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GEOLOGY, PETROLOGY AND THE AGE OF PEGMATITES IN ALINCI LOCALITY (NORTH MACEDONIA)

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Abstract. This paper presents the latest studies on petrographic composition and chemical and geochemical characteristics of metamorphic (alkaline gneisses) and igneous rocks (alkaline syenites) from the locality of Alinci, as well as research related to the age of pegmatite occurrences in the locality Alinci, with the application of the K/Ar method on the mineral microcline. In terms of the occurrence of minerals, Alinci is a highly exotic locality, with the occurrence of numerous minerals (quartz, albite, microcline, arfvedsonite, augite, titanite, zircon, apatite, magnetite, davidite, macedonite and others). The age of the Alinci pegmatites is determined as the Cretaceous period, and the formation of the pegmatites is the consequence of the partial melting of gneisses and the formation of alkaline syenites during the metamorphic and tectono-magmatic processes, which took place within the Pelagonian metamorphic complex.

Keywords: Alinci, pelagonian metamorphic complex, age determination

ГЕОЛОГИЈА, ПЕТРОЛОГИЈА И СТАРОСТ НА ПЕГМАТИТЕ ОД ЛОКАЛИТЕТОТ АЛИНЦИ (СЕВЕРНА МАКЕДОНИЈА)

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Апстракт. Во трудот се прикажани најновите испитувања на петрографскиот состав, хемиските и геохемиските карактеристики на метаморфните (алкални гнајсеви) и магматските карпи (алкални сиенити) од локалитетот Алинци, како и испитувањата кои се однесуваат на староста на пегматиските појави во локалитетот Алинци со примена на К/Ар методата направени на минералот микроклин. Локалитетот Алинци е во поглед на појавувањето на минералите многу егзотичен локалитет со појава на бројни минерали (кварц, албит, микроклин, арфедоснит, аугит, титанит, циркон, апатит, магнетит, давидит, македонит и др.). Староста на пегматитите од Алинци е одредена како кредна и постанокот на пегматитите се последица на делумните топења на гнајсевите и формирањето на алкалните сиенити за време на метаморфните и тектно-магматските процеси кои се случиле во рамките на Пелагонискиот метаморфен комплекс.

Клучни зборови: Алинци, пелагониски метаморфен комплекс, одредба на староста

1. Introduction

The locality Alinci is situated near the village Alinci, approximately 3 km from the Prilep-Bitola regional road (North Macedonia). The locality itself is within the Pelagonian metamorphic complex, in a metamorphic beam separating the Prilep field from the Bitola field. Here, the metamorphic rocks (gneisses) build three heights that descend from the northern branches of the Selecka Mountain into the Pelagonija valley (Fig 1). The site itself lies on the elevation known as Crn Kamen (Maric, 1949). Pegmatite occurrences are located in the series of alkaline syenites and gneisses (Fig 2). The pegmatite occurrences are composed of microcline, arfvedsonite, albite, titanite, augite, zircon and apatite (Fig 3)(Baric, 1964) minerals. A specific trait of the deposit is its rare mineral paragenesis, which includes uranium minerals. It is important to note that there are frequent nests several centimeters in size, filled with needle-like arfvedsonite crystals (Jovanovski et al, 2012). Arfvedsonite is a mineral of the amphibole group, occurring as acicular shapes of greenish, dark or blue tinge. It appears as an inclusion in other mineral forms. Albite is also common, appearing as platy-white to totally transparent crystals. The largest crystals are 10 cm in size. Twinned individual grains (poly-synthetically twinned) or Carlsbad's twins are common. Arfvedsonite crystals are frequent inclusions in albite. Of note are the well-developed quartz crystals, the large titanite crystals (attaining 2 cm in size) and the crystals of monazite and macedonite.

There is also the occurrence and specific association of rare minerals with uranium content (*e.g.*, davidite) (Damjanovic, 1961, Žorž et al., 1988/1989, 1999).

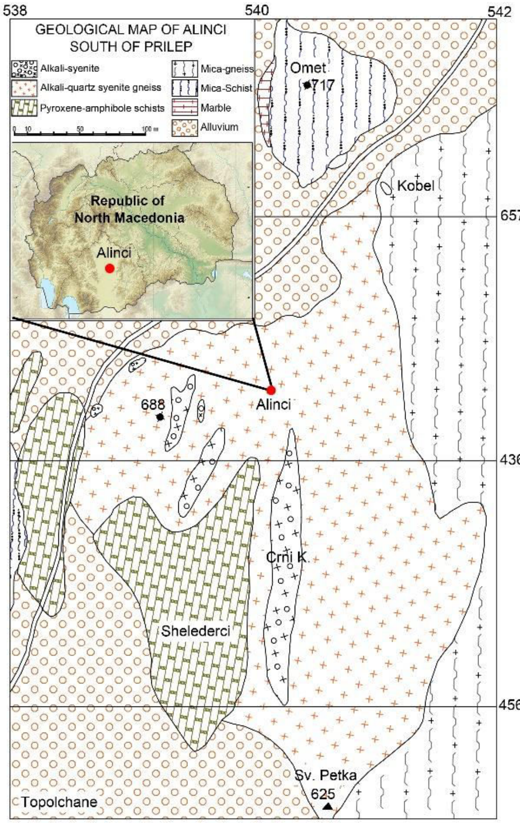


Fig.1. Geological and geographical map of Alinci locality

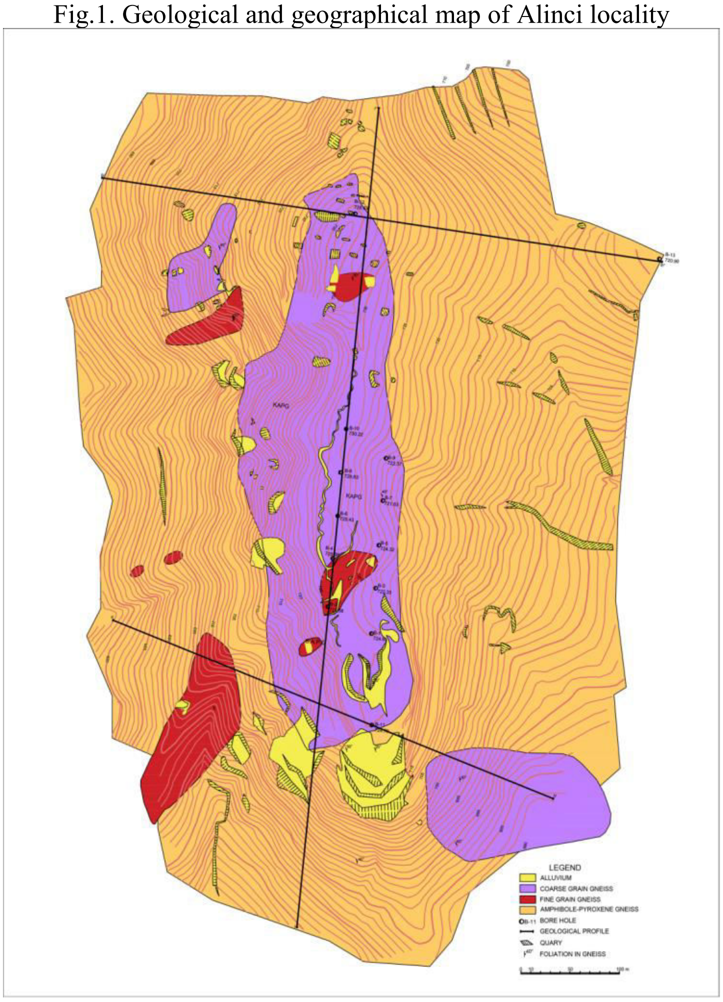
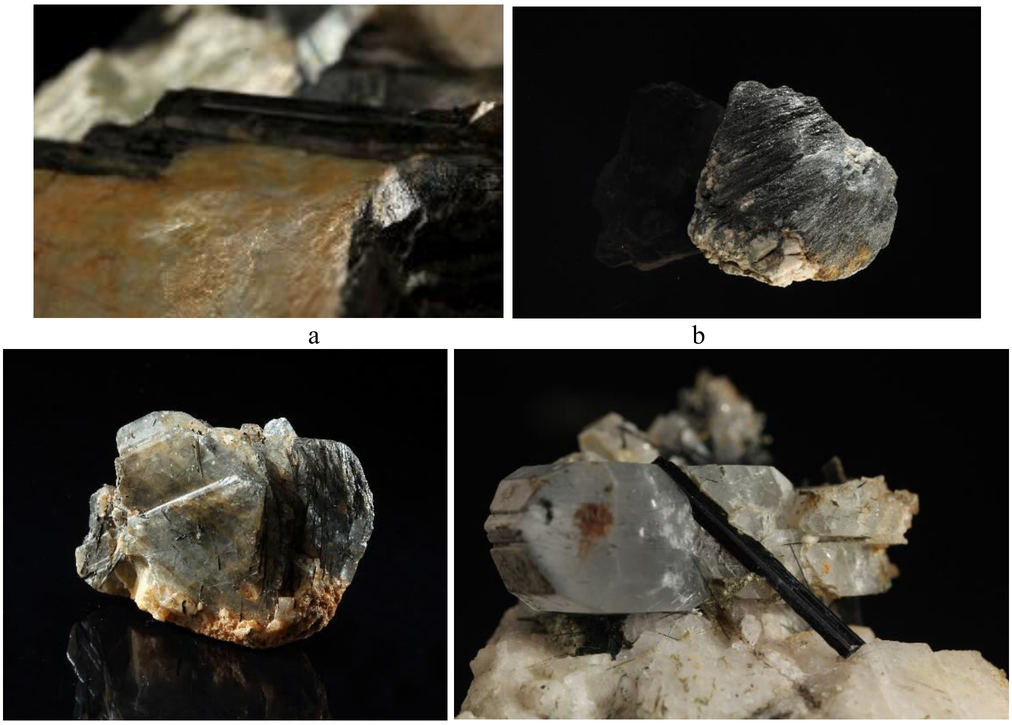


Fig.2. Geological map of pegmatite of Alinci



a b
c d

Fig. 3. Photographs of minerals of Alinci (a) Actinolite, (b) Arfedsonite, (c) Albite + Quratz, (d) Albite + Microcline + Arfedesonite

2. Methodology

During the field visit to the Alinci locality, several samples of alkaline syenites and alkaline gneisses (the most common rocks) were collected. Microscopic preparations were made, and samples were microscopically determined using the polarized light method. Using the ICP-MS method, chemical and geochemical tests were performed, and the presence of trace elements and elements from the group of rare earth elements (REE) was determined. A mineralogical separation of a microcline was performed, and an age determination was performed using the K-Ar method.

K-Ar methodology:

An aliquot of the sample was weighed into an Al container, loaded into the sample system of extraction unit, and degassed at ~100°C over 2 d to remove the surface gases. Ar was extracted from the sample in a double vacuum furnace, at 1700°C. The determination of radiogenic Ar content was performed twice on an MI-1201 IG mass spectrometer by the isotope dilution method, with ^{38}Ar as a spike, which is introduced to the sample system prior to each extraction.

The extracted gases were cleaned using a two-step purification system. Then, pure Ar was introduced into a custom-built magnetic sector mass spectrometer (Reynolds-type). It shall be noted that the test was done twice per sample, in order to ensure consistency of results. Two globally-accepted standards (Bern-4M Muscovite and 1/65 "Asia" rhyolite matrix) were

measured for ^{38}Ar spike calibration. For age calculations, the international values for constants were used, as follows: $\lambda K = 0.581 \times 10^{-10}\ y^{-1}$, $\lambda\beta- = 4.962 \times 10^{-10}\ y^{-1}$, $^{40}K = 0.01167$ (at. %).

3. Geology and petrology

Within the Pelagonia metamorphic complex, approximately 10 km south of Prilep there is an occurrence of alkaline syenites and alkaline quartz-syenite gneisses, which, together with pyroxene-amphibole schists, make up the composition of the Alinci site, with an area of approximately 25 km^2. On the north side the locality is limited by the Omet hill (717 m above sea level), and on the south side by the Sv. Petka hill (625 m above sea level). The eastern border of the locality goes along the slopes of the Komarchin and Cuculin hills, and the western border goes towards the villages of Veselcani and Topolcani.

The syenite rocks, as well as the pyroxene-amphibole schists, according to their occurrence, are limited to the locality of Alinci within the Pelagonija metamorphic complex. Марић (1949), Protic (1959) discusses these rocks in his paper on the metamorphic rocks of Bakarno Gumno and Veslec, and also mentions the locality of Crn Kamen (Alinci). Based on the mineral compositions and structures, the following types of rocks can be distinguished within the locality of Crn Kamen (Alinci) (Fig 4).

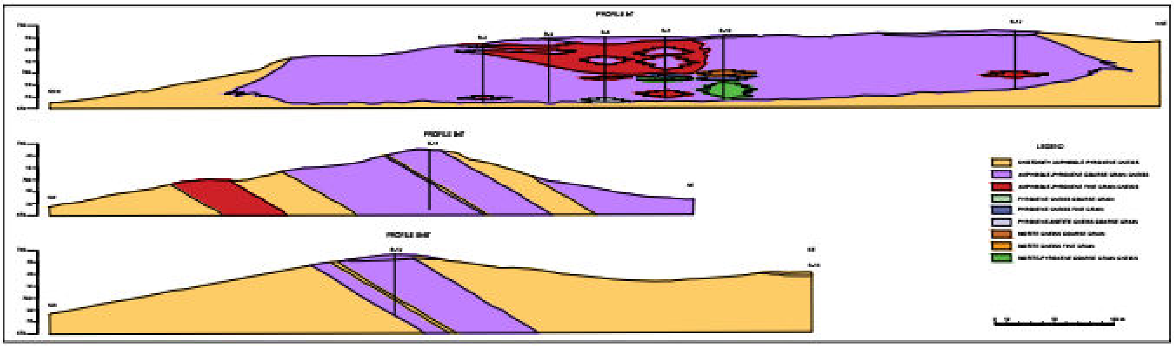
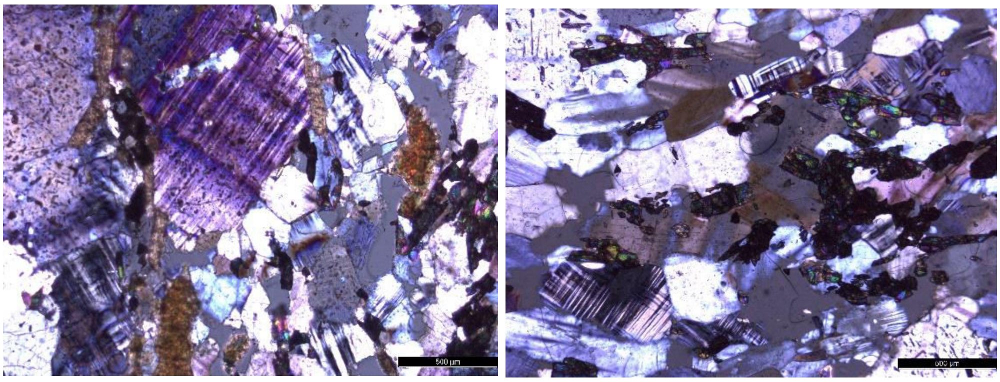


Fig. 4. Geological profile of pegmatite of Alinci

Coarse-grained syenite

Coarse-grained syenite is a fresh, hard rock, which is greenish-grey in colour and has a coarse-grained structure with a clear lineation (orientation) of coloured minerals. The presence of greenish microcline, up to 2 cm in size, and of dark green amphibole can be easily observed in the rock macroscopically (Fig 5. a,b).



a b

Fig. 5. Micro photographs of syenite (a) (b) Pob 25 x

Under the microscope, it can be seen that this rock is made up of microcline, arfvedsonite and aegirine-augite as the main components, with smaller quantities of quartz and albite, while zircon, apatite, sphene and barite occur as secondary minerals.

Microcline is the dominant mineral in the rock structure, composing nearly three quarters of the rock, appearing as large crystals and as smaller crystals in other areas. Large crystals have irregular shapes and a pronounced lattice structure, observable under a microscope. Large crystals of microcline near-consistently contain inclusions of arfvedsonite, and albite allocations are occasionally found in the microcline. The green colour of the microcline comes from the inclusions of arfvedosnite (amphibole). The fine-grained microcline builds granular aggregates, and, in the cracks of the coarse-grained microcline, a third generation of microcline also appears in the veins.

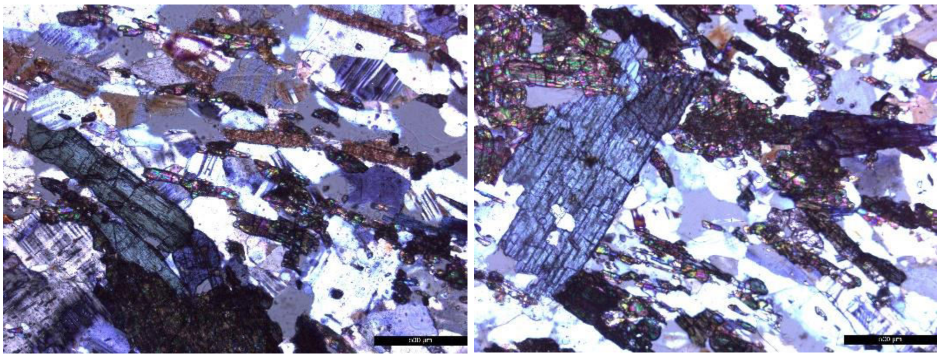
Arfvedsonite occurs spontaneously in the form of prismatic grains with a greenish to black colour, with clearly-marked directions of cleavage. Arfvedsonite is sometimes accompanied by aegirine-augite. Arfvedsonite has a clearly-pronounced indigo blue—coloured pleochroism. Aegirine-augite occurs in fine-grained aggregates and has a pronounced yellow-green pleochroism. Quartz occurs less frequently, in the form of fine aggregates, while albite occurs in the form of non-twinned individuals crystals. Sphene occurs as crystals between 2–3 mm in size. Zircon, apatite and barite are less common as secondary components.

Fine-grained syenite

Fine-grained syenite has a uniform grain size and occurs together with coarse-grained syenite, from which it differs macroscopically only in the grain size (less than 1 mm), and has a lighter colour, due to being composed of a lower amount of coloured minerals. In terms of mineral composition, fine-grained syenite has an identical composition to coarse-grained syenite, with the differences being that fine-grained syenite contains more quartz and coarse-grained microcline is not present.

Alkaline gneisses-quartz syenite gneisses

Most of the Alinci massif (Crn Kamen) is composed of alkaline gneisses. These rocks are bound on the west by pyroxene-amphibole schists, and on the east by two-mica gneisses (Fig. 6. a,b). The rocks have a schist (gneiss) texture in which the dominant orientation is that of the coloured minerals. The structure of the rock is porphyroblastic. The mineral composition of these rocks is as follows: microcline, quartz, aegirine-augite and arfvedsonite, while also containing albite, biotite, epidote, zircon, sphene and apatite as secondary minerals. Regarding the quantities of quartz, there are two types of gneisses: gneisses rich in quartz and gneisses poor in quartz. Microcline occurs in fine and larger crystals, ranging from a few mm to a few cm in size, with very frequent inclusions of arfvedsonite and quartz. Quartz occurs as irregular grains and aggregates, with variable dimensions. Aegirine-augite occurs as grains between 1–2 mm in size, in isometric forms and, in some cases, in elongated forms. Arfvedsonite occurs in elongated crystal shapes of varying sizes, with a pronounced orientation in the rock, and occurs in places associated with aegirine-augite. Biotite occurs in small, leaf forms, and, muscovite may occasionally occur instead of biotite.



a b

Fig. 6. Micro photographs of alkaline gneisses-quartz syenite gneisses (a) (b) Pob 25

The most common mineral is zircon. It occurs in crystalline forms with a clearly-pronounced zonation. Several colours of zircon are found, from lemon yellow to red, dark and colourless. Zircon occurs in the form of jets in the rock.

Pyroxene-amphibole schists

Pyroxene-amphibole rocks occur in the southern and southwestern parts of the terrain at the locality of Alinci. Within this series, two members stand out: pyroxene-biotite schists and amphibole schists with pyroxene. The composition of these rocks includes diopside, biotite and occasionally hornblende, with apatite, zircon and sphene as secondary components.

4. Geochemistry

Five samples of alkaline syenites and two samples of alkaline gneisses were taken, and complete chemical and geochemical analyses were performed using the ICP-MS method. The results obtained are shown in Table 1.

Table 1: Chemical and geochemical composition of rocks from the locality of Alinci (ICP-MS method)

	1	2	3	4	5	6	7
SiO2	61,23	66,8	67,53	67,57	62,34	64,76	67,68
TiO2	0,4	0,17	0,19	0,38	0,7	0,53	0,35
Al2O3	16,1	13,96	14,11	14,7	13,97	14,4	16,61
Fe2O3	2,58	2,8	3,02	4,17	4,98	4,83	2,17
FeO	1,11	0,26	0,24	0,23	1,16	0,98	0,14
MnO	0,1	0,02	0,01	0,02	0,16	0,16	0,11
MgO	1,94	1,1	0,68	1,36	1,21	1,11	1,02
CaO	2,26	0,94	0,45	0,72	2,6	1,7	0,65
Na2O	3,04	2,92	2,2	2,17	2,11	1,29	0,72
K2O	10,01	10,64	9,85	7,9	7,8	7,6	9,4
P2O5	0,64	0,12	0,11	0,1	2,25	2,15	1,11
H2O-	0,14	0,08	0,5	0,2	0,27	0,25	0,06
H2O+		0,27	0,61	0,33	0,64	0,28	0,24
	99,55	100,08	99,5	99,85	100,19	100,04	100,26
Li	31,3	33,2	34,5	33,2	48,2	50.3	51,2
Be	8,6	8,6	7,8	6,9	9,4	8,7	8,9
B	515	617	580	570	256	245	265
Na	20054	20019	19869	21545	16537	17235	16987
Mg	8697	9632	9152	8891	9676	9854	9787
Al	66280	66528	64587	65321	65872	66251	66541
P	1587,1	1486,1	1421,3	1587,2	1572,2	1584	1651
S	<100	<100	<100	<100	<100	<100	<100
K	69874	68454	71258	70141	65948	66254	67321
Ca	13875	14743	1521	1489	14432	14568	14874
Sc	17,5	18,2	17,2	18,5	17,0	17	18
Ti	577	455	521	531	577	580	590
V	124	144	135	141	112	115	118
Cr	41,0	44,0	43	42	30,2	31	32
Mn	560	581	592	578	483	501	490
Fe	28582	29585	30241	28654	27695	28254	27898
Co	5,0	5,0	4,9	4,7	6,3	7	7
Ni	4,5	4,6	4,2	4,1	15,1	16	15
Cu	8,7	8,4	9,1	9,5	13,4	14	15
Zn	32,5	31,8	32,1	33,2	31,6	32	33
Ga	21,3	22,1	21,3	20,5	22,2	23	24
Ge	2,0	2,0	2	2	2,0	2	2
As	10,2	11,4	12,1	11,2	8,0	9	10
Se	2,2	3,2	3,3	3,4	2,2	3	3
Rb	298	287	288	296	301	302	305
Sr	565	542	532	548	443	450	448
Y	31,0	30,8	32,1	32,3	54,9	55	56
Nb	51,2	50,4	52,1	53,2	108,2	110	112
Mo	<1	<1	<1	<1	<1	<1	<1
Pd	1,4	1,4	1,4	1,4	1,4	1,4	1,4
Ag	<1	<1	<1	<1	<1	<1	<1
Cd	<1	<1	<1	<1	<1	<1	<1
(In)	1,6	1,6	1,6	1,6	1,6	1,6	1,6
Sn	17,9	17,2	16,5	17,4	17,9	18,2	18,3
Sb	<1	<1	<1	<1	<1	<1	<1
Te	11,5	11,2	12,3	12,5	12,8	13,2	14,1
Cs	12,5	11,9	12,4	11,9	13,8	14,2	14,5
Ba	11250	10790	10654	11121	12731	13214,0	12451,0
La	65,3	63,7	64,2	65,3	114,3	115,3	116,2
Ce	150	141	151	148	253	265,0	245,0
Pr	15,8	16,7	15,2	15,4	29,8	30,0	31,0
Nd	63	59,3	61,2	60,4	112	115,0	114,0
Sm	12,1	11,4	12,3	11,8	21,9	22,0	24,0
Eu	2,5	2,4	2,3	2,4	4,5	4,7	4,6
Gd	7,6	7,7	7,6	7,4	14,0	15,0	15,0
Tb	0,8	0,8	0,8	0,7	1,6	1,7	1,7
Dy	4,2	4,1	4,3	4,4	7,1	7,2	7,4
Ho	0,5	0,6	0,5	0,4	1,0	1,0	1,0
Er	1,4	1,5	1,5	1,5	2,6	2,7	2,7
Yb	1,1	1,2	1,21	1,12	1,9	2,0	2,0
Lu	0,14	0,15	0,14	0,15	0,22	0,2	0,2
Hf	10,4	10,8	10,3	10,5	10,4	11,0	12,0
W	0,2	0,2	0,2	0,2	0,2	0,3	0,3
Re	<1	<1	<1	<1	<1	<1	<1
Au	<1	<1	<1	<1	<1	<1	<1
Tl	2,0	1,8	1,9	1,8	2,0	2,0	2,0
Pb	11,5	10,6	11,2	11,3	35,5	36,0	37,0
Bi	<1	<1	<1	<1	<1	<1	<1
Th	8,3	7,9	8,2	8,6	149,3	151,0	154,0
U	4,5	3,5	3,9	4,2	9,7	10,0	10,0

1, 2, 3, 4 – syenites; 5, 6, 7- alkaline gneisses

From the results shown in Table 1, it can be concluded that the rocks have highly similar chemical and geochemical compositions. The SiO_2 content ranges from 61.23–67.68%, which clearly indicates that these are acid rocks. This large amount of SiO_2 is also clearly manifested by the large presence of quartz in these rocks. The Al_2O_3 content ranges from 13.96–16.61%, and the Na_2O content is in the range of 0.72–3.04%. It is interesting to note the large amount of K_2O in the composition of these rocks. The K_2O content is within the interval of 7.6–10.64%. This large amount of K_2O is also reflected in the mineral composition of the rocks, with an increased amount of alkaline feldspars and alkaline amphiboles. A classification of these rocks is made based on the content of $SiO_2/Na_2O + K_2O$ (Middelmost, 1994) (Fig.7), and it was concluded that these rocks belong to the syenite- and monzonite-type groups of acid rocks; *i.e.*, that these are rocks of the same origin.

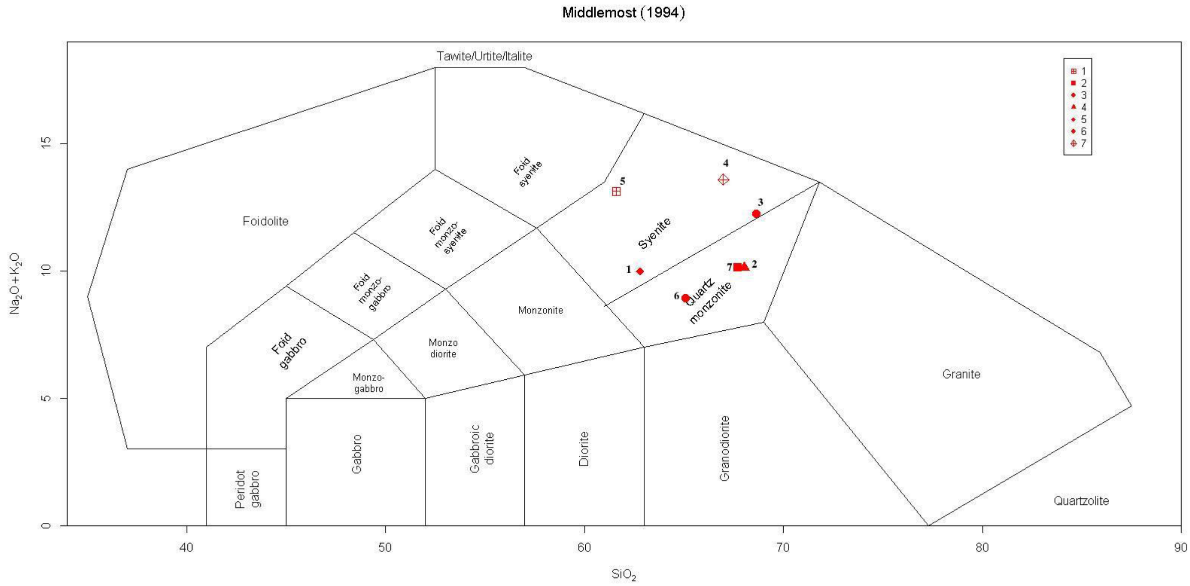


Fig 7. Total Alkali vs Silica (TAS) diagram after Middlemost (1994)

The results obtained from the geochemical investigation and the distribution of the elements from the group of REE, in rocks from the locality of Alinci (Table 2), lead us to draw the following conclusions:

- The concentration of REE in alkaline gneisses ranges from 574–592.8 mg/kg, while the concentration of REE in alkaline syenites ranges from 321.2–335 mg/kg.
- The concentration of elements from the REE group in alkaline gneisses is almost twice as high as the concentration of REE in alkaline syenites.
- The distribution of elements from the REE group shown in (Fig 8) (gneisses [L1] and alkaline syenites [L2]) shows a similar curve of the normalized values of REE with respect to the primitive mantle.
- From the concentrations of REE shown for alkaline gneisses and alkaline syenites (Table 2), as well as from the position of the distribution curves (Fig 8), it can be concluded that alkaline syenites were formed as a consequence of partial melting of alkaline gneisses, during metamorphic processes in the Pelagonia metamorphic complex (Braun et al, 1996: Meyer et al, 2009).

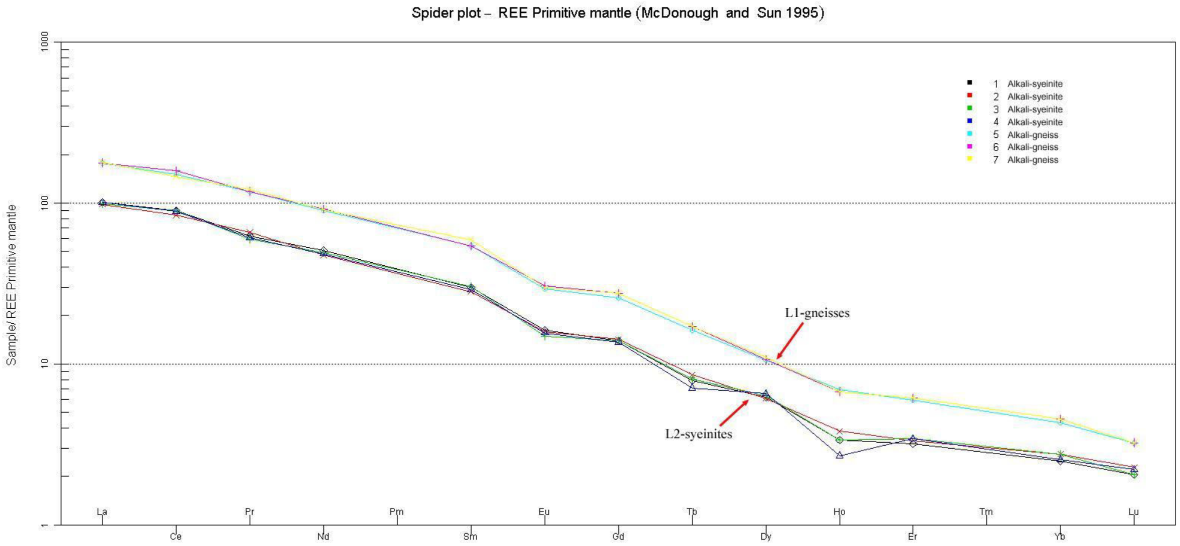


Fig.8. Spider diagram of REE in gneisses and syenites in locality Alinci (McDonough and Sun 1995)

Table 2: Concentration of elements from the REE group in gneisses and syenites from Alinci (ICP-MS method)

	1	2	3	4	5	6	7
La	65,3	63,7	64,2	65,3	114,3	115,3	116,2
Ce	150	141	151	148	253	265,0	245,0
Pr	15,8	16,7	15,2	15,4	29,8	30,0	31,0
Nd	63	59,3	61,2	60,4	112	115,0	114,0
Sm	12,1	11,4	12,3	11,8	21,9	22,0	24,0
Eu	2,5	2,4	2,3	2,4	4,5	4,7	4,6
Gd	7,6	7,7	7,6	7,4	14,0	15,0	15,0
Tb	0,8	0,8	0,8	0,7	1,6	1,7	1,7
Dy	4,2	4,1	4,3	4,4	7,1	7,2	7,4
Ho	0,5	0,6	0,5	0,4	1,0	1,0	1,0
Er	1,4	1,5	1,5	1,5	2,6	2,7	2,7
Yb	1,1	1,2	1,21	1,12	1,9	2,0	2,0
Lu	0,14	0,15	0,14	0,15	0,22	0,2	0,2
Hf	10,4	10,8	10,3	10,5	10,4	11,0	12,0
Sum	335,0	321,2	332,55	329,47	574,0	592,8	576,8

1, 2, 3, 4 – syenites; 5, 6, 7- alkaline gneisses

5. Geochronology

The age of the pegmatite occurrences at the locality of Alinci was determined by applying the isotopic K/Ar method on microcline mineral sample. Microcline is a widespread mineral within pegmatite occurrences, appearing in larger and smaller crystals. The performed isotopic examinations show that the pegmatite bodies in the locality of Alinci are from the Cretaceous period (Table 3).

Table 3: The table below presents the results of the K-Ar geochronology test. The certainty of the ages calculated falls within 2σ error.

Minerals	K (% ± σ)	40Ar rad, (ng/g) %	40Ar air	Age (MA)	2σ
Microcline	12.39 ± 0.13	93.1 ± 0.3	5.5	105.2	2.3

6. Conclusion

The Pelagonian metamorphic complex has long been exposed to polyphasic tectonic deformations and metamorphism, making its thermal evolution highly complex. Based on investigations of the age of biotites using the K-Ar method (Most et al., 2001), four tectonic-magmatic phases are distinguished which occurred pre-

Cambrian era. One group of processes occurred within the interval from 447 ± 17 MA to 267 ± 10 MA, and the second group of dynamo thermal metamorphic processes, which were accompanied by the processes of partial melting, occurred within the interval from 148 ± 6 to 114 ± 4 MA, the third group of processes occurred within the interval from 102 ± 4 to 86 ± 34 MA, and the fourth group of processes occurred within the interval from 64 to 36 MA. In summary of the aforementioned, it can be concluded that the Pelagonia metamorphic complex has a highly diverse and complex thermal evolution, over a long period of approximately half a billion years. The formation of pegmatite bodies within the locality of Alinci occurred as a consequence of partial melting, which occurred in gneisses during the Cretaceous period (105.2 ± 2.3 MA), in the so-called third phase of the thermal evolution of the Pelagonian metamorphic complex. It should be mentioned here that the formation of pegmatite bodies in the localities of Caniste occurred during the second phase of the thermal evolution of the Pelagon, within the interval of 252.4 ± 3 MA.

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