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MINERALOGICAL CHARACTERIZATION OF RIEBECKITE FROM ALINCI, REPUBLIC OF MACEDONIA

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Abstract: In this paper are presented the preliminary mineralogical characterization of riebeckite from Alinci, Republic of Macedonia. Several crystals of riebeckite were collected for research. The following three methods were used for the examination: scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectrometer (EDS), X-ray powder difraction (XRD) and Fourier Transform Infrared Spectroscopy using Diffuse Reflectance method (FTIR/DRS). With these methods was established that the investigated mineral is riebeckite. Riebeckite from Alinci appears in needle crystals with dark green-black colour, vitreous luster and greenish brown streak. The concentration of elements in riebeckite crystals is: Na (2.97–4.94%), Mg (4.89–6.96%), Fe (10.83–27.21%), Si (21.90–26.42%), Ca (0.89–4.38%). The Fe/Mg ratio is from 1.8 to 3.8. Riebeckite (with Fe/Mg >> 1) is common mineral in alkaline granites and syenites. In alkaline granites and syenites, a continuous series exists between arfvedsonite and the riebeckite. Outer surface of riebeckite is covered with the crust various thickness and width. In this crust concentration of elements is: P (0.60–15.22), Mg (0.58–5.14%), Fe(4.98–13.13%), Si (3.50–25.39%), Ca (0.59–1.63%), Al (0.73–17.33%), Ti (0.12–0.40%). There is proportional dependence between phosphorus and silicon in riebeckite crystals and crust. In the crust content of phosphorus increases, while the content of silicon decreases. Fine-grained phosphates are formed by superficial alteration processes. The nucleation and crystallization of Al and Fe phosphate phases are directly from aqueous solutions. Al and Fe phosphate phases readily precipitate from supersaturated solutions. This crust is likely a result of surface chemical reaction through altered surface layers and riebeckites dissolution at Earth surface temperatures. The most intense registered maxima in the studied powder pattern [*d* values (in Å), *I*, (*hkl*)] are: 8.44 (100), 3.12 (51), 2.80 (17), 3.14 (10), 3.27 (10), 2.71 (5), 4.20 (4), 1.65 (4), 3.25 (3).

Key words: riebeckite; X-ray powder diffraction; scanning electron microscopy;
Fourier transform infrared spectroscopy

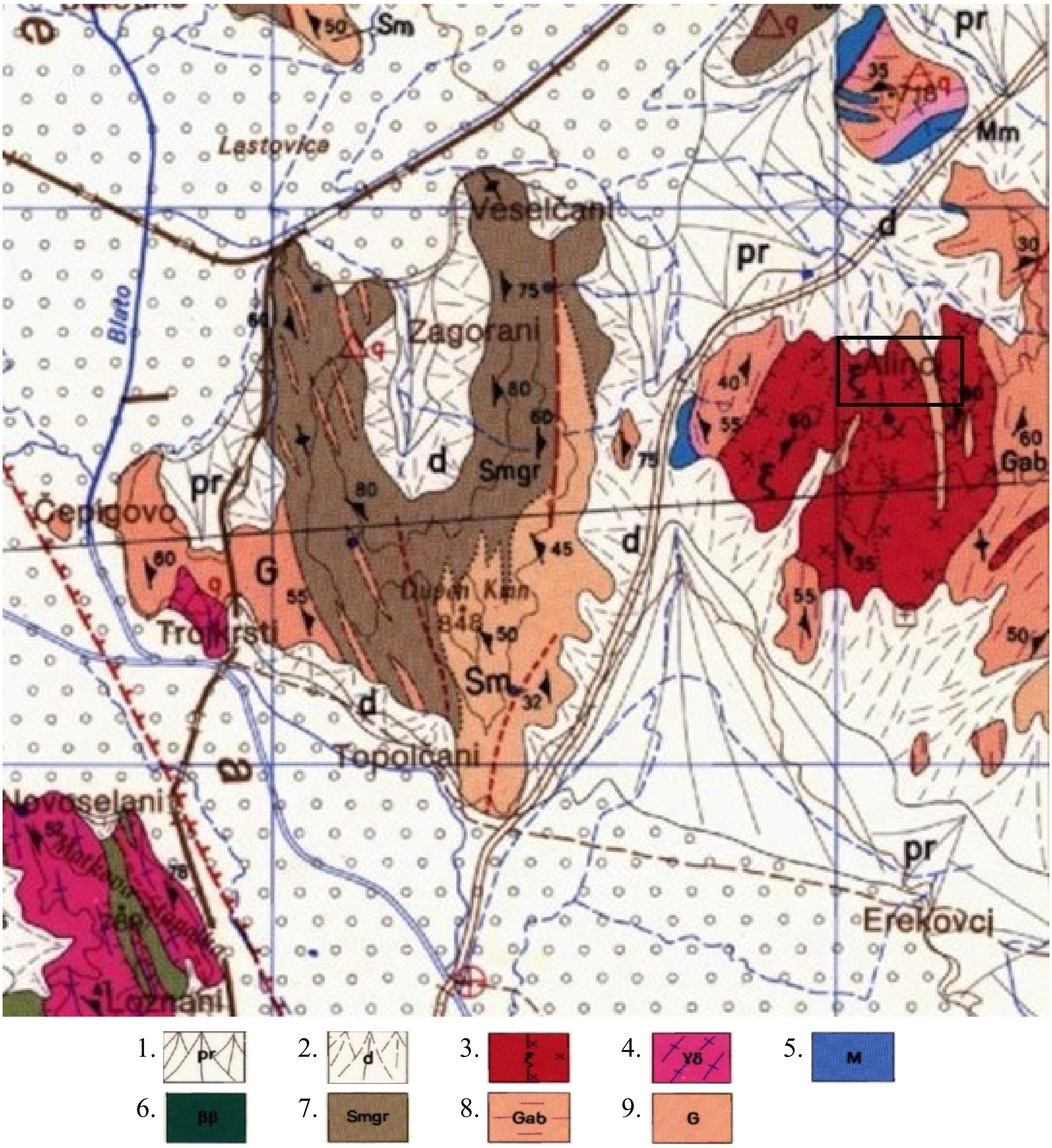
INTRODUCTION

The Alinci locality is situated 11 km southwest of Prilep. It covers an area of 4 km^2 and is built up of gneisses, syenites, marbles and schists (Figure 1). The first data on geological research at the locality Alinci are given by Kossmat (1924) and Protić (1959). Bermanec (1992) examines the mineral monazite and sennait from this locality.

Syenite is present as a magmatic body length 3 km and width 2 km. Syenite body has a fine-grained structure and a massive texture. Fine grained syenites are grayish white. They are composed of microcline, albite, quartz, arfvedsonite, augite, aegirine, biotite, sphene, apatite and zircon. Also are found coarse grains of syenite. Coarsely grain syenites are also compact, hard with green-white colour. Texture is massive. They are composed of feldspar, quartz, amphibole, pyroxene, sphene and apatite.

So far, investigations on this locality are mostly related to the geology of the locality and is given a description of only certain minerals among which is not the mineral riebeckite. Chukanov (2013) give infrared spectra of magnesioriebeckite from Alinci and Nežilovo. With our investigation in these syenites we found small lens bodies with pegmatite structure and coarse grains of microcline and quartz in which are present crystals of mineral that looked like such as riebeckite.

For this purpose we took out several representative samples from this mineral for examination.



Legend: 1. proluvium; 2. diluvium; 3, syenite; 4. granodiorite; 5. marble; 6. metamorphosed diabases; 7. graphite schist; 8. albite gneiss; 9. gneiss

Fig. 1. Geological map of locality Alinci 1:100 000 (M. Karajanović, T. Ivanovski, 1964–1972)

ANALYTICAL METHODS

For our research were used the following three methods: Fourier Transform Infrared Spectroscopy using Diffuse Reflectance method (FTIR/DRS), scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectrometer (EDS) and X-ray diffraction (XRD).

The use of these three methods showed that they are very useful methods for rapid mineral analysis contributing important analytical information.

IRPrestige 21 spectrophotometer (Shimadzu, Japan), capable of Diffuse Reflectance Spectroscopy (DRS), was employed in this study. The DRS analyses were performed by using a DRS-8000 attachment (Shimadzu). About 1 mg of the powdered samples were diluted to about 5 % by weight in dry KBr and then placed into a sample cup (2 mm diameter; 1 mm depth) which is a component of the DRS equipment. The spectra was recorded in the spectral range 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with 62 scans. For spectra manipulation was used IR Solution 1.5 software (Shimadzu Corporation).

SEM is model VEGA3LMU, increasing 2× 1000 000, W-wire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr.

Results of SEM/EDS analyses of mineral phases demonstrated usefulness of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

According to semi-quantitative results of SEM /EDS analyses, it can be concluded that SEM/EDS possesses adequate accuracy to obtain stoichiometric mineral from atomic ratios of constituent elements and identify analyzed mineral phases.

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray researches were performed using an XRD-6100 Diffractometer (Shimadzu) with X-ray Cu (1.54060 Å) radiation operating at 40 kV and 30 mA. The powdered samples were scanned over the 5–80° range with step size of 0.02° and scanning speed of 1.2°/min. The most intense registered maxima in the studied powder diagrams were compared with the corresponding diagrams from PDF-2 software.

RESULTS AND DISCUSSION

The name "riebeckite" was first used by Sauer (1888) when describing a blackish amphibole collected in Socotra (Yemen) by Dr. E. Riebeck. Riebeckite is mineral of the amphibole (alkali) group. The ideal formula of riebeckite is $[Na_2]$ $[Fe_3^{2+}]$ $Si_8O_{22}(OH)_2$ (Palache, 1951; Burke and Lake, 2004; Hawthorne, 2012). The first refinements of the crystal structures of magnesio-riebeckite and riebeckite were done by Whittaker (1949) and Colville and Gibbs (1964), respectively. Oberti et al. (2017) reported some unique peculiarities in riebeckite at high temperature. A complete set of new optical and x-ray data is given by Borg (1967) for eleven analyzed alkali amphiboles $[Na_2(Mg, Fe^{2+})_3(Al, Fe^{3+})_2 Si_8O_{22}(OH)_2]$.

Complete physical, chemical and crystallographic data on a single sample are missing in the literature.

Riebeckite from Alinci usually appears in very elongated prismatic fibrous or radial fibrous aggregates (Figures 2 and 3). Riebeckite is with dark green-black colour, vitreous luster and greenish brown streek.

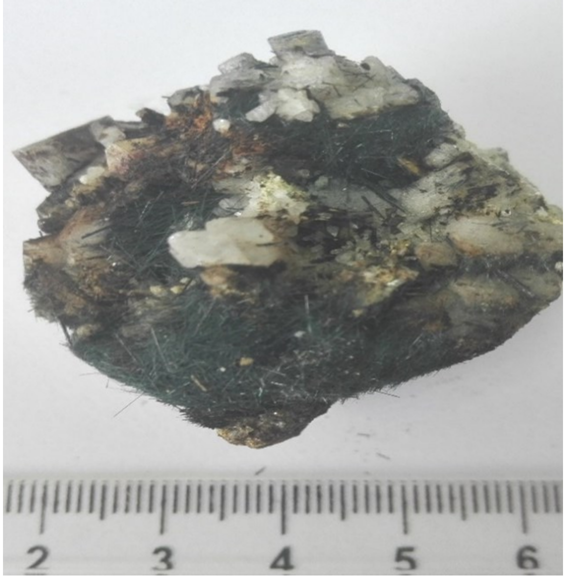


Fig. 2. Crystals of riebeckite from Alinci locality, Republic of Macedonia

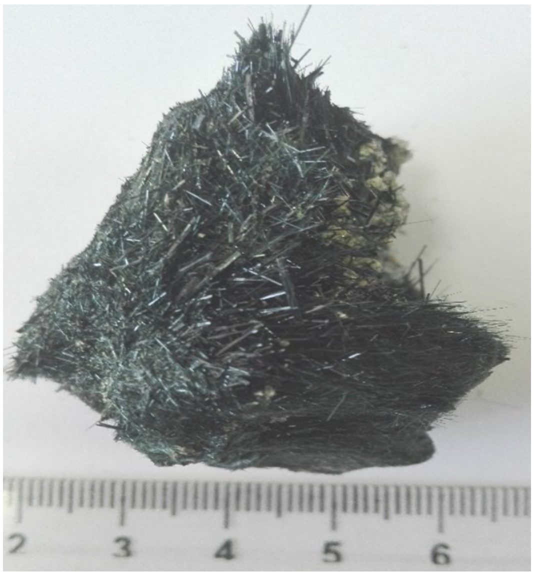


Fig. 3. Crystals of riebeckite from Alinci locality, Republic of Macedonia

The infrared spectrum of the analyzed sample is given in Figure 4. In order to *achieve resolution enhancement* of the original absorption spectrum (Figure 4a) we used the second derivative spectroscopy (Figure 4b). The second derivative profile of the original spectrum reveals a series of resolved bands which could not be assigned in a straight-forward manner.

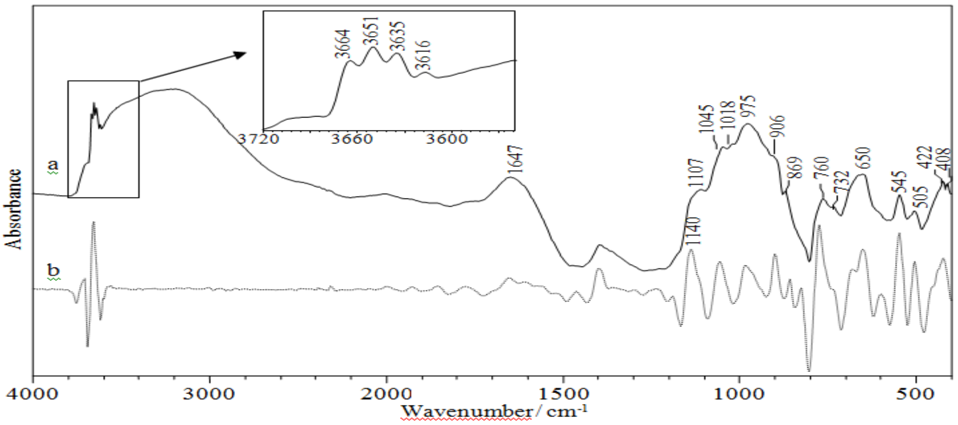


Fig. 4. (a) Infrared spectrum of the analyzed sample. **(b)** Second derivative profile (inverted curve)

The spectra inspection led to following assessments:

– The hydroxyl stretching region exhibits a series of four bands at 3664, 3651, 3635 and 3616 cm^{-1} assigned to MOH vibrations. The strong absorptions observed at 3030–3400 cm^{-1} is due to OH stretching vibrations of water, while the band at around 1650 cm^{-1} corresponds to the bending mode.

– The IR spectrum shows complexity in the region at about 1100 to 900 cm^{-1}, with several over lapping bands. This region is attributable to the antisymmetric stretching modes of Si–O–Si (Makreski, 2006; Jovanovski, 2009; Apopei, 2011), but also it can be associated with the PO_4 stretching vibrations (Frost, 2002, 2003; Capitelli, 2014; Chukanov, 2013). The presence of phosphate groups could be also assessed by the bands observed at 545 and 505cm^{-1}, ascribed to the PO_4 bending modes.

– The spectral region 900–650 cm^{-1} consists of absorption bands that could be assigned to the symmetric stretching vibrations of the Si–O and Al–O linkage.

– However, the presented spectrum indicates the presence of different mineral phases in the analyzed sample rather than a single phase of riebeckite.

The literature search revealed IR data for magnesio-riebeckite species [$Na_2(Mg_3\,Fe_2^{3+})(Si_8O_{22})(OH)_2$] from different localities (Chukanov, 2013, Apopei, 2011). The results from this work in comparison with the literature data are listed in Table 1.

The chemical properties of the riebeckite are given by Murgoci (1906), Miayshiro (1957) and Deer et al. (1963). Oberti et al. (2018) give crystal-chemical characterization of magnesio-riebeckite.

Riebeckite is found in a wide variety of paragenesess. It is a common constituent of alkalic granites and syenites (Borley, 1963; Lyons, 1972, 1976). Distinct compositional differences occur between riebeckites from different parageneses.

The results for the chemical composition of the riebeckite from the Alinci obtained by SEM-EDS for sample 1 are given in the Figures 5–8 and Table 2.

On Figures 5 and 6 is given a crystal of riebeckite wrapped with secondary crust of varying size. The crust is quite cracked. From Table 2 can be seen that there is a presence of phosphorus. The content of phosphorus is proportional to the thickness of the crust. By increasing on the content of phosphorus in the range of 2.78–13.53%, the contents of Si (19.59–4.38%), Fe (11.78–4.98%), Ca (1.07–0.81%) and Mg (5.14–0.58) decrease. The contents of Al also increase (3.25–15.12%).

SEM image and EDX spectrum for sample 2 are given in Figures 9–12 and chemistry is given in Table 3.

SEM image and EDX spectrum for sample 3 are given in Figures 13–16 and chemistry is given in Table 4.

In Table 4 is given the chemistry of the riebeckite from which can be seen that there is no presence of phosphorus.

SEM image and EDX spectrum for sample 4 are given in Figures 17–20 and chemistry is given in Table 5. From Table 5 can be seen that there is a presence of phosphorus in range 0.64–7.56%, while the silicon content is 22.88–15.99%.

SEM image and EDX spectrum for sample 5 are given in Figure 21–24 and chemistry is given in Table 6. From Table 6 can be seen that the spectrum 1 is the riebeckite, while the spectrum 2 is the crust located on the riebeckite.

SEM image and EDX spectrum for sample 6 are given in Figure 25–28 and chemistry is given in Table 7. From Table 7 can be seen that the spectrum 1 is the riebeckite, while the spectrum 2 is the crust which coveres the riebeckite and in which part of the silicon is repleaced with phosphorua.

SEM image and EDX spectrum for sample 7 are given in Figures 29–32 and chemistry is given in Table 8.

In Table 8 is given the chemistry of riebeckite (spectrum 1) and the chemistry of crust (spectrum 2). Content of silicon in riebeckite is 21.90% while in crust is 7.10. Content of phosphorus in crust is 11.66%.

Table 1

IR bands of the analyzed sample in comparison with literature data

This study	Chukanov, 2013			Apopei, 2011 [1]
	Locality: Alinci, Pelagonia, Macedonia	Locality: Skopje, Macedonia	Locality: Karelia, Russia	
408s, 422s	404, 458s	445sh 468s	451s	451
505m, 545 m	509s, 545sh	514, 556	503, 513, 544	499, 538sh
650s	655sh, 670s, 690sh	649w, 672s, 695s	666s, 691	635, 660, 692
732w		730w	732 w	
761s	767, 782	794	784	773
869sh		887	886w	879sh
906sh	900sh	910sh	901	
975s	968s	980s	977s	972s
1018sh		1000sh	1020	
1045s	1082s	1043s	1053	1033
1107s	1135sh	1103s 1150sh	1100 1145	1100 1137
3616w, 3635s, 3651s, 3664s	3615, 3640, 3680sh, 3710w,	3635w, 3655w	3655w, 3635w	3609, 3620, 3630, 3651, 3656

s – strong; m – medium; w – weak; sh – shoulder

Table 2

Chemistry of sample 1 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	52.85	O	60.20
Na	3.55	Mg	0.58
Mg	5.14	Al	15.12
Al	3.25	Si	4.38
Si	19.59	P	13.53
P	2.78	Ca	0.81
Ca	1.07	Ti	0.40
Fe	11.78	Fe	4.98
Totals	100.00	Totals	100.00

Table 3

Chemistry of sample 2 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	55.91	O	52.89
Al	16.33	Na	4.14
Si	7.45	Mg	5.14
P	12.93	Al	0.73
K	0.59	Si	22.48
Ca	0.64	P	0.60
Ti	0.47	Ca	0.77
Fe	5.68	Ti	0.12
		Fe	13.13
Totals	100.00	Totals	100.00

Table 4

Chemistry sample 3 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	48.76	O	37.29
Na	4.41	Na	3.62
Mg	6.96	Mg	4.87
Si	24.08	Si	25.39
Ca	1.76	Ca	1.63
Fe	14.03	Fe	27.21
Totals	100.00	Totals	100.00

Table 5

Chemistry of sample 4 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	50.76	O	50.24
Na	4.46	Na	1.52
Mg	5.27	Mg	3.02
Si	22.88	Al	8.40
P	0.64	Si	15.99
Ca	0.91	P	7.56
Fe	13.56	Ca	0.89
Br	1.52	Ti	0.32
		Fe	12.07
Totals	100.00	Totals	100.00

Table 6

Chemistry of sample 5 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	55.52	O	58.29
Na	4.94	Na	1.17
Mg	5.91	Mg	1.55
Si	21.90	Al	12.97
Ca	0.89	Si	7.10
Fe	10.83	P	11.66
Totals	100.00	Ca	0.73
		Fe	6.52
		Totals	100.00

Table 7

Chemistry of sample 6 (%)

Spectrum 1		Spectrum 2	
Element	Weight	Element	Weight
O	41.66	O	58.00
Na	4.02	Al	17.33
Mg	5.36	Si	3.50
Si	26.42	P	15.22
Ca	1.86	Ca	0.59
Fe	20.68	Fe	5.36
Totals	100.00	Totals	100.00

Table 8

Chemistry of sample 7

Spectrum 1		Spectrum 2	
Element	Weight%	Element	Weight%
O	41.88	O	58.89
Na	2.97	Mg	1.27
Mg	6.17	Al	15.62
Si	24.08	Si	4.13
Ca	4.38	P	12.99
Fe	20.52	Ca	0.45
		Fe	6.65
Totals	100.00		
		Totals	100.00

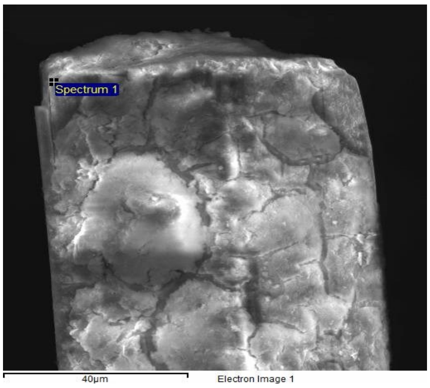


Fig. 5. SEM image of sample 1 (spectrum 1)

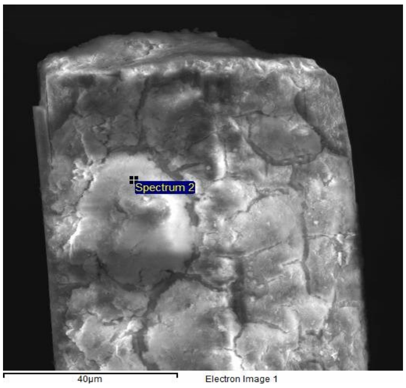


Fig. 6. SEM image of sample 1 (spectrum 2)

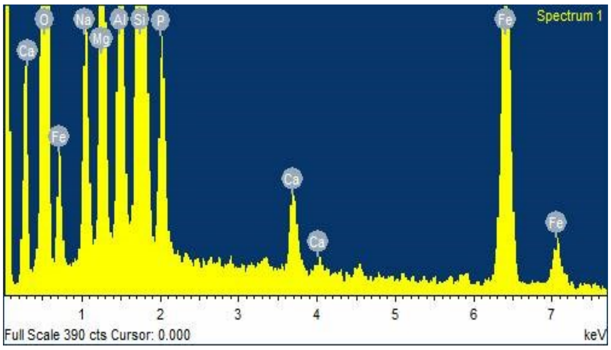


Fig. 7. EDX of sample 1 (spectrum 1)

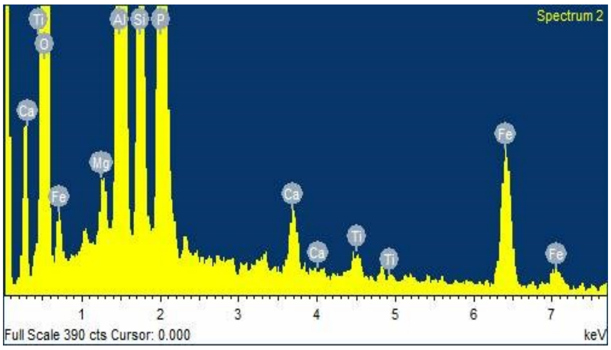


Fig. 8. EDX of sample 1 (spectrum 2)

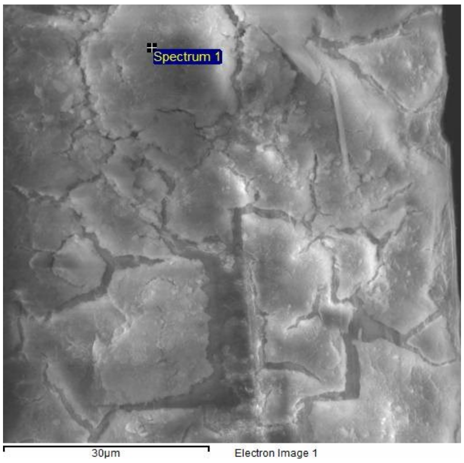


Fig. 9. SEM image of sample 2 (spectrum 1)

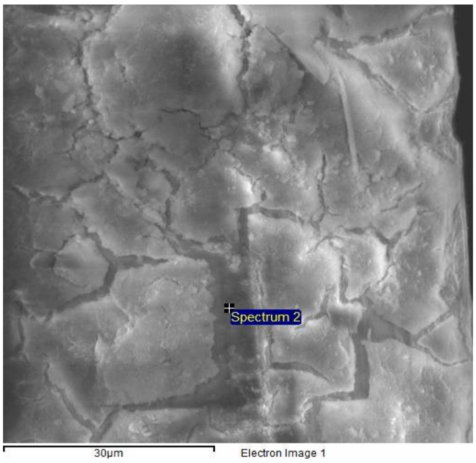


Fig. 10. SEM image of sample 2 (spectrum 2)

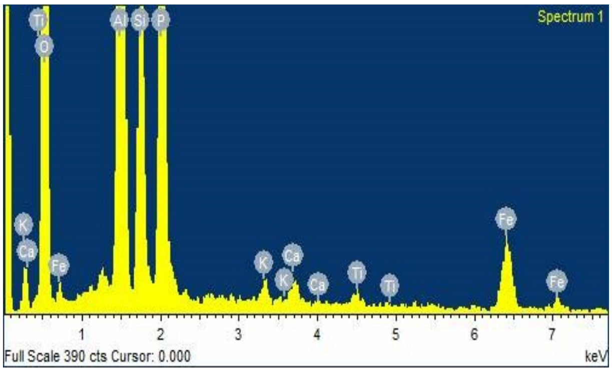


Fig. 11. EDX of sample 2 (spectrum 1)

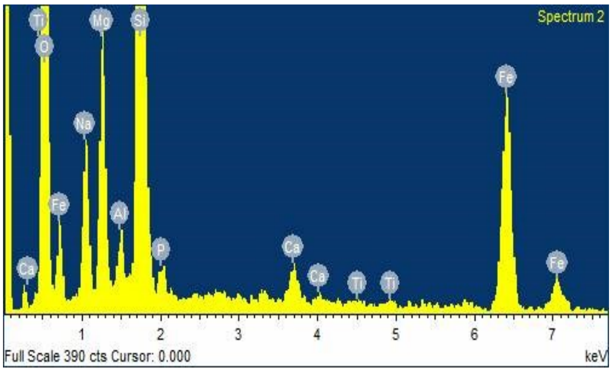


Fig. 12. EDX of sample 2 (spectrum 2)

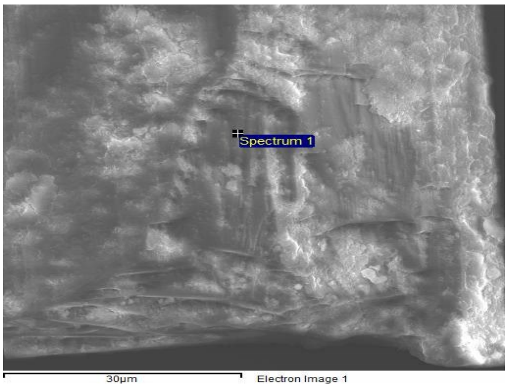


Fig. 13. SEM image of sample 3 (spectrum 1)

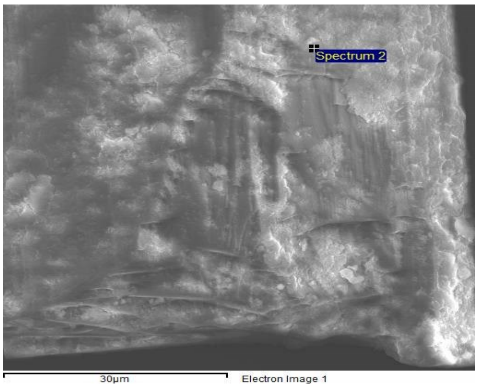


Fig. 14. SEM image of sample 3 (spectrum 2)

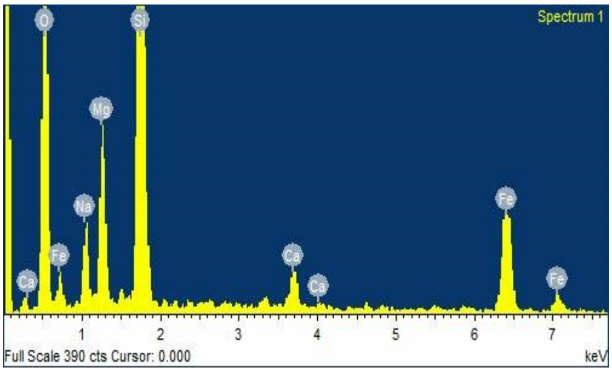


Fig. 15. EDX of sample 3 (spectrum 1)

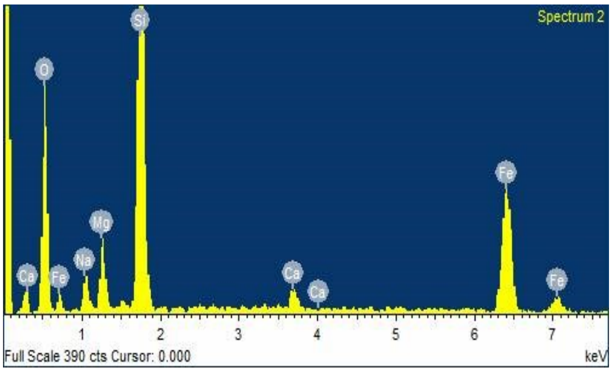


Fig. 16. EDX of sample 3 (spectrum 2)

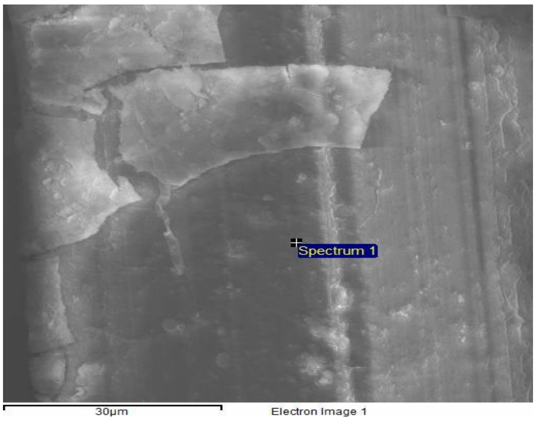


Fig. 17. SEM image of sample 4 (spectrum 1)

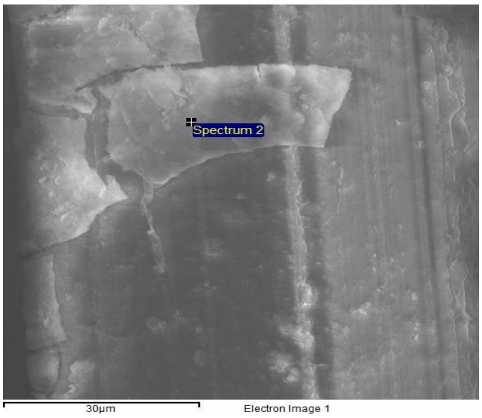


Fig. 18. SEM image of sample 4 (spectrum 2)

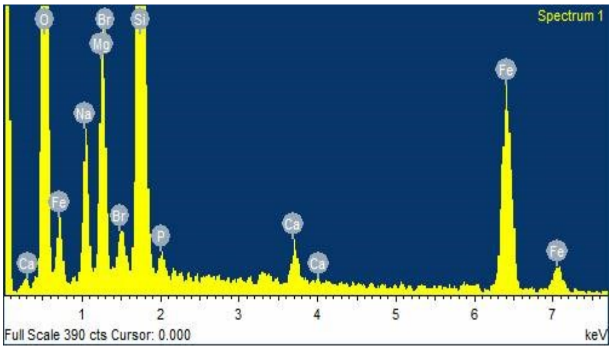


Fig. 19. EDX of sample 4 (spectrum 1)

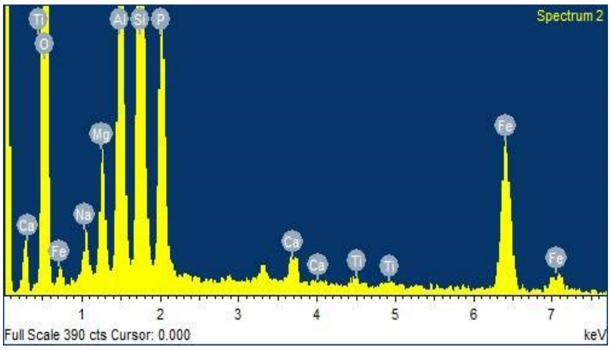


Fig. 20. EDX of sample 4 (spectrum 2)

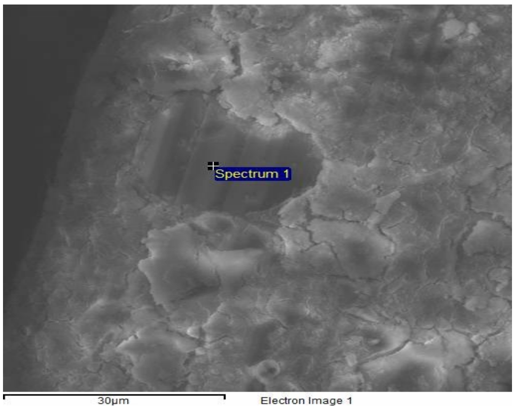


Fig. 21. SEM image of sample 5 (spectrum 1)

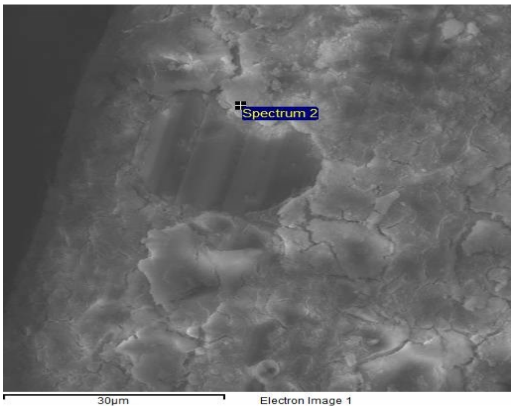


Fig. 22. SEM image of sample 5 (spectrum 2)

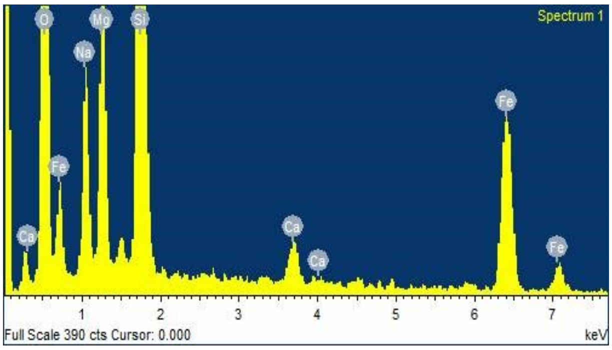


Fig. 23. EDX of sample 5 (spectrum 1)

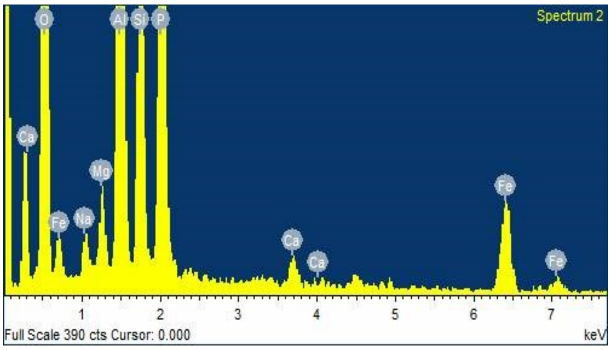


Fig. 24. EDX of sample 5 (spectrum 2)

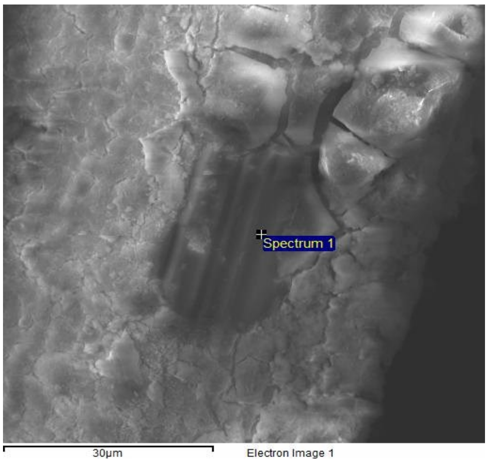


Fig. 25. SEM image of sample 6 (spectrum 1)

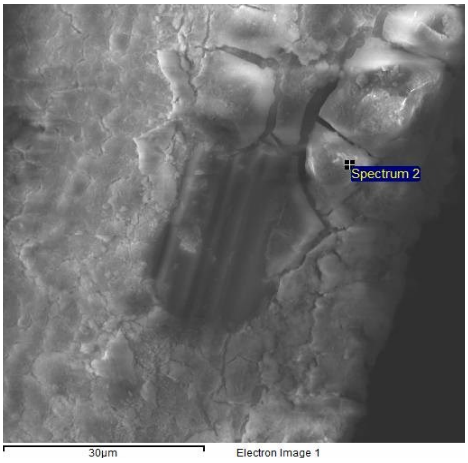


Fig. 26. SEM image of sample 6 (spectrum 2)

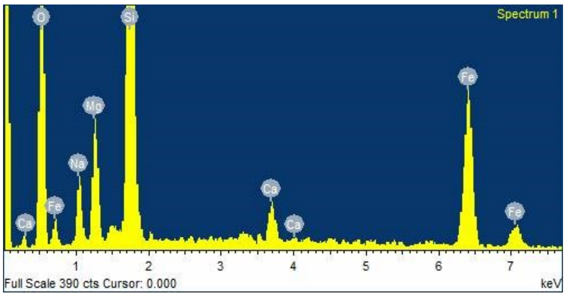


Fig. 27. EDX of sample 6 (spectrum 1)

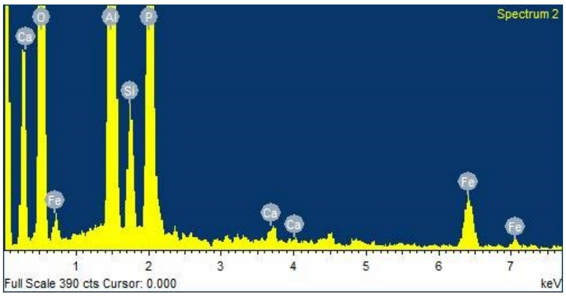


Fig. 28. EDX of sample 6 (spectrum 2)

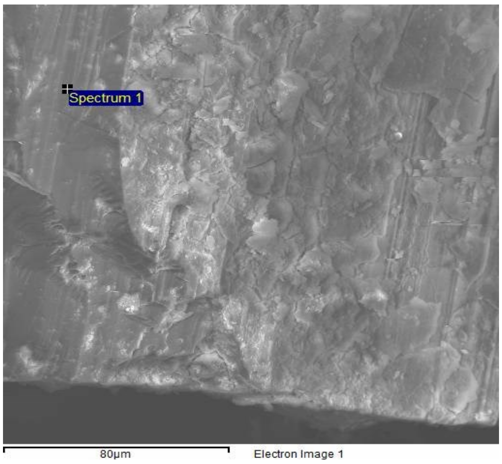


Fig. 29. SEM image of sample 7 (spectrum 1)

Fig. 30. SEM image of sample 7 (spectrum 2)

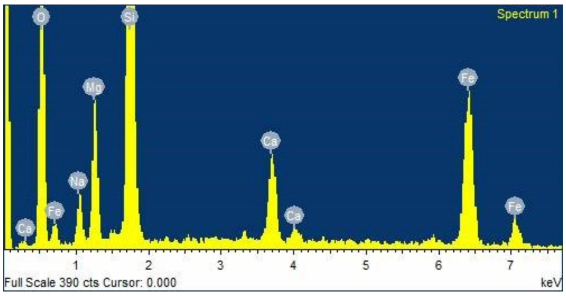


Fig. 31. EDX of sample 7 (spectrum 1)

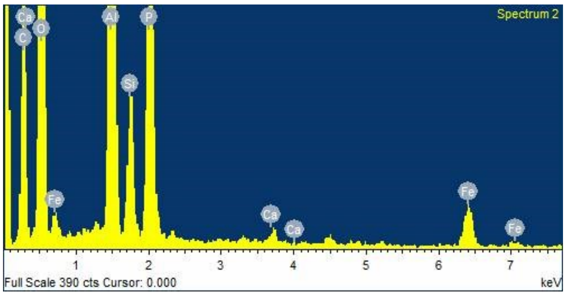


Fig. 32. EDX of sample 7 (spectrum 2)

From the data on the chemical composition given in Tables 2–8 can be concluded that the investigated samples are riebeckite. The Fe/Mg ratio in studied samples is from 1.8–3.8. Riebeckite (with Fe/Mg >> 1) is a common mineral in alkaline granites and syenites. In alkaline granites and syenites, continuous series exist between arfvedsonite and the riebeckite.The general rule of thumb is that riebeckite is found in the more silica rich alkaline rocks, although this rule is not without exceptions.

Kauko 1973 gives chemistry of magnesioriebeckite from different localities. According to him, the theoretical content of the MgO in magnesioriebeckite is 14.37%. We compared data from studied samples with data given by Kauko and the comparison is given in Table 9.

From Table 9 can be seen that in studied samples the content of MgO is lower, while the content of Fe_2O_3 is much higher.

Table 9

Comparison of data from studied samples with the data given by Kauko 1973 (%)

	Studied samples Alinci, R. Macedonia (average value)	Magnesioriebeckite from Polanka-Finland	Magnesioriebeckite from Japan	Magnesioriebeckite from West Afrika
MgO	6.59	15.55	11.98	15.8
Fe_2O_3	27.19	14.85	12.99	14.5
FeO		0.57	3.53	2.3

Outer surface of riebeckite is usually covered with the crust which has various thickness and extention. According Berner et al. (1980), amphiboles are undergo dissolution during weathering by means of the formation, growth and coalescence of distinctive, parallel, lens-shaped etch pits. The presence of phosphorus is determined in the crust. There is a proportional dependence between concentration of phosphorus and silicon. When the content of phosphorus increases, the content of silicon decreases. The content of P is in ranges from 0.60 to 15.22%, while the content of the Si is 3.50–22.88%. The identification of phosphate minerals under the microscope is not an easy task, mainly because they are mostly present in cryptocrystalline form, both as pedofeatures and as groundmass components. The development of a fine-grained phosphate is formed by superficial alteration processes.

The nucleation and crystallization of Al and Fe phosphate phases is directly from aqueous solutions. Al and Fe phosphate phases readily precipitate from supersaturated solutions. These crystallize at $T = 100$ °C to either variscite and metavariscite or strengite and phosphosiderite, respectively. Variscite is a secondary mineral formed by direct deposition from phosphate-bearing water that has reacted with aluminium-rich rocks in a near-surface environment. It occurs as fine-grained masses in nodules, cavity fillings and crusts.

In Figure 33 are given XRD patterns of the investigated riebeckite.

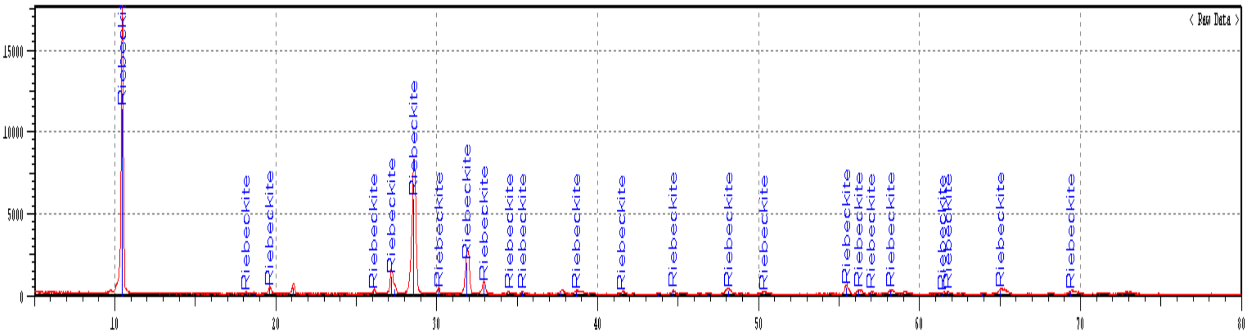


Fig. 33. XRD patterns of the investigated riebeckite

Obtained XRPD data [2θ, *d*-values (in Å), *I*, (*hkl*)] for investigated samples are given in Table 10.

Table 10

XRPD data [2θ, d*-values (in Å), I, (hkl)] for riebeckite from Alinci*

2*θ*	*d* (Å)	I	hkl
10.4655	8.4461	100	110
19.7000	4.5028	1	040
26.1200	3.4088	1	131
27.1903	3.2770	10	240
27.4200	3.2501	3	310
28.3400	3.1466	10	330
28.5798	3.1207	51	310
31.8958	2.8035	17	330
32.9165	2.7188	5	151
35.2400	2.5447	1	260
38.6200	2.3294	1	–351
41.5800	2.1702	2	261
44.5600	2.0317	1	351
44.6600	2.0274	2	242
48.1200	1.8894	2	242
55.4466	1.6558	4	461
56.0800	1.6558	1	481
56.2800	1.6332	2	480
57.0400	1.6133	1	110
58.3000	1.5814	1	660
65.0200	1.4332	2	–661
69.3400	1.3541	1	263

The most intense registered maxima in the studied powder pattern (Figure 33) area compared with the corresponding maxima of riebeckite sample from ICDDcard:00019 1061 (riebeckite from Doubrutscha [Dobrudja], Romania). The comparison has shown that the X-ray powder pattern of the natural riebeckite taken from the ICDD card are practically identical with the studied powder pattern. We also made a comparison of the obtained X-ray powder pattern with all X-ray powder patterns of the magnesioriebeckite from the PDF-2 softwer. Some of them are given in Table 11.

From the Table 11 can be seen that the obtained X-ray powder pattern completely coincides with the X-ray powder pattern on riebeckite ICDD 00 019 1061.

Table 11

X-ray powder pattern [2θ, d*-values (in Å), I, (*hkl*)] on the studied powder diagram and ICDD cards for riebeckite and magnesioriebeckite from PDF-2 softwer*

Studied powder diagram			
2*θ*	d	*I*	*hkl*
10.46	8.44	100	110
28.57	3.12	51	310
31.89	2.80	17	330
Riebeckite, ICDD 00 019 1061			
10.52	8.40	100	110
28.58	3.12	55	310
31.92	2.80	18	330
Magnesioriebeckite, ICDD 00 029 1236			
10.58	8.35	99	110
20.98	4.23	20	220
28.87	3.09	100	310
Magnesioriebeckite, ICDD 00 020 0656			
10.46	8.45	100	110
28.58	3.12	90	310
30.91	2.89	60	221

CONCLUSION

After summarizing the data collected in this research, we can confirm that the investigated minerals are riebeckite. Riebeckite from Alinci appears in needle-shaped crystals with dark green-black colour, glassy luster and greenish brown streak. The concentration of the elements in the crystals of riebeckite is: Na (2.97–4.94%), Mg (4.89–6.96%), Fe (10.83–27.21%), Si (21.90–26.42%), Ca (0.89–4.38%). The Fe/Mg ratio is from 1.8 to 3.8. Riebeckite (with Fe/Mg >>1) is a common mineral in alkaline granites and syenites. In alkaline granites and syenites, continuous series exist between arfvedsonite and the riebeckite. The general rule of thumb is that riebeckite is found in the more silica rich alkaline rocks, although this rule is not without exceptions.

The outer surface of the riebeckite is covered with crust of different thickness and width. The concentrations of elements in the crust are: P (0.60–15.22), Mg (0.58–5.14%), Fe (4.98–13.13%), Si (3.50–25.39%), Ca (0.59–1.63%), Al (0.73–17.33%), Ti (0.12–0.40%).There is a proportional dependence between phosphorus and silicon in the riebeckite and crust. In the crust the content of phosphorus increases, while the content of silicon decreases. The identification of phosphate minerals under the microscope is not an easy task, mainly because they are mostly present in cryptocrystalline form. SEM studies provide additional information on their submicroscopic structure. The development of a fine-grained phosphate are formed by superficial alteration processes.The crystallization of Al and Fe phosphate phases is a result of aqueous solutions. The phases of Al and Fe phosphates are easily deposited from over-soluble solutions.

This crust is most likely the result of a surface chemical reaction that changes the surface layers of riebeckite to temperatures on the surface of the Earth.

With the X-ray examinations the following data has been obtained: [d-values (in M), *I*, (hkl)]: 8.44 (100), 3.12 (51), 2.80 (17), 3.14 (10), 3.27 (10), 2, 71 (5), 4.20 (4), 1.65 (4), 3.25 (3).

The results obtained from all three methods confirmed that the studied samples are riebeckite.

REFERENCES

[1] Apopei, A. I., Buzgar, N., Buzatu, A.: Raman and infrared spectroscopy of kaersutite and certain common amphiboles, *Analele Stiintifice ale Universitatii“Al. I. Cuza” din Iasi Seria Geologie*, **57** (2) 35–58 (2011), Available online at http://geology.uaic.ro/auig/

[2] Bermanec, V. et al.: Monazite in hydrothermal veins from Alinci, Yugoslavia, *Mineralogy and Petrology*, Vol. **38**, Iss. 2, pp. 139–150 (1992).

[3] Bermanec, V. et al.: Uranium-rich metamictsenaite from Alinci, Yugoslavia. *European Journal of Mineralogy*, **4** (2), 331–335 (1992).

[4] Berner, R. et al: Dissolution of pyroxenes and amphiboles during weathering, *Science*, **207**, 1205–1206, (1980).

[5] Borley, G. D.: Amphiboles from the younger granites of Nigeria. Part 1. Chemical classification. *Mineral. Mag*., **33**, 358–376 (1963).

[6] Burke, E. A. J. & Leake, B. E.: “Named amphiboles”, a new category of amphiboles. *Can. Mineral*., **42**, 1881– 1883 (2004).

[7] Capitelli, F. et al.: Crystal-chemical study of wavellite from Zhirov, Czech Republic, *Mineralogical Magazine*, Vol. **78** (4), 1057–1070 (2014).

[8] Chukanov, N. V.: Infrared spectra of mineral species: Extended library, Springer Geochemistry / Mineralogy, Springer Science & Business Media, 2013.

[9] Colville, A. A. and Gibbs, G. V.: Refinement of the crystal structure of riebeckite. Geological Society of America, *Abstracts Annual Meetings*, **82**, 31 (1964).

[10] Deer, W. A., Howie, R. A., Zussman, J.,: *Rock-forming Minerals*, Volume **2**, *Chain Silicates*, 1963, pp. 333–351.

[11] Frost, R. L., Martens, W., Williams, P. A. and Kloprogge, J. T.: Raman and infrared spectroscopic study of the vivianite-group phosphates – vivianite, baricite and bobierrite, *Mineralogical Magazine*, Vol. **66** (6), 1063–1073 (2002).

[12] Frost, R. L., Erickson, K. L., Weier, M. L., & Mills, S.: Raman spectroscopy of the phosphate minerals: cacoxenite and gormanite, *Asian Chemistry Letters*, **7** (4), pp. 197–203 (2003).

[13] Hawthorne, F. C., Oberti, R.: On the classification of amphiboles. *The Canadian Mineralogist*, **44**, 1–21 (2006).

[14] Jovanovski, G., Makreski, P., Kaitner, B., Boev, B.: Silicate minerals from Macedonia. Complementary use of vibrational spectroscopy and X-ray powder diffraction for identification and detection purposes, *Croatia Chemica Acta*, **82**, 363–386 (2009).

[15] Hawthorne, F. C., Oberti, R., Harlow, G. E., Maresch, W. V., Martin, R. F., Schumacher, J. C., Welch, M. D.: Nomenclature of the amphibole supergroup. *American Mineralogist*, **97**, 2031–2048 (2012).

[16] Kossmat, F: Geologie der zentralen Balkanhalbinsel. Mit einer Ueber-sicht des dinarischen Gebirgsbaus. Die Kriegsschauplatze 1914–1918 geologisch Dargestellt, H. 12, Berlin, 1924.

[17] Kauko Laajoki and Pentti Ojanperä: Magnesioriebeckite and penninite from a shear zone in Puolanka, N E Finland, *Bull. Geol. Soc. Finland,* **45**, 143–153 (1973).

[18] Lyons, P. C.: Significance of riebeckite and ferrohastingite in microperthite granites. *Arnel. Mineral*. **57**, 1404–1412 (1972).

[19] Lyons, P. C: The chemistry of riebeckite of Massachusetts and Rhode Island. *Mineral. Mag.* **40**, 473–479 (1976).

[20] Makreski, P., Jovanovski, G., Gajovic, A.: Minerals from Macedonia – XVII. Vibrational spectra of some common appearing amphiboles, *Vibrational Spectroscopy* **40**, 98–109 (2006).

[21] Miyashiro, A.: Cordierite-indialite relations. *Am. J. Sci.* **255**, 43–62 (1957).

[25] Murgoci G. M.: Contribution to the classification of the amphiboles. On some glaucophane schists and syenites. *Bull. of the Department of Geology*, *University of California*, 4, 359–395 (1906).

[22] Oberti, R. et al.: Magnesio-riebeckite from the Varenche mine (Aosta Valley, Italy): crystal-chemical characterization of a grandfathered end-member. *Mineralogical magazine*, **81** (6), 1431–1437 (2017).

[23] Oberti, R. et al.: The high-temperature behaviour of riebeckite: expansivity, deprotonation, selective Fe oxidation

and a novel cation disordering scheme for amphiboles., *Eur. J. Mineral*. (2018) in press,

[24] Palache, C. et al.: *The System of Mineralogy of the Danas*, Vol 2. John Wiley and Sons, New York, 1951.

[25] Protić, M., Cvetić, S.: Alkali syenite and related rocks of Crni Kamen south of Prilep (Macedonia). Geološki anali Balkanskoga poluostrva, Issue 26, 205–2018. Beograd, 1959.

[26] Sauer, A.: Ueber Riebeckit, ein neues Glied der Hornblendegruppe, sowie über Neubildung von Albit in granitischen Orthoklasen. *Zeitschrift der Deutschen geologischen Gesellschaft*, **40**, 138–152 (1888) (in German).

[27] Whittaker, E. J. W.: The structure of Bolivian crocidolite. *Acta Crystallographica,* **2**, 312–317 (1949).

Резиме

МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА РИБЕКИТОТ ОД АЛИНЦИ, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: рибекит; инфрацрвена спектроскопија; скенирачки електронски микроскоп; рендгенска дифракција

Во овој труд се презентирани прелиминарните резултати за минералошка карактеризација на рибекитот од Алинци, Р. Македонија. Испитувањата се вршени со следниве три методи: IR – инфрацрвена спектроскопија, SEM/EDS – скенирачка електронска микроскопија, X-ray – рендгенска дифракција. Рибекитот од Алинци се појавува во игличести кристали со темна зеленоцрна боја, стаклеста сјајност и зеленикаво кафеав огреб. Концентрацијата на елементите во рибекитот е: Na (2,97–4,94%), Mg (4,89–6,96%), Fe (10,83–27,21%), Si (21,90–26,42%), Ca (0,89–4,38%). Соодносот Fe/Mg е од 1,8 до 3,8. Рибекитот (со Fe/Mg >> 1) е чест минерал во алкалните гранити и сиенити. Во алкалните гранити и сиенити постои континуирана серија помеѓу арфведсонит и рибекит, а општо правило е дека рибекитот се наоѓа во алкалните карпи богати со силициум, иако ова правило не е без исклучоци. Надворешниот дел на рибекитот е покриена со кора со различни големина и дебелина. Концентрација на елементи во кората е: P (0,60–15,22%), Mg (0,58–5,14%), Fe (4,98–13,13%), Si (3,50–25,39%), Ca (0,59–1,63%), Al (0,73–17,33%), Ti (0,12–0,40%). Постои пропорционална зависност помеѓу фосфорот и силициумот во рибекитот и во кората. Во кората содржината на фосфор се зголемува, а содржината на силициум се намалува. Кристализацијата на фосфатните фази на Al и Fe е резултат на водните раствори. Фазите на фосфатите на Al и Fe лесно се таложат од презаситени раствори. Оваа кора е најверојатно резултат на површинска хемиска реакција со која се врши промена на површинските слоеви на рибекитот на температури на површината на земјата. Со рендгенските испитувања се добиени следниве податоци [*d* вредности (во Å), *I*, (*hkl*)]: 8,44 (100), 3,12 (51), 2,80 (17), 3,14 (10), 3,27 (10), 2,71 (5), 4,20 (4), 1,65 (4), 3,25 (3). Резултатите добиени од сите три методи дадоа јасна идентификација и потврдија дека испитуваните примероци се рибекит.