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Апстракт

Вулканската калдера Алшар се наоѓа во западните делови од вулканскиот комплекс на Кожуф Планина и таа е сместена во рабниот дел на Вардарската зона и метаморфниот комплекс Елен Шупе кој претставува реликт од старата прекамбриска континентална кора. Во овој дел од вулканскиот комплекс на Кожуф Планина вулканската активност е претставена со вулкански карпи кои имаат дацитско-риолитски состав. Во градбата на калдерата влегува поголема количина на седиментни пирокластични карпи кои се претставени со вулканокластични туфови во кои има појава на слоеви од тридимит и слоеви на перлит. Тридимитот се појавува во слој со дебелина од неколку метри а по боја е бел. Тридимитот и перлитот обично се асоцирани со силицискиот вулканизам. Во составот на тридимитот има појава и на кристобалит и на помала количина на опал. Појавата на опал е последица на дијагенетските промени на високотемпературното SiO₂ стакло. Во трудот се прикажани хемискитре и геохемиските испитувања на тридимитот и перлитот со примена на методите на FUS-ICP-MS. Нормализираните вредности на ретките земји укажуваат на дистрибуција по ист тип како во вулканските карпи од вулканската калдера на Алшар.

Клучни зборови: вулканизам, силициски, тридимит, перлит.

SILICIC VOLCANISM ON KOZUF MOUNTAINS EVIDENCED BY TRIDIMITE AND PERLITE IN HIGH-SiO₂ SEDIMENTARY ROCK AT ALSAR CALDERA

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Abstract

The volcanic caldera Allchar is located in the western area of the volcanic complex in the Kozuf Mountain at the frontier of the Vardar zone and the metamorphic complex Elen Supe, a relic of the old Precambrian continental crust. The volcanic activity in this area of the volcanic complex in the Kozuf Mountain is represented by igneous rocks with Dacitic-Rhyolitic composition. There are many sediment pyroclastic rocks in the composition of the caldera, represented by volcanoclastic tuffs with layers of tridymite and layers of perlite. Tridymite appears in layers, few meters thick and its color is white. Tridymite and perlite are usually associated with Silicic volcanism. There is also cristobalite and smaller amount of opal in tridymite's composition. The appearance of opal is due to the diagenetic changes of the high temperature SiO₂ glass. This paper presents the mineralogical and geochemical investigations of tridymite and perlite using XRD, FUS-ICP-MS, SEM-EDS methods. Normalized values of the rare element earth show distribution in the same manner as in the igneous rocks at the volcanic caldera of Allchar.

Key words: volcanism, silicic, tridymite, perlite.

1. Introduction

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 (Boev, 1988).

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 - Kilis transverse zone (Arsovski, Ivanov, 1977) 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 - Kilikis (E - W) fault structure formed during the neotectonic period. This type of volcanism is characterized by ring-radial structures. (Boev, 1988).

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, 1994) prolonged in Pliocene and finished in Quaternary (Boev, 1988).

The volcanic activities produced volcanic necks, frozen supply channels, large quantities of pyroclastic 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, occasionally 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 boron 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.

2. Geology of Alsar Caldera

Allchar locality is in fact settled in the volcanic complex of Mtn. Kožuf having a common frontier with Mtn. Kozjak. This volcanic complex is east-west oriented being about 30 km long. On the east the complex spreads to the Demir Kapija-Gevgelija ophiolitic complex, whereas to the west it reaches the overthrust structure which separates the Pelagonian metamorphic complex and Vardar zone (Boev, 1988). The development and evolution of this volcanism is closely related to the development and evolution of the Vardar zone. Thereby the labile geotectonic unit is formed in the period from the Mio-Pliocene to the Quarter (Arsovski, 1962. In the Neotectonic period (from the end of Oligocene to the Pliocene) the territory of the Republic of Macedonia is characterized by the processes of radial tectonics and formations of longitudinal and transversal grabens structures (Kochneva et al, 2006, Volkov et al, 2006). Formation of some of these grabens is related to the activation of the neogen magmatism in the territory of the Republic of Macedonia (Boev, 1988) as well as with the neogen volcanism in the Mtn. Kožuf region. This volcanism is of central type and is localized on the cross section between the transversal structure Kožuf-Kilikis (E-W) and the structures of Vardar zone (NW-SE to N-S) (Ivanov, 1963). This central type of volcanism is pointed out by the numerous ring structures characteristic for the Mtn. Kozuf region (Boev, 1988, Kochneva et al, 2006).

From the geological point of view, the surroundings of the Allchar locality consists of several geological formations arranged in five stratigraphic complexes (Fig. 1):

- complex of Precambrian metamorphic rocks,
- complex of Mesozoic (Triassic-Jurassic) rocks,
- complex of upper Kreda sediment rocks,
- complex of Pliocene sediments, pyroclastites and volcanic rocks,
- complex of quaternary sediments.

Complex of Precambrian metamorphic rocks is presented by albite gneisses and marbles in the metamorphic block of Mala Rupa region (in the Eastern part of Mtn. Kožuf), and by gneisses and mica schists in the tectonic block Elen Šupe (in the Western part of Mtn. Kožuf) (Arsovski, 1962).

Complex of Mesozoic (Triassic-Jurassic) rocks consists of rocks with sediment and metamorphic genesis as well as rocks of magmatic genesis. The complex of rocks with sediment and metamorphic genesis is presented by facies of colourful clay schists with intercalations of limestones, and with the facies of limestones and dolomite limestones of Triassic-Jurassic age. The rock series of Jurassic age is presented by facies of plate and massive limestones and facies of sandstones and clay schists, quartzites and cherts. The rock series of Triassic age is presented by marbleized limestones and dolomites, clay schists and sandstones with intercalation of diabases and green schists. In this complex of mesozoic rocks the magmatic rocks are also included being presented by ophiolitic rocks (serpentinized dunites, serpentinized harzburgites, gabbros, basalts, diabases and gabbropegmatites).

The complex of Upper-Cretaceous sedimentary rocks consists of series of sandstones and conglomerates of Alb and Baramian age and series of limestones of Turonian age.

The complex of Pliocene sediments, pyroclastites and volcanic rocks consists of lake sediments laying over the sediments of upper Eocene. Pliocene sediments are presented by roughly grained conglomerates and claystone sediments, clay carbonate sediments and marls. In this series sometimes horizons of diatomaceous earth appear. The complex of Pliocene sediments terminates with the appearance of tufas and travertines overlaid by a

series of pyroclastite rocks. This series of pyroclastite rocks is presented by various types of lakustrian tuffs, volcanic agglomerates and volcanic glasses.

The volcanic rocks of Pliocene age are widely spread on the Mtn. Kozuf (Republic of Macedonia (Boev, 1988), and Mtn Voras (Greece) (Kolios e al, 1980). This complex of volcanic rocks spreads on about 2000 km² and, in general, consists of alkali basalts, andesites, latites, trachites and rhyolites. Their age ranges from 1.8 to 6.5 million years (Boev, 1988).

The complex of quaternary sediments consists of various terrace sediments, fluviglacial sediments and alluvial sediments.

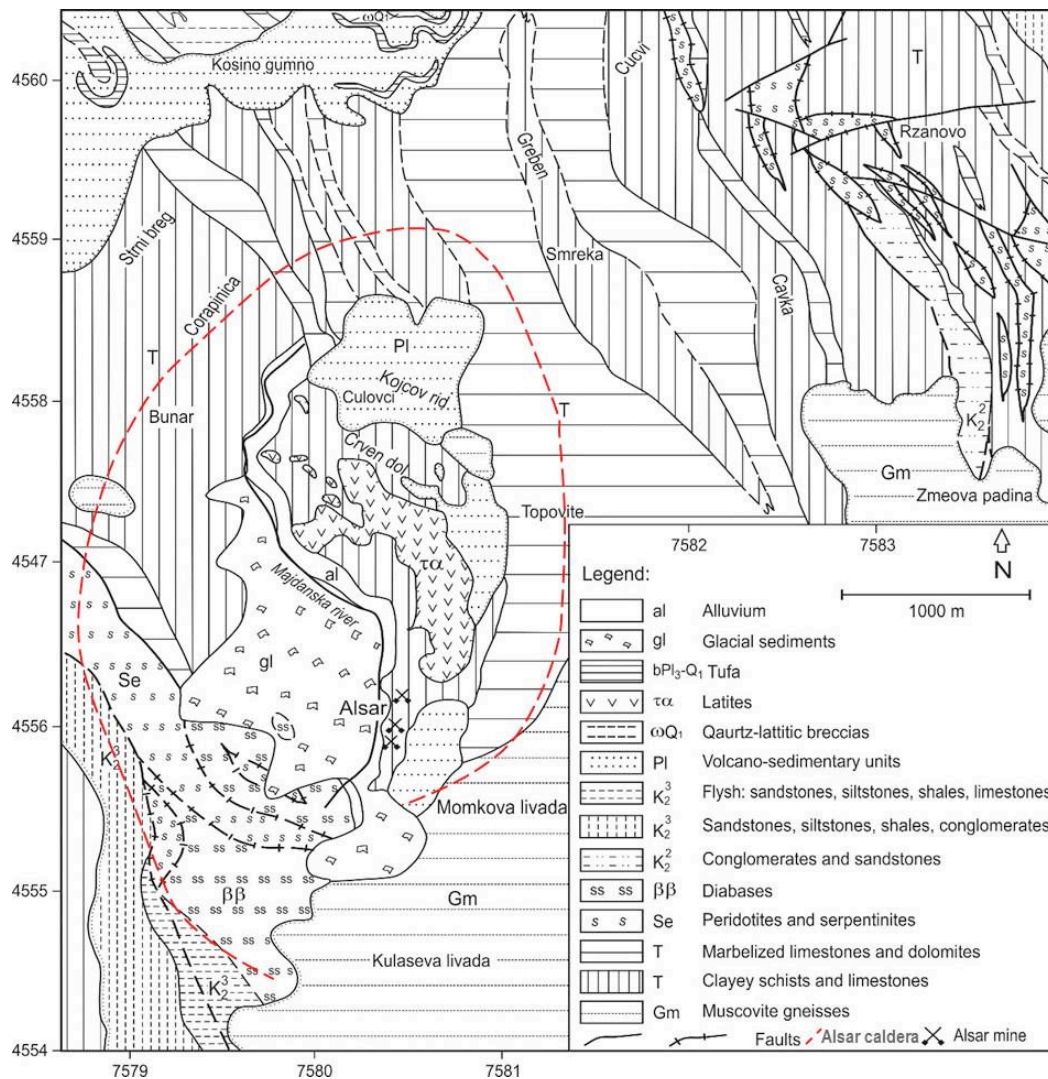


Figure 1. Geological position and geological composition of Alsar Caldera

3. Volcanica activity in Alsar Caldera

The Alsar volcanic complex was investigated in detail by Frantz (1944), Frantz et al. (1944) 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 1).

Table 1. Absolute age determination of volcanic rock from Alshar based on $^{40}\text{Ar} / ^{39}\text{Ar}$ of plagioclase (Troesh and Frantz (1994)

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

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).

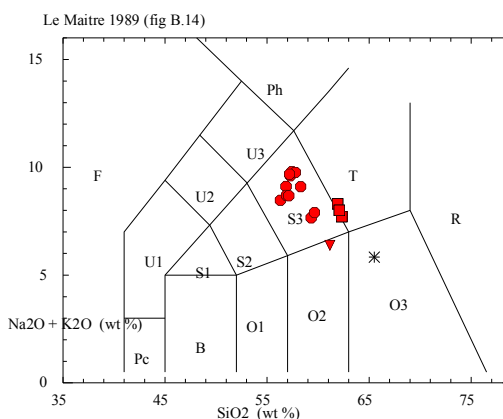
Results obtained from determination of age by K/Ar method of andesines affected by hydrothermal processes indicate to absolute age of 3.9 to 5.1 m.y. (Lipolt and Fuhrman, 1986). Determination of the age of volcanic rocks from Alshar was also carried out on sanidine and plagioclase (Table 2).

Table 2. The age of volcanic rocks from Alshar determined ba $^{40}\text{Ar} / ^{39}\text{Ar}$ method (Troesh and Frantz, 1994)

Mineral	Temperature (°C)	$^{40}\text{Ar} / ^{39}\text{Ar}$
Sanidine	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

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).

a)



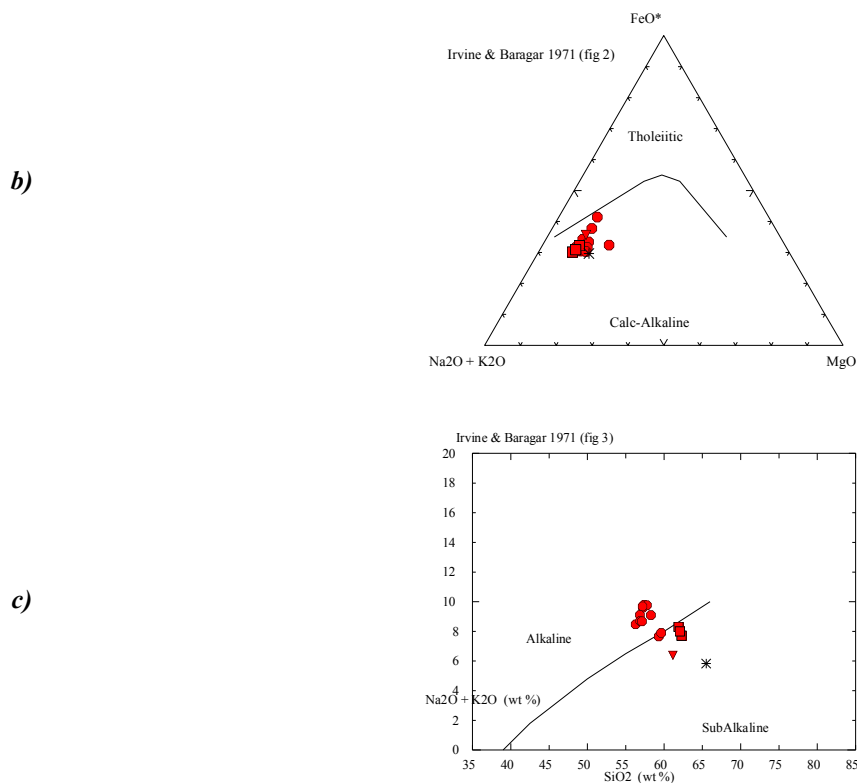


Figure 2. Diagrams of a: SiO₂/Na₂O+K₂O ; b: SiO₂ - K₂O. and c: Na₂O+K₂O-MgO-FeO of volcanic rocks in the vicinity of Ashar (Lepitkova, 1995)

Volcano-intrusive rocks of Alshar include latite, quartz- latite, trachyte, sporadically andesite and dacite (Fig. 2). The volcanics of Alshar contain variable amounts of trace elements and REE. Table 25 shows the values of trace elements and REE from three samples of trachytes (Frantz, 1994). Fig. 3 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 impoverishment in heavy elements. The Nd content is also high.

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 tholeiitic 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, Jankvic et al, 1977).

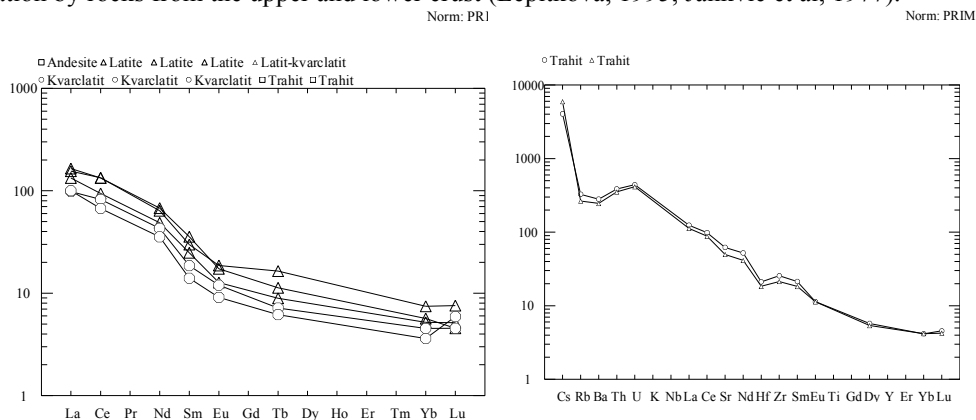


Figure 3. Distribution pattern of rare elements (left) and REE of the trachytes from Alshar (right) (Frantz, 1994) (Lepitkova, 1995)

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 clinopyroxene, 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 3.

Table 3. Chemical composition of the latites of Alsar (%) (Lepitkova, 1995)

	1	2	3	4	5	6
SiO₂	57.28	57.43	57.77	56.30	57.20	59.32
TiO₂	0.72	0.77	0.75	0.70	0.68	0.70
Al₂O₃	17.29	17.41	17.68	17.31	18.00	17.90
Fe₂O₃	5.60	5.84	5.73	5.20	5.62	5.25
MnO	0.06	0.08	0.06	0.06	0.06	0.10
MgO	1.89	1.60	2.00	3.21	1.80	1.66
CaO	4.42	4.23	5.35	5.18	4.68	5.07
Na₂O	4.01	4.10	4.31	3.65	4.15	3.65
K₂O	5.60	5.70	5.45	4.82	5.53	4.01
P₂O₅	0.57	0.51	0.50	0.44	0.51	0.52
H₂O	2.30	2.30	1.10	3.14	1.95	1.56
Total	99.74	99.97	100.7	100.01	100.18	99.74

Note: The method applied in determination of the chemical composition of the rocks is Inductive Connected Plasma (ICP - method)

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. The chemical composition of the trachytes of the Alsar deposit is shown in Table 4.

Table 4. Chemical composition of the trachytes of Alsar (%) (Lepitkova, 1995)

	1	2	3
SiO₂	61.90	62.30	62.08
TiO₂	0.70	0.65	0.72
Al₂O₃	17.80	18.01	17.23
Fe₂O₃	4.60	4.80	4.65
MnO	0.10	0.09	0.09
MgO	1.30	1.39	1.35
CaO	4.72	4.30	4.18
Na₂O	4.01	3.61	3.85
K₂O	4.30	4.10	4.15
P₂O₅	0.50	0.50	0.50
H₂O	0.85	0.88	1.11
Total	100.78	100.63	100.63

Method (Inductive Connected Plasma, ICP)

Dacite and **andesite** occur sporadically. Their chemical composition is shown in Table 5.

Table 5. Chemical composition of andesite and dacite of Alsar (%) (Lepitkova, 1995)

	1 (andesite)	2 (dacite)
SiO ₂	61.17	65.50
TiO ₂	0.53	0.58
Al ₂ O ₃	15.91	16.45
Fe ₂ O ₃	4.68	3.43
MnO	0.04	0.10
MgO	1.24	1.49
CaO	3.37	3.84
Na ₂ O	3.82	2.33
K ₂ O	0.24	3.50
P ₂ O ₅		0.24
H ₂ O	4.77	6.79
Total	98.31	98.97

Applied method: Inductive Connected Plasma, ICP method.

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 alkalis than latite and trachyte-andesite.

4. Tridimite and Riolite (Perlite)

Tridimite are presented by layer in the pyroclastic materials with the thiknes of 2 meters, white color. Chemical and geochemical analysys was performed by ICP-FUS method and the results are presented in the Table.6. In Fig 4 is presented noramalized value of rare elements of tridimite/chondrite. Type of normalized diagrams for tridimite is similar to diagram of volcanic activity in the Alsar volcanic caldera.

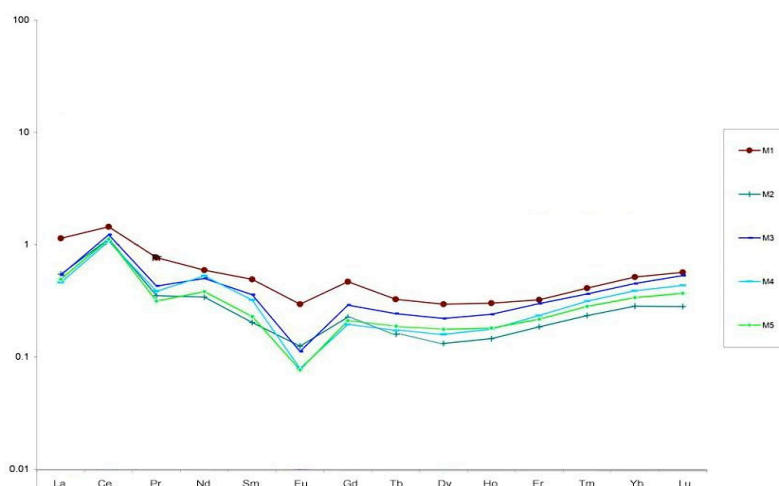


Figure 4. Distribution pattern of rare elements for tridimite of Alsar caldera

Table 6. Chemical and geochemical composition of tridimite from Alsar caldera (ICP-FUS-MS)

Analyte Symbol	Unit Symbol	M1	M2	M3	M4	M5
SiO ₂	%	87,84	91,46	90,16	90,66	90,75
Al ₂ O ₃	%	2,77	1,36	2,17	1,18	1,48
Fe ₂ O ₃ (T)	%	0,45	0,31	0,31	0,28	0,29
MnO	%	0,005	0,004	0,003	0,003	0,004

MgO	%	0,2	0,19	0,27	0,18	0,2
CaO	%	0,16	0,14	0,12	0,13	0,11
Na2O	%	0,78	0,12	0,14	0,1	0,13
K2O	%	0,72	0,41	0,71	0,35	0,44
TiO2	%	0,046	0,048	0,095	0,041	0,046
P2O5	%	< 0.01	< 0.01	0,01	< 0.01	< 0.01
LOI	%	5,82	6,4	6,15	6,36	6,05
Total	%	98,79	100,4	100,1	99,28	99,51
Sc	ppm	< 1	< 1	< 1	< 1	< 1
Be	ppm	29	31	33	27	26
V	ppm	9	10	16	12	13
Cr	ppm	< 20	< 20	20	< 20	< 20
Co	ppm	< 1	< 1	< 1	< 1	< 1
Ni	ppm	< 20	< 20	< 20	< 20	< 20
Cu	ppm	< 10	< 10	< 10	< 10	< 10
Zn	ppm	< 30	< 30	< 30	< 30	< 30
Ga	ppm	3	2	3	1	2
Ge	ppm	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
As	ppm	9	7	7	7	12
Rb	ppm	18	13	24	12	15
Sr	ppm	6	4	4	4	4
Y	ppm	0,8	< 0.5	0,6	< 0.5	< 0.5
Zr	ppm	16	15	24	15	16
Nb	ppm	1	1,1	2,1	1	1,1
Mo	ppm	< 2	< 2	< 2	< 2	< 2
Ag	ppm	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
In	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	ppm	< 1	< 1	< 1	< 1	< 1
Sb	ppm	2,7	2,9	3,2	2,8	3
Cs	ppm	1	1	1,3	1,1	1,4
Ba	ppm	23	22	34	23	30
La	ppm	0,36	0,17	0,17	0,14	0,15
Ce	ppm	1,17	0,91	1	0,87	0,91
Pr	ppm	0,09	0,04	0,05	0,04	0,04
Nd	ppm	0,35	0,2	0,3	0,31	0,23
Sm	ppm	0,09	0,04	0,07	0,06	0,04
Eu	ppm	0,021	0,009	0,008	0,006	0,006
Gd	ppm	0,12	0,06	0,07	0,05	0,05
Tb	ppm	0,02	< 0.01	0,01	< 0.01	< 0.01
Dy	ppm	0,1	0,04	0,07	0,05	0,06
Ho	ppm	0,02	0,01	0,02	0,01	0,01
Er	ppm	0,07	0,04	0,06	0,05	0,05
Tm	ppm	0,013	0,007	0,012	0,01	0,009
Yb	ppm	0,11	0,06	0,09	0,08	0,07
Lu	ppm	0,018	0,009	0,017	0,014	0,012
Hf	ppm	0,4	0,3	0,6	0,4	0,4
Ta	ppm	0,07	0,05	0,12	0,08	0,05
W	ppm	0,7	0,8	1,9	1,7	3,7
Tl	ppm	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Pb	ppm	< 5	< 5	< 5	< 5	< 5
Bi	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	ppm	0,14	0,08	0,17	0,1	0,06
U	ppm	1,11	1,11	1,4	1,06	1,08

The Rhyolites are represented by lava extrusions of perlitic composition. Chemical analyses (Table 7) show that they are the most acid rocks occurring in the vicinity of Gradesnica west of Kozjak Mt.

Table 7. Chemical composition of rhyolites of Alsar caldera (%)

	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 ₂ O ₃	11.22	12.85	10.20	9.46	9.78	13.30
Fe ₂ O 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 ₂ O	2.87	3.21	2.15	2.32	2.46	3.24
K ₂ O	4.83	4.85	3.95	3.84	4.31	4.79
P ₂ O ₅	0.06	0.60	0.08	0.03	0.07	0.03
H ₂ O	1.08	0.60	3.23	2.18	1.52	1.95

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 porphyritic. 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.

5. Conclusion

The appearance of layers of tridymite and perlite in the pyroclastic products of Kozuf volcanism clearly demonstrates the presence of Silicic volcanism in particular phases of volcanic activity evolution. It is not rare to have acid volcanism in the western part of the volcanic activity (Allchar caldera), in the frontier with the metamorphic complex of Elen Supe. The appearance of this volcanism is due to the high contamination of the primary magmas with materials in the continental crust.

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