stratigraphic section and the beginning of volcanic activity during which dolomite deposition took place (Percival, 1990). The basal contact zone is of particular interest as a preferred environment of hydrothermal alteration and mineralization, particularly in the central and southern parts of the deposit.

The unit of Pliocene felsic tuffs covers a large portion of the Alshar deposit. This volcanic sequence includes ash, crystal tuffs, tuff breccia and lacustrine tuffaceous sediments.
According to Percival (1990) the lowest level of felsic tuffs consists of soft and friable ash tuffs, grading upwards to a crystal lithic tuff and then into a crystal tuff. These tuffs contain sanidine, biotite and quartz phenocrysts in an aphanatic ground mass.
The composition of tuff braccia is similar to the crystal tuff. The tuffs deposited in the sublacustrine basins in the southern part of Alshar show bedding and contain tuffaceous sedimentary clay material (a volcano-sedimentary series).

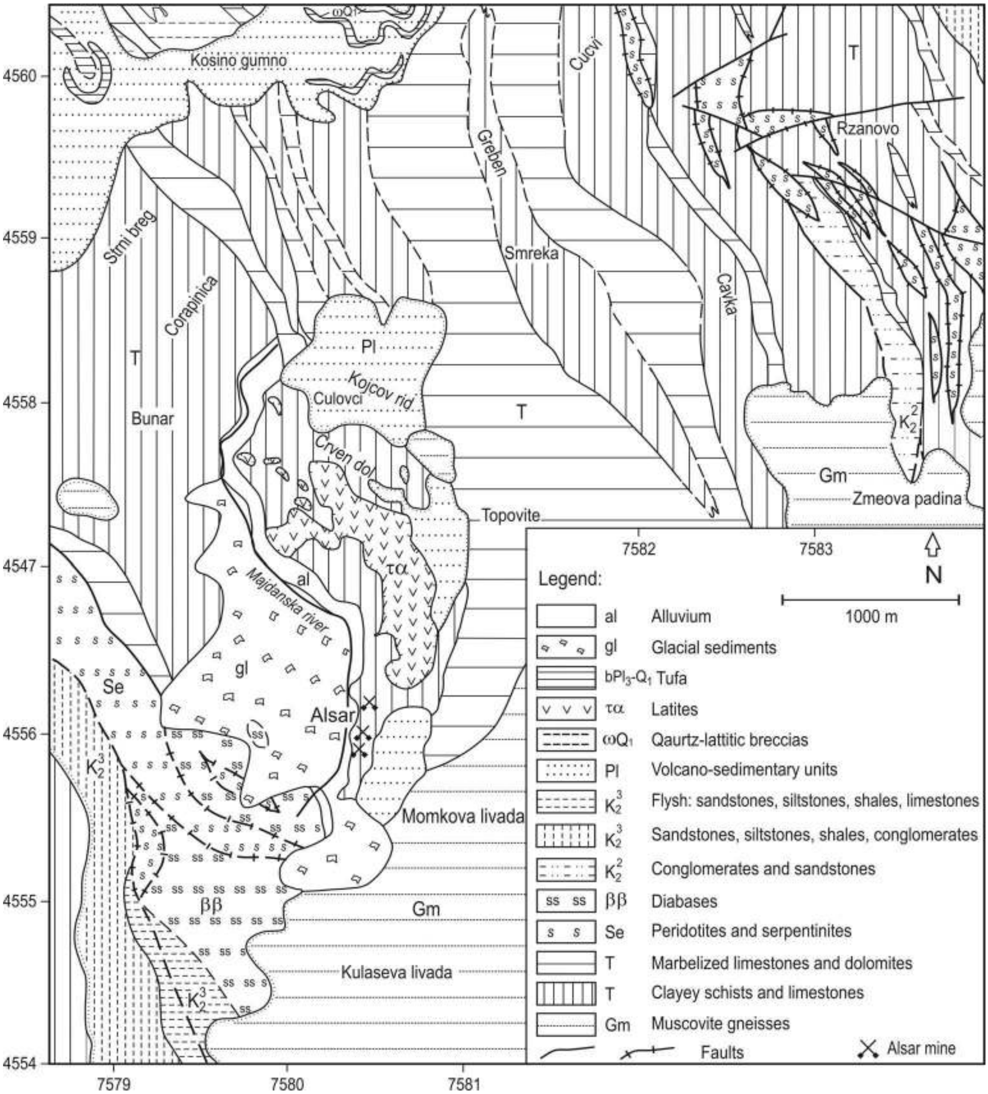


Fig. 11. Geological map of the Alsar area

The Alsar volcanic complex was investigated in detail by Frantz (1994), Frantz et al. (1994) and Lepitkova (1995).

Two principal volcano-intrusive phases have been identified in Alsar based on investigations carried out so far:

a. a Miocene phase of calc-alkaline rocks ccurring as dikes. Troesch and Frantz (1994) have determined a Miocene age (14.3 - 8.2 m.y.) for the volcanic phase. The age was determined based on Ar/ Ar data obtained for plagioclase from Crven Dol (Table 12).

Minerals	Temperature (°C)	^{40}Ar / ^{39}Ar
Plagioklase	800	9.222 ±0.842
	1000	8.279 ±1.183
	1200	12.256±0.762
	1400	14.323±0.776

Table 12. Absolute age determination of volcanic rock from Alshar based on ^{40}Ar /^{39}Ar of plagioclase (Troesh and Frantz (1994)

The volcano-intrusive rocks of this volcanic phase were completely altered by hydrothermal solutes during the Pliocene.

b. The most significant volcanic rocks in Alshar developed as part of the Kozuf volcano-intrusive activities. Subvolcanic hypoabyssal intrusions formed, based on data from K-Ar investigations, during the period from 4.5 to 5.0 m.y. (Lepitkova, 1995; Frantz et al. 1994).

Results obtained from determination of age by K/Ar method of andesines affected by hydrothermal processes indicate to absolute age of 3.9 to 5.1 m.y. (Lipolt and Fuhrman, 1986).

Determination of the age of volcanic rocks from Alshar was also carried out on sanidine and plagioclase (Table 13).

	Temperature (°C)	^{40}Ar / ^{39}Ar
Sanidinee	800	3.657 ± 0.137
	1000	3.334 ± 0.065
	1200	3.271 ± 0.063
	1400	3.261 ± 0.067
	1600	3.289 ± 0.170
Plagioklase	800	3.923 ± 0.319
	1000	3.328 ± 0.708
	1200	3.283 ± 0.757
	1400	5.027 ± 0.511
	1600	2.927 ± 0.058

Table 13. The age of volcanic rocks from Alshar determined by 40Ar / 39 Ar method (Troesh and Frantz, 1994)

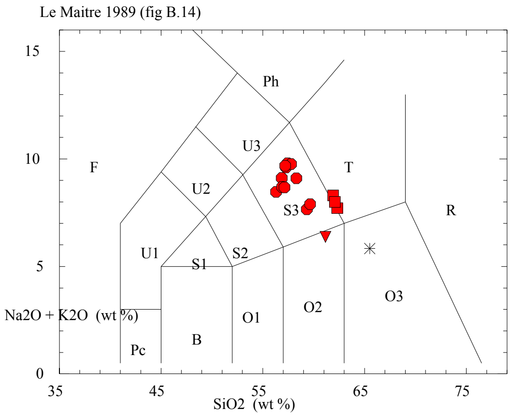


Fig. 12. Clasification of the Kozuf volcanic rocks based on the Le Maitre (1989)diagram (from Lepitkova, 1995)

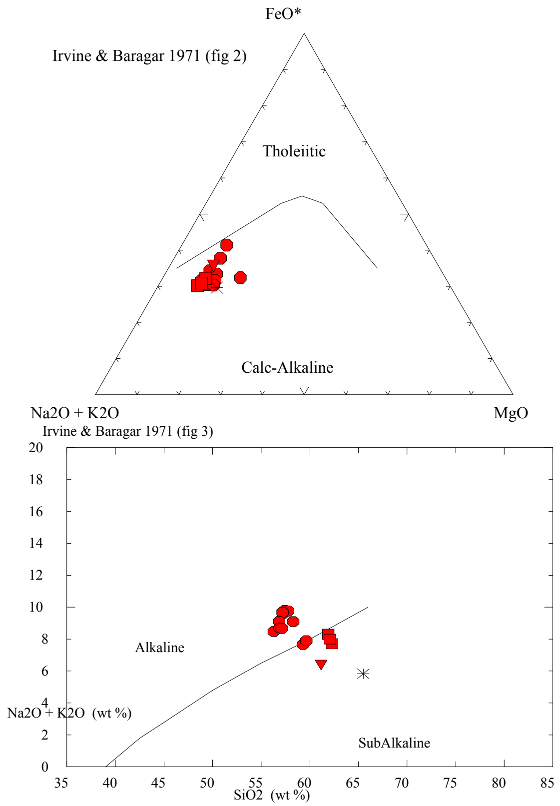


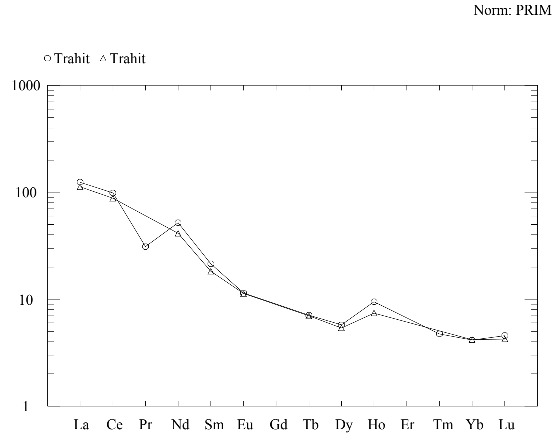
Fig. 13. Diagrams of (Na_2O+K_2O-FeO-MgO and Na_2O+K_2O/SiO_2) of volcanic rocks in the vicinity of Ashar (from Lepitkova, 1995)

It can be inferred that the volcanic activity in Alshar took place in the period between 3.9 to 5.1 m.y.. Based on Sr/ Sr ratio for latite (0.70856) it can be inferred that parent magma derived from lower continental crust/upper mantle domain (Boev, 1990/91).
Volcano-intrusive rocks of Alsar include latite, quartz-latite, trachyte, sporadically andesite and dacite (Fig. 12 and Fig.13).
The volcanics of Alshar contain variable amounts of trace elements and REE.Table 14 shows the values of trace elements and REE from three samples of trachytes (Frantz, 1994). Fig. 14

element	in ppm	error %	element	in ppm	error %
Li			Sn		
B			Sb	0.5270	10
C			Te		
F			J		
Na	167.0	3.0	Cs	1.330	6.0
P			Ba	34.80	13
S			La	6.340	3.0
Cl			Ce	7.300	5.0
K	41.00	15	Pr		
Sc	2.780	3.0	Nd	11.00	11
V			Sm	2.440	6.0
Cr	18.00	5.0	Eu	0.3400	6.0
Mn	38000	3.0	Gd	1.000	
Co	88.86	3.0	Tb	0.2400	13
Ni	< 20.00		Dy		
Cu	< 30.00		Ho	0.4700	20
Zn	593.0	4.0	Er		
Ga	< 0.6000		Tm	0.2700	20
Ge			Yb	1.200	6.0
As	637.8	3.0	Lu	0.1980	11
Se	< 0.40		Hf	0.2400	15
Br			Ta	0.03200	12
Rb	< 3.500		W	8.440	3
Sr	< 80.00		Re		
Y			Os		
Zr	10.0		Ir	< 0.00200	
Nb			Pt		
Mo	3.0	20	Au	0.494	3.0
Ru			Hg	0.7560	16
Rh			Tl		
Pd			Pb		
Ag	1.300	20	Bi		
Cd	12.00	20	Th	0.8000	14
In			U	8.520	5.0

Table 14. Trace elements of the trachytes from Alshar in ppm (Frantz, 1994)

shows the distribution of REE in the volcanic rocks of Alshar. It can be inferred that there is certain enrichment in light REE in regard to heavy elements. The relative enrichment in La is characteristic for the volcanic rocks of Alshar, whereas the Ce content (140-157 ppm), as well as Ce/Y (around 6) point to certain empoverishment in heavy elements. The Nd content is also high.



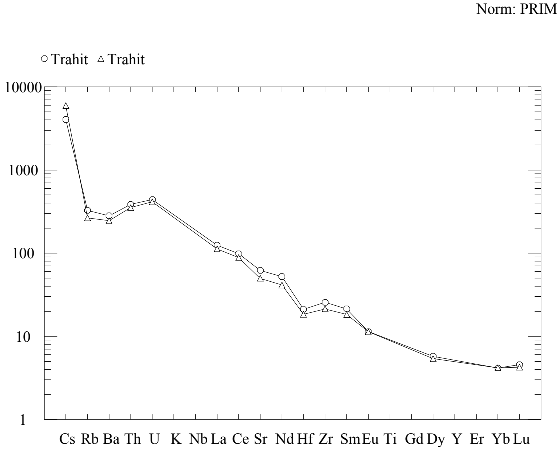


Fig. 14. Distribution pattern of REE (left) and trace elements of the trachytes from Alshar (right) (Frantz, 1994) (Lepitkova, 1995)

From the analysis it can be inferred that the enrichment in light REE elements indicates that magma originated from the continental crust and that it distinguishes it from toleitic basalts. The slightly pronounced minimum of Eu and the pronounced minimum of Dy indicate to the fractionation processes of primary magma and its contamination by rocks from the upper and lower crust (Lepitkova, 1995).

14. General characteristics of the volcanic rocks

Pliocene volcanic rocks occur either as subvolcanic intrusions in the shape of dikes and /or small intrusions, and extrusive volcanic material. Unlike Miocene volcanics, the younger rocks are relatively fresh and less affected by hydrothermal alteration processes (Lepitkova, 1995).

Latites.- Phenocrysts are clynopyroxene, andesine, sporadically biotite located in the ground mass of sanidine, andesine, Fe-Ti oxides and apatite.

The latites are the most common volcanic rock in the Alsar deposit. Their chemical compositions are displayed in Table 15.

	1	2	3	4	5	6	7	8	9	10
SiO_2	57.28	57.43	57.77	56.30	57.20	59.32	59.65	56.86	56.90	57.12
TiO_2	0.72	0.77	0.75	0.70	0.68	0.70	0.81	0.90	0.88	0.83
Al_2O_3	17.29	17.41	17.68	17.31	18.00	17.90	18.12	17.70	17.90	17.49
Fe_2O_3	5.60	5.84	5.73	5.20	5.62	5.25	5.38	5.30	5.32	5.48
MnO	0.06	0.08	0.06	0.06	0.06	0.10	0.10	0.10	0.10	0.09
MgO	1.89	1.60	2.00	3.21	1.80	1.66	1.78	1.88	1.98	2.01
CaO	4.42	4.23	5.35	5.18	4.68	5.07	4.87	5.12	4.95	4.88
Na_2O	4.01	4.10	4.31	3.65	4.15	3.65	3.79	4.01	3.95	3.88
K_2O	5.60	5.70	5.45	4.82	5.53	4.01	4.11	5.10	4.75	4.80
P_2O_5	0.57	0.51	0.50	0.44	0.51	0.52	0.50	0.48	0.44	0.47
H_2O	2.30	2.30	1.10	3.14	1.95	1.56	1.20	2.60	2.90	2.88
Total	99.74	99.97	100.7	100.01	100.18	99.74	100.31	100.05	100.01	99.93

Table 15. Chemical composition of the latites of Alsar (%)(from Lepitkova, 1995)

Trachyte is characterized by holocrystalline porphyry texture with phenocrysts represented by sanidine, plagioclase, amphibole and biotite. The groundmass consists of microliths of the same minerals.Chemical composition is presented on Table 16.

	1	2	3
SiO_2	61.90	62.30	62.08
TiO_2	0.70	0.65	0.72
Al_2O_3	17.80	18.01	17.23
Fe_2O_3	4.60	4.80	4.65
FeO			
MnO	0.10	0.09	0.09
MgO	1.30	1.39	1.35
CaO	4.72	4.30	4.18
Na_2O	4.01	3.61	3.85
K_2O	4.30	4.10	4.15
P_2O_5	0.50	0.50	0.50
H_2O	0.85	0.88	1.11
Total	100.78	100.63	100.63

Table 16. Chemical composition of the trachytes of Alsar (%) (Lepitkova, 1995)

Dacite and *andesite* occur sporadically. Their chemical composition is shown in Table 17.

	1 (andesite)	2 (dacite)
SiO_2	61.17	65.50
TiO_2	0.53	0.58
Al_2O_3	15.91	16.45
Fe_2O_3	4.68	3.43
FeO		
MnO	0.04	0.10
MgO	1.24	1.49
CaO	3.37	3.84
Na_2O	3.82	2.33
K_2O	0.24	3.50
P_2O_5		0.24
H_2O	4.77	6.79
Total	98.31	98.97

Table 17. Chemical composition of andesite and dacite of Alsar (%)(from Lepitkova, 1995)

Dacite consists of phenocrystas such as andesine, biotite, hornblende and minor quartz and sanidine, and of groundmass composed of microliths of andesine and sanidine as well as minor quartz, biotite, hornblende, apatite and Fe-Ti oxides.

Andesite is rare in the Alsar deposit. It is characterized by less alkalies than latite and trcahyte- andesite.

15. 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 of 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.

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, Kojčov Rid, Rudina, ADR and Vitačevo),

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, Kojčov 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 Kojčov 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 do ~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 ± 0.1 to 4.31 ± 0.2 My, according to Neubauer and coworker (Neubauer at al., 2009a), the biotite ages of 5.0 ± 0.1 and 5.1 ± 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 ± 0.2 to 3.3 My (Experiments with amphibole from a subvolcanic latite body result in disturbed $^{40}Ar/^{39}Ar$ release patterns and an age of 4.8 ± 0.2 My. Biotites yield slightly varying ages ranging between 4.6 ± 0.2 and 4.8 ± 0.2 My. K-feldspar disturbed, staircase patterns with ages increasing from 3.3 ± 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 ± 0.2 and 3.3 ± 0.2 My).

16. Conclusion

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. The prevalent lithological members in the central part of the deposit are carbonaceous 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.

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.The age determinations of the volcanic rocks in the Alsar deposit indicate pliocene time.

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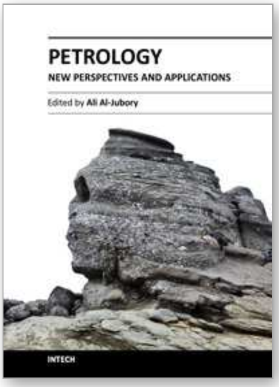

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