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SPODUMENE AND BERYL FROM CONȚU LITHIUM - PEGMATITES, CINDREL (CIBIN) MOUNTAINS, CENTRAL GROUP, SOUTH CARPATHIANS, ROMANIA

Nicolae CĂLIN[1], Ciprian CONSTANTINA[1], & Elena Ramona BĂLĂȘCUȚĂ[1]
[1]Geological Institute of Romania, Caransebeş Str., No. 1, sector 1, RO-012271, Bucharest, Romania
nickcalin@gmail.com, cconstantina@yahoo.com, ramona.balascuta@yahoo.com,

Abstract: Spodumene, now in the everyday life, represent a critical source of the chemical element known as lithium. For principle reducing emissions of CO_2, now and in the future, we can find an alternative resource like green resources – spodumene. The first step is to identify the field with minerals - prospecting, then the second is exploration, and culminates with exploitation. In Romania, we find probably the only fields with lithium pegmatites in Conțu. Pegmatitic bodies are known as Conțu Superior and Conțu Inferior. Spodumene appears in the form of crystals and massive aggregates, with long habitus – prismatic, sometimes tabular, and with dimensions of 25 cm – 70 cm. Its color varies from white–greenish with vitreous luster, to gray – greenish, color due to the alteration processes, which led to the appearance in green – yellow colors on the spodumene has a good cleavage on the plane (010). Spodumene has monoclinic symmetry and C2/c space group (15), and cell parameters: a = 9.466 Å, b = 8.394 Å, c = 5.221 Å. The analytical method (EPMA) indicated a lithium oxide content between 7.43 % and 7.50 %, these percentages were calculated. Beryl (the emerald variety) macroscopically, has a greasy luster, colors in light green to dark green tones, in the mass of quartz and albite. Beryl crystallizes in the hexagonal system, space group P6/mcc (192), and the cell parameters are a = 9.267 Å, b = 9.187 Å. Infrared transmittance spectroscopy indicated the presence of beryl. BeO_4 vibrates at frequencies around 900 cm^{-1} and 1000 cm^{-1}, we find in sample N118, valence vibrations at: 1094 cm^{-1}, 1039 cm^{-1}, and 957 cm^{-1}.

Keywords: lithium – pegmatites, green – beryl, spodumene, lithium, Conțu pegmatites

1. INTRODUCTION – GENERAL CONSIDERATION

The pegmatites with spodumene that have emerged in the Conțu brook, lithium pegmatites, may be the only lithium pegmatites with rare metals in Romania. Due to its exotic character, the lithium pegmatite from Conțu has been researched petrographically, mineralogically, geochemically, and genetically by several authors: Dittler & Kimbauer, (1931); Vendl, (1932); Pomârleanu et al., (1967); Maier et al., (1968); Diaconu et al., (1976); Hann, (1987); Hîrtopanu et al., (1989); Săbău et al., (1987, 1989), Săbău, (1994, 1995); Murariu, (1992-1993), Murariu et al. (2008); Androne, (2005a, b), Androne et al. (2009); Buzgar et al., (2006); Călin et al., (2009, 2010, 2020a, b). Research has shown that lithium pegmatites have a granitic composition characterized by the mineralogical association consisting of albite, spodumene, quartz, and muscovite. These minerals considered the main minerals, are associated with accessory minerals such as staurolite - sillimanite - almandine - spessartine - zircon - eucryptite - topaz - chloritoid - titanite - dumortierite - zoisite - epidote - beryl - cordierite - tourmaline - biotite - chlorite - fengite - lepidolite - paragonite - kaolinite - celadonite - illite - cookeite - sericite - microcline - microcline-perthite - oligoclase - bikitaite - rutile - cassiterite - magnetite - hematite - uraninite - mangano-columbite - columbite-tantalite - spinel - ilmenite - zirconolite - purpurite - heterosite - triphyline - lithiophilite - ferrisicklerite - amblygonite - montebrasite - monazite - fluorapatite - hydroxylapatite - hureaulite - tavorite - alluaudite - variscite - xenotime - graphite - pyrite - fluorite – sphalerite. The genesis of lithium pegmatites was first attributed to magmatic origin due to the complex mineralogy that encompasses rare minerals. Based on the relationship between pegmatites and host rocks, inter-mineral relationships, and the lack of magmatic bodies, it was concluded that these pegmatites are metamorphic. Most likely, these pegmatites formed under metasomatic-anatectic conditions, crystallizing from a pegmatitic fluid, without an observable melting Săbău, et al., (1987). This process involves temperatures and pressures belonging to the Precambrian metamorphic event, suffered by the Sebeș - Lotru group, and developed in the conditions of the amphibolite facies, the area with kyanite and staurolite. The genesis of pegmatites consists of a complex geochemical evolution given by the alkaline fluid that can produce the pegmatitic field Conțu, Murariu, et al., (2008).

Our goal is to indicate perhaps the only pegmatites with rare elements in Romania.

The objectives can be achieved if we have data about the minerals in the area, one of the most important is the economic one.

2. ANALYTICAL METHODS USED

We use for this study:

A) Polarized light microscopy (PLM) to identify minerals on thin sections. The optical microscopes are Leica type and Jenapol U type.

B) Scanning electron microscopy (SEM) Rem 100U uses an energy dispersive system equipped with an Edax Oxford ISIS GO 3.2., for the calibration of the device, it was used as standards: fluorapatite $Ca_5(PO_4)_3F$, alkaline feldspar – orthoclase $KAlSi_3O_8$, MnO and metallic Fe.

C) Powder X-ray diffraction (XRD) – with Bruker D8 ADVANCE (CuKα radiation, $\lambda = 1.54056$ Å), accelerating voltage of 40 kV and beam current of 40 mA, with software PDF-2/Release 2013 and EVA 13 database ICDD.

D) Infrared Transmittance Spectroscopy (ITS) made with Bruker TENSOR 27 spectrometer with Fourier transform and software called OPUS 6.5., Anason, et al., (2010).

E) Electron probe micro–analyzer (EPMA)-was conducted with a CAMECA SX-50, operating in wavelength–dispersion mode, with a beam current of 20 mA, an accelerating voltage of 15 kV, the device is calibrated using: titanite $CaTiSiO_5$, jadeite $NaAlSi_2O_6$, graftonite $(Fe^{2+},Mn,Ca)_3(PO_4)_2$; topaz $Al_2SiO_4(F,OH)_2$, pyrope $Mg_3Al_2(SiO_4)_3$, andradite $Ca_3Fe_2(SiO_4)_3$, spessartine $Mn_3Al_2(SiO_4)_3$.

F) With Raman spectroscopy we obtained spectra on minerals using the micro-Raman spectrometer Renishaw In Via coupled with a Peltier-cooled CCD detector. Excitation was provided by a 532 nm laser with a nominal power of 50 mW at room temperature. Data acquisition was carried out using Wire software version 3.2. The micro-Raman spectra were acquired using an exposure time of 10 s per frame, and 10–20 acquisitions at a laser power of 0.5%–1%, to improve the signal-to-noise ratio. Spectra were obtained using 20× magnification objectives. Calibration was performed using a 520.5 cm^{-1} line of silicon.

3. THE PEGMATITES BODIES

Geological research highlights the presence of pegmatitic bodies on the left and right slopes of the Conțu Valley, in the area called Conțu Inferior, and in the area upstream of the Dinamitierii brook, known as the Conțu Superior area. The pegmatites developed in these fields are associated with the outcrops with mica-schists and micaceous gneisses, geological formations belonging to the Sebeș - Lotru group (Figure 1-3). The pegmatites from the Conțu field are located on the homonymous tributary of the Sadu river, belonging to the Precambrian group Sebeș - Lotru, Săbău, et al., (1989).

Pegmatites in the Conțu area appear in the form of tabular veins, or the form of irregular lenses or bodies generally arranged by the schistosity of the host of metamorphic rocks. The pegmatitic veins have a thickness that varies between 2 and 10 meters in the central area and development in the direction between 170 and 475 meters. The veins are affected by transverse and directional fractures in general with low amplitude jumps (0.5 - 5 meters) and delimit the area of pegmatites with spodumene. Most of the pegmatitic bodies emerge on the left slope of the Conțu Valley, are thick from a few tens of centimeters to a few meters, are strongly fragmented and cracked, and show supergene alteration phenomena, Androne, (2005a), tavorite and apatite are the result of processes supergene, Roda, et al., (1998). Fractures lead to strong tectonization of pegmatite bodies.

The contact between pegmatites and metamorphic rocks is highlighted by the presence of mafic minerals, especially tourmaline and biotite. Frequent tourmaline is reported at the contact between pegmatites and mica, the thickness of the tourmaline (shorl) being of centimeter order, and the crystals oriented parallel to the plane of the contact line. The appearance of mafic minerals is explained by metasomatic processes, generated by the reactions between the host rock and the pegmatitic fluid. In the central area, block structures are reached Maier et al., (1968). In a pegmatite vein from Conțu, it was possible to observe the decrease of the quartz content from the upper to the lower part of the vein, noting an incipient asymmetrical zonation. The aplitic areas of the pegmatites are represented by albite–oligoclase, quartz, biotite, kyanite, and garnet; the intermediate zone has a macro granular structure due to the presence of spodumene, quartz, plagioclase feldspars, potassium feldspars, beryl, garnets, muscovite; lithium, iron, manganese and calcium phosphates and cassiterite.

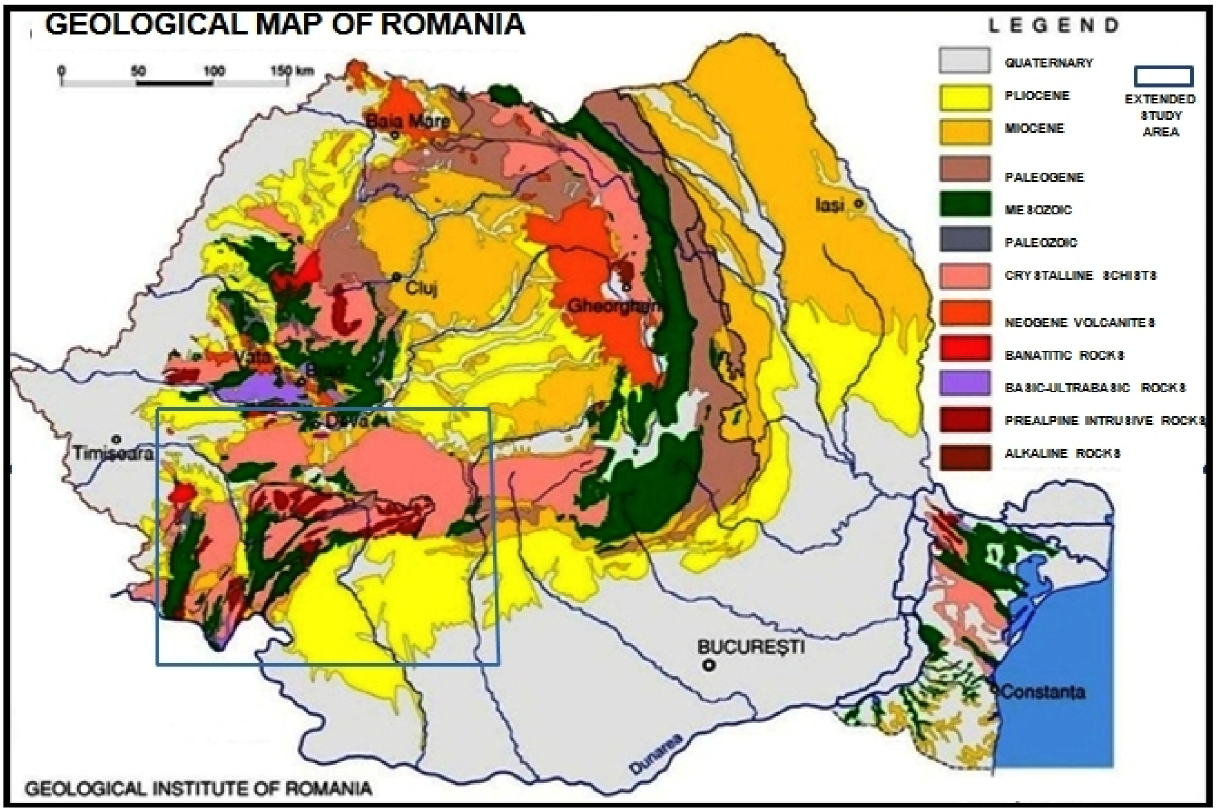

Figure 1. Geological map of Romania, after Geological Institute of Romania.

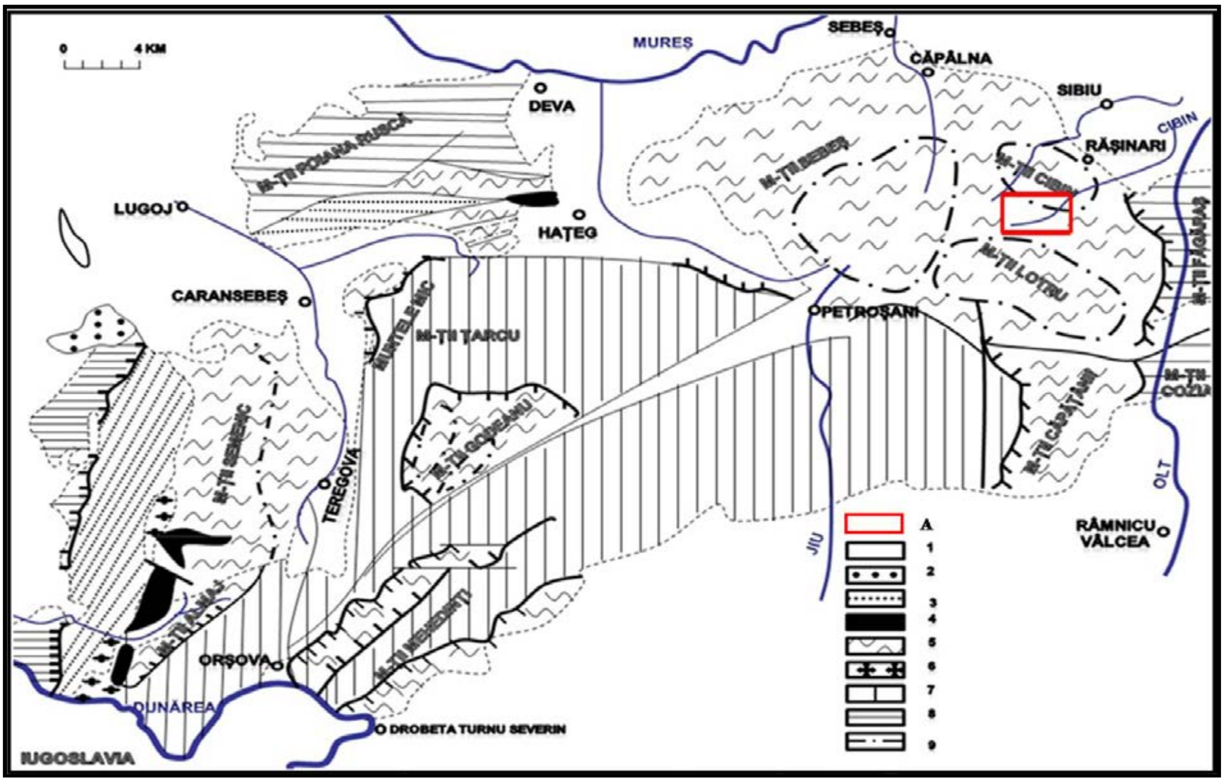

Figure 2. Areas of development of pegmatites in the Southern Carpathians: 1 = post-Austrian sedimentary cover; 2 = banatites rocks; 3 = Upper Paleozoic and Mesozoic sedimentary cover; 4 = Buceava, Miniș, Dăbâca, and Căpâlna series; 5 = Sebeș - Lotru group - Upper Precambrian; 6 = massive granitoid; 7 = Danube units; 8 = supragetic units; 9 = areas with pegmatites mobilizations, A = study area; after Hann, (1987).

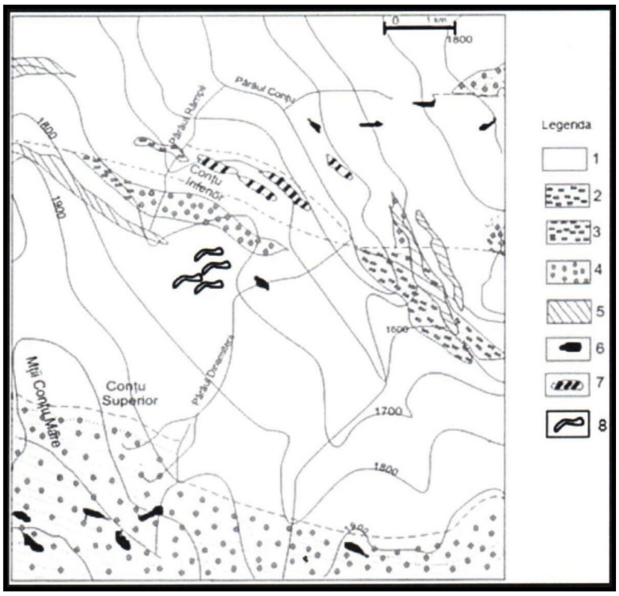

Figure 3. Geological sketch of the pegmatitic field Conțu - Negovanu: 1 = gneisses micacee and mica-schists; 2 = mica-schists with kyanite; 3 = mica-schists with staurolite; 4 = mica-schists with garnets; 5 = amphibolites, gneisses and amphibolic schists; 6 = pegmatites; 7 = albite-spodumene pegmatites; 8 = graphic pegmatites (Săbău, et al., 1989).

These minerals are growing towards the center of the pegmatitic body, highlighting quartz, feldspars, and spodumene; the latter measuring 50-70 centimeters Androne, (2005a).

From the point of view of mineralogical composition, pegmatites can be divided into two types: muscovitic-feldspar pegmatites - and lithium pegmatites - characterized by the association of albite + spodumene. Muscovite-feldspar pegmatites have a mineralogical association: feldspars, quartz, muscovite, biotite, and accessory minerals.

They are located on the surface, have supergene alteration processes, and depending on the predominant alkalis in their composition, can be: potassium – sodium, in which feldspar minerals are represented by microcline and microcline - perthite and sodium–potassium (Figure 5), in which the predominant mineral is represented by albite. including the cleavelandite variety, to which is added plagioclase.

Macroscopically, these pegmatites have a light color, white, yellowish-white, white-gray, or even white-pink, they are hard, compact, and intensely cracked. Microscopically, it has a simple composition: polysynthetic spotted plagioclase feldspars, quartz, microcline, microcline-perthite, muscovite, biotite, sometimes tourmaline, and rarely epidote–zoisite, apatite, and sphene (titanite).

The second type of pegmatite: lithium pegmatites - is characteristic of the Conțu field. Lithium pegmatites are located in veins and lens-shaped bodies located mostly in-depth and to a lesser extent on the surface. The mineralogical association consists of albite (cleavelandite), spodumene, quartz, and muscovite. Macroscopically, lithium pegmatites have a massive, white-gray appearance due to the presence of smoky quartz that can carry chemical elements such as Al and Li, Calas, (2011), sometimes slightly greenish, due to the presence of large amounts of spodumene and muscovite (Figure 4). They are hard rocks and have a gradual transition to adjacent rocks. In the mass of these types of lithium pegmatites, there are large aggregates of spodumene, with dimensions of up to a few centimeters, a mineral that appears associated with white-bright tabular masses of feldspars (albite); there are also aggregates of white quartz – purplish, glassy and greenish packets of muscovite, Androne, (2005b). Subordinate “nests” of Li, Fe, Mn, Ce, and Ca phosphates appear.

Phosphate tends to penetrate the spodumene prism, Călin, et al (2020a), and accumulate in the initial phase at the base of the prism, after which, at a later stage, it migrates to the cracks encountered in the mineral, (Figure 4).

Microscopically, a predominance of plagioclase, polysynthetic twin, can be observed over potassium feldspars (microcline and microcline-perthite).

The spodumene is usually cracked and has quartz inclusions (Figure 4), and feldspars (Figure 4), with which it is overgrown; exsolutions between spodumene and quartz have been indicated which lead to the intergrowth between spodumene and quartz (Figure 4), intergrowth due to the breakdown of the petalite during the cooling of the pegmatitic melt, London, (1984). Muscovite inclusions have also been observed, which appear to come from two different sin- and post-kinematic generations (Figure 5), and phosphates with the same characteristics as muscovite appear accompanied by both sin-kinematic and kinematic quartz, and post-kinematic in the prismatic crystal of the spodumene (Figure 5).

The microcline shows the crosshatched, crystal twinning, and the microcline-perthite is characterized by perthitic separations with the appearance of vines or beaches, (Figure 5).

Microcline + sillimanite, resulting association based on the balance equation according to Le Châtelier's, (1884) principle: Muscovite + Quartz = Potassium Feldspar + Sillimanite + H_2O. Microcline replacing oligoclase; areas with crosshatched crystal twinning represent microcline, and areas without crosshatched crystal twinning represent oligoclase, (Figure 5).

Quartz occurs in large quantities, and muscovite is most often associated with feldspars and

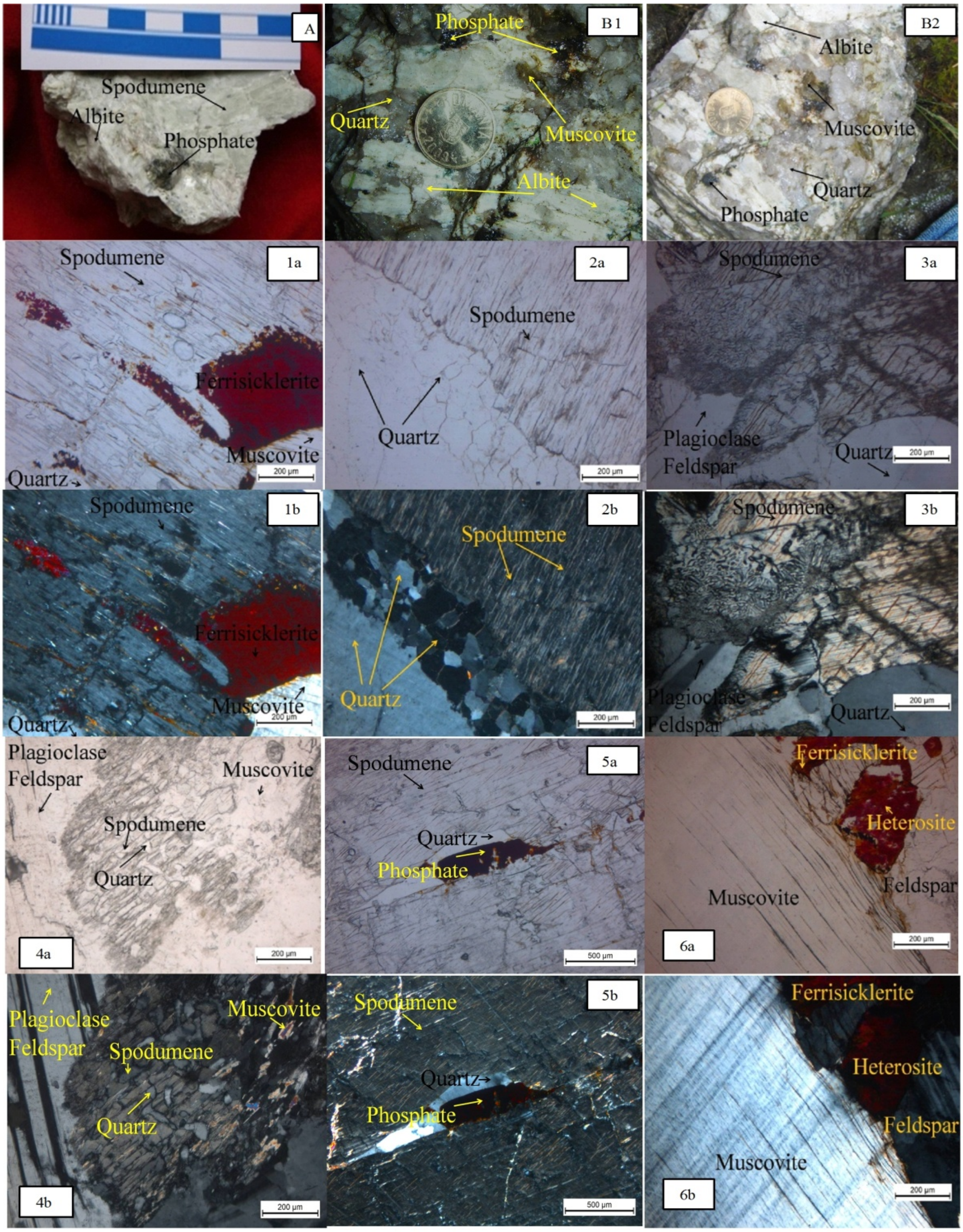

Figure 4. A B1 B2 Macroscopic images of spodumene in association with phosphate, quartz, feldspar, and muscovite 1a.b = It can be seen how the phosphate tends to penetrate the spodumene prism. (1a = plane polarized light = N II; 1b = cross polarized light = N +. 2a.b = PLM of mineralogical association: spodumene – quartz. We observe how between the two minerals, quartz recristallization (2a = N II. 2b = N +). 3a.b – PLM = Quartz shows an intergrowth with feldspar (feldspar and quartz seem to replace spodumene) (3a = N II. 3b = N +). 4a.b – PLM of Spodumene relict (pseudomorphosis) is replaced by quartz and muscovite, in the pegmatites from Conțu. (4a = N II. 4b = N+). 5a.b = PLM of pyroxene, phosphate, and quartz, spodumene prism are penetrated by phosphate-bearing quartz (5a = N II, 5b = N +). 6a.b = PLM of the feldspar+phosphates (heterosite - yellow and purple tones, ferrisicklerite - red tones) + muscovite. (6a = N II, 6b = N+). PLM–(polarized light microscopy).

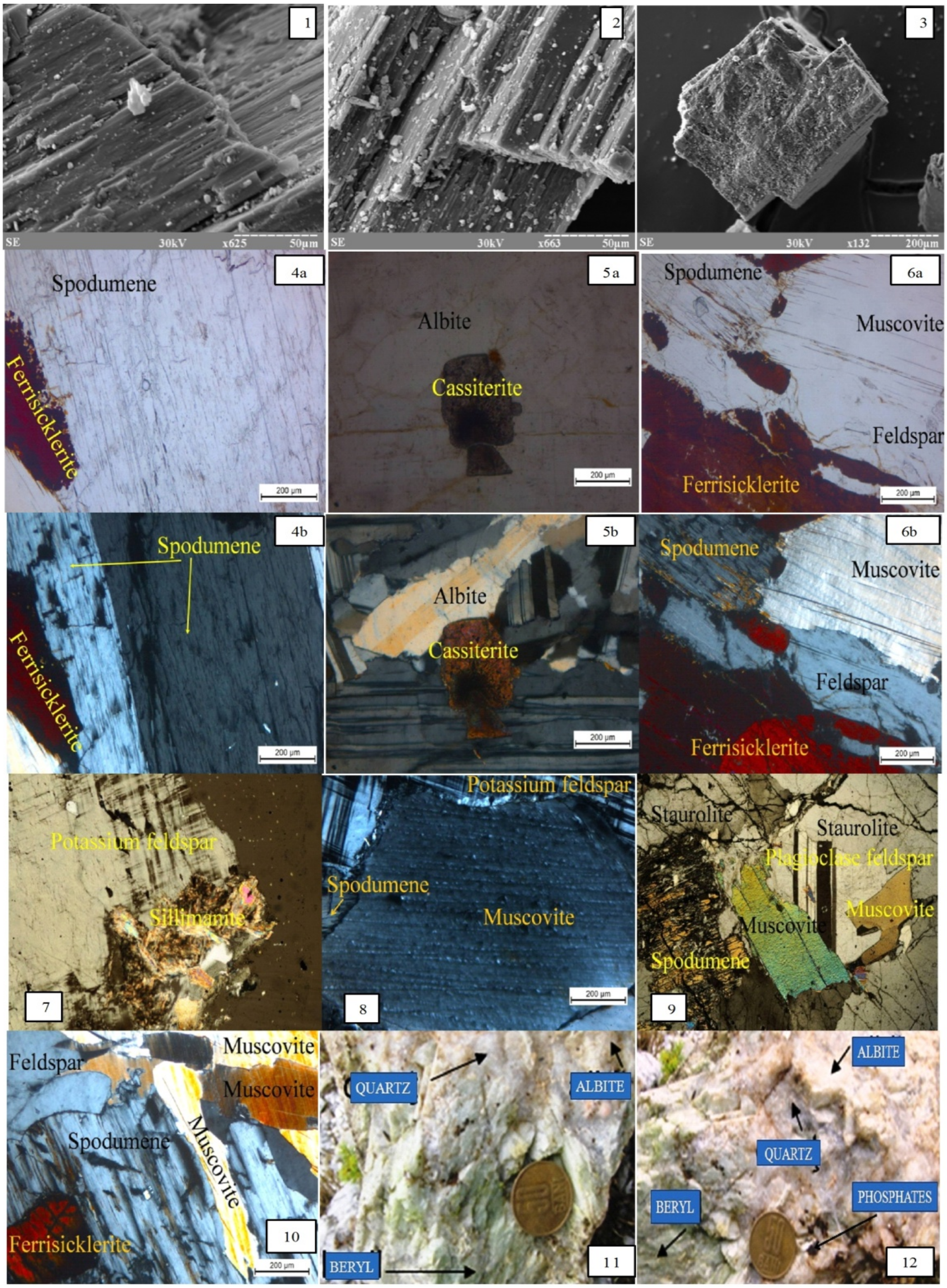

Figure 5. 1 = SEM of a spodumene crystal, with details of the location of the face in steps (100). 2 = SEM of a spodumene crystal, in which we observe a structure in stairs. 3 = SEM image of a fragment of a feldspar crystal. 4a, b= (PLM) of spodumene with ferrisicklerite. 4a=plane polarized light N II; 4b = cross polarized light N +, we observe the spodumene twins. 5a, b – PLM = 5a = N II; 5b = N +, the cassiterite present in the albite mass can be observed. 6a.b – PLM = spodumene (with phosphate inclusions) + quartz + phosphate (ferrisicklerite) + muscovite (6a = N II, 6b = N +. 7– PLM = microcline + sillimanite (N+) (5x). 8 - PLM = Muscovite is associated with feldspars, spodumene, and quartz (N +), 9 = PLM with spodumene, staurolite, muscovite and feldspar, (N +) (10x). 10 - PLM = mineralogical association: spodumene + muscovite + quartz + phosphates (ferrisicklerite), (N +), 11, 12 = Macroscopic images of beryl in light green tones present in the smoky-white and albite-quartz mass. SEM - (scanning electron microscopy).

quartz, but also with spodumene (Figure 5). The percentage mineralogical composition of lithium pegmatites indicates the following values: albite 30 - 35%, quartz 30 - 35%, spodumene 15 - 20%, microcline 10 - 15%, muscovite 3 - 5%, Androne, (2005a).

Microcline with smooth beaches, resulting from the substitution of plagioclase feldspar; microcline associated with muscovite (fine myrmekitic texture can be observed on contact) (Figure 5).

The mineralogical characteristics of the albite-spodumene lithium pegmatites from the Conțu field determine their classification in the granitic families: (NYF and LCT), Černý & Ercit, (2005).

Černý, (1992) and Černý & Ercit, (2005) state that rare-earth pegmatites are located within the metamorphic fields characteristic of the amphibolite facies (500 - 600° C and 2 - 4.5 Kbar).

The albite–spodumene type belongs to the subclass REL - Li - class of rare elements, but also has components from the subclass REL - REE with chemical elements such as U and Ti materialized in minerals such as monazite, rutile, ilmenite, titanite, and uraninite.

Conțu field pegmatites fall into the NYF and Mixed families (NYF and LCT), the dominant subclasses of REL-REE and REL-Li pegmatites, with a composition of sub-aluminous to meta-aluminous pegmatites. The composition of the boundaries considered as a plutonic source is sub-aluminous to meta-aluminous type A. The lithological source is represented by the medium to a low crust of the granulitic facies, as well as by mixed protoliths of supra-crustal rock boundaries assimilations by NYF, Černý & Ercit, (2005). Potassium feldspars are represented by microcline and rarely by microcline – perthite, sodium feldspars in acceptable proportions are represented by albite cleavelandite variety, feldspar responsible for pegmatite albitization and its classification in the rare elements, according to Černý, (2005). The lithium pegmatites, the albite-spodumene type, constitute an evolved stage within the pegmatitic process, a stage that corresponds to the accumulation of minerals that incorporate in their structure important chemical elements that are found in the class of rare elements.

4. RESULTS

4.1. SPODUMENE - $LiAlSi_2O_6$

The Dana classification places the spodumene in the category of inosilicates - lithium pyroxene. Macroscopically, the spodumene appears in the form of crystals and massive aggregates, with long habitus – prismatic, sometimes tabular. Its color varies from white-greenish with vitreous luster to gray-greenish, color due to the alteration processes, which led to the appearance of green-yellow colors on the spodumene (Figure 4). The mineral has a good cleavage on the plane (010).

4.1.1. Polarized light microscopy (PLM)

Under the microscope, the spodumene appears in shades of gray to yellow, has a moderate relief, and is strongly cracked, on these cracks develops quartz which shows intergrowth (Figure 4), which is due to the breakdown of the petalite during the cooling of the pegmatitic melt, London, (1984). Muscovite and a number of phosphates may also appear, (Figure 4; 5).

4.1.2. X-ray powder diffraction (XRD)

The mineral was also detected by X-ray powder diffraction; 14 diffractograms were recorded, which were indexed by comparison with ICDD 00-033-0786, according to which the mineral has monoclinic symmetry and C 2 / c space group (15). The values given in the mentioned sheet were chosen as starting values during the calculation program, Appleman & Evans, (1973), Benoit, (1987) of the cellular parameters, namely: a = 9.466 Å; b = 8.394 Å; c = 5.221 Å, $\beta = 110.170^0$. The values of the reticular parameters for the 14 samples can be found in (Table 1), values that correspond to data from the literature. The most representative diffractogram can be traced in (Figure 6). Along with the spodumene also appear: vivianite, fluorapatite, cookeite, feldspars, heterosite, and quartz. The X-ray powder diffraction data for spodumene ore can be found in (Table 2).

4.1.3. Scanning electron microscopy (SEM)

The observations made with the scanning electron microscope revealed a prismatic habitus sometimes tabular of the mineral, with longitudinal striations, parallel to the edges of the crystal faces. Spodumene appears with details of the location of face in steps (100) - (Figure 5), but also a structure in stairs, - (Figure 5).

4.1.4. Electron microprobe analyzer (EPMA)

The fourth analytical method used to highlight the mineral spodumene is the electron microprobe analyzer. The analytical method indicated a lithium oxide content of between 7.43% and 7.50%, 6 analyzes were performed, the most representative of which are listed in (Tables 3a and 3b). In addition to the lithium oxide content, the spodumene also has low concentrations of Fe, the average value of FeO around 0.53%, because pyroxene is also associated with phosphates (Figure 4).

4.1.5. Raman spectroscopy

Raman micro-spectral anlaysis indicate values: between 301 cm^{-1} and 1271 cm^{-1} (356, 391, 394, 523, 562, 708, 710, 1073, 1074 cm^{-1}), values that correspond to the data from specialized literature, Cameron, et al., (1973) for the spodumene mineral. The most representative Raman spectra are shown in (Figure 7).

4.1.6. Genesis

According to data from the literature, the spodumene was born in the third stage of crystallization, Săbău, et al., (1989). A large amount of spodumene was closely accompanied by albite in much larger quantities. Along with these minerals, the authors Săbău, et al., (1989), Săbău (1995), sporadically mention muscovite, spessartine, beryl, tavorite, sphalerite, cassiterite, magno-columbite, hureaulite, and alluaudite.

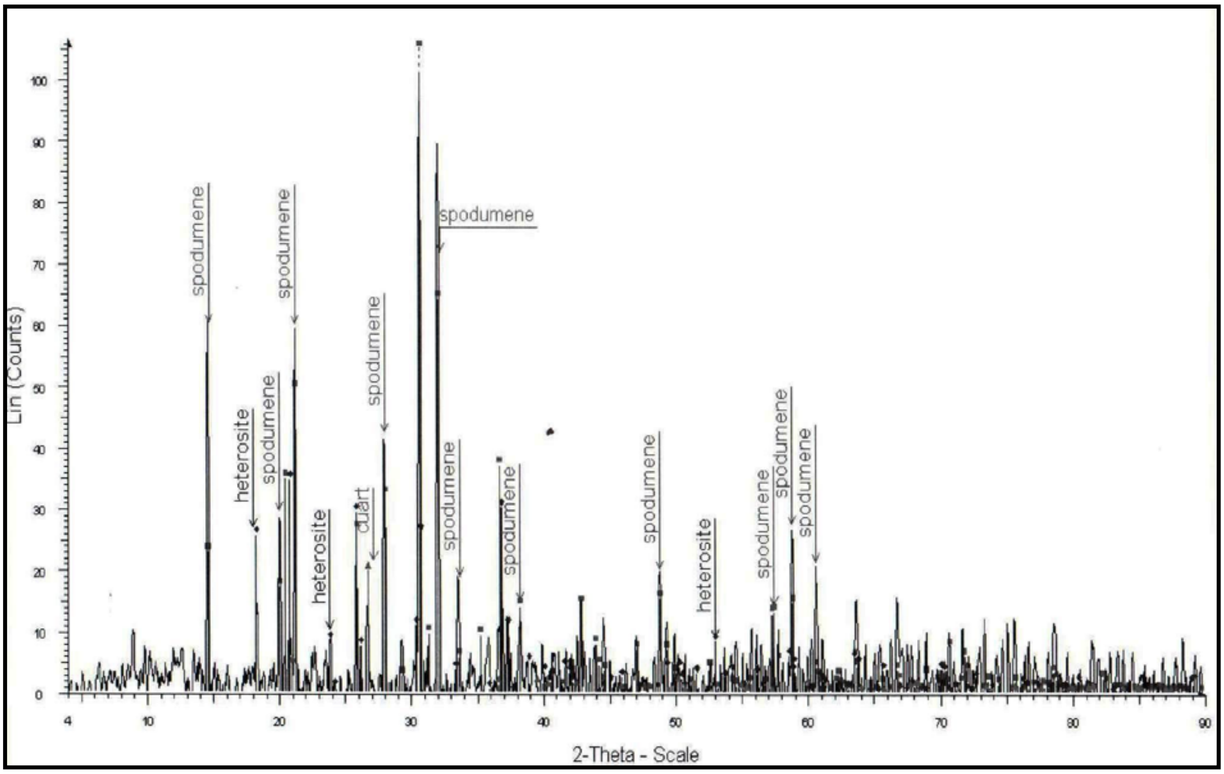

Figure 6. Powder X-ray diffractogram for a sample of spodumene associated with heterosite and quartz, from Conțu lithium pegmatites.

Table 1. Elemental cell parameter values for 14 spodumene samples from the Conțu area

Sample	a(Å)	b(Å)	c(Å)	β(⁰)	V (A³)
N1	9.454(3)	8.405(5)	5.220(3)	110.00(3)	389.77(2)
N2	9.478(5)	8.406(5)	5.225(9)	110.08(3)	391.20(3)
N3	9.481(3)	8.405(9)	5.226(2)	110.29(2)	390.62(2)
N4	9.482(8)	8.413(4)	5.230(4)	110.01(1)	392.02(2)
N5	9.482(5)	8.401(3)	5.236(2)	110.28(2)	391.25(2)
N6	9.456(2)	8.411(1)	5.223(1)	110.06(1)	390.72(3)
N7	9.478(1)	8.404(5)	5.222(6)	109.96(4)	390.91(4)
N8	9.472(4)	8.397(9)	5.230(8)	110.22(1)	390.39(1)
N9	9.483(3)	8.396(2)	5.223(2)	110.20(2)	390.28(1)
N10	9.471(2)	8.399(2)	5.232(2)	110.17(1)	390.68(1)
N11	9.473(3)	8.399(3)	5.225(2)	110.19(2)	390.15(2)
N12	9.489(2)	8.390(9)	5.229(2)	110.11(2)	390.90(2)
N13	9.473(6)	8.396(6)	5.226(3)	110.06(3)	390.46(3)
N14	9.474(5)	8.396(1)	5.224(8)	110.12(1)	390.22(7)
Charoy et al., (1992)	9.476(3)	8.397(2)	5.226(2.6)	110.16(4)	390.27
Fosu et al., (2021)	9.471	8.400	5.223	110.2	-

Table 2. Powder X-ray diffraction data were obtained for three representative samples of spodumene 3 from the Conțu pegmatitic field. (monochromatized CuKα radiation, λ = 1.54056 Å).

Nr. crt.	Sample 1A s			Sample 1B s			Sample 1C s			(hkl)
	d_{meas}(Å)	$d_{calc.}$ (Å)	I/I_0	d_{meas} (Å)	$d_{calc.}$ (Å)	I/I_0	d_{meas}(Å)	$d_{calc.}$ (Å)	I/I_0	
1	6.1913	6.1068	3.5	6.1281	6.109	3.6	6.1561	6.1152	53.8	(110)
2	4.4342	4.4492	4.8	4.4721	4.4542	4.8	4.4473	4.4527	18.4	(200)
3	-	-	-	3.4378	3.4521	6.2	3.454	3.4455	32.5	(111)
4	3.2068	3.1905	25.4	3.2023	3.1911	25.4	3.1961	3.1929	89	(021)
5	2.9288	2.9192	32	2.923	2.9208	32	2.9283	2.9277	100	(-221)
6	-	-	-	2.8555	2.8636	1.3	2.7945	2.7993	83.7	(-311)
7	2.6574	2.6698	1	2.6763	2.6692	2.1	2.6752	2.6746	12.2	(130)
8	2.452	2.4537	5.6	2.4543	2.4538	5.6	2.4579	2.4586	29.4	(-131)
9	2.452	2.4546	5.6	2.4543	2.4567	5.6	2.4579	2.4525	29.4	(002)
10	1.8609	1.8648	1.6	1.8681	1.8648	4.5	1.8645	1.8691	17.2	(-241)
11	1.7396	1.741	3.7	1.7413	1.7429	3.7	1.7404	1.7424	12.4	(510)
12	1.7396	1.7409	3.7	1.7413	1.7417	3.7	1.7404	1.7407	12.4	(331)
13	1.5695	1.5661	2.2	-	-	-	1.5708	1.5699	13.5	(-441)

Table. 3 a. Chemical analysis results for 4 representative samples of spodumene from the Conțu area

Sample	21/c10	169/c1	170/c1	173/c1
	%	%	%	%
SiO_2	66.73	66.58	66.28	66.27
Al_2O_3	27.44	28.09	28.27	28.18
FeO	0.67	0.56	0.39	0.52
Total 1	94.84	95.23	94.94	94.97
Li_2O	7.49	7.45	7.43	7.5
Total 2	102.33	102.68	102.37	102.47
	the base 12 cat. +	the base 12 cat. +	the base 12 cat. +	the base 12 cat. +
Si	2.19	2.17	2.17	2.17
Al	1.06	1.08	1.09	1.08
Fe	0.01	0.01	0.01	0.01

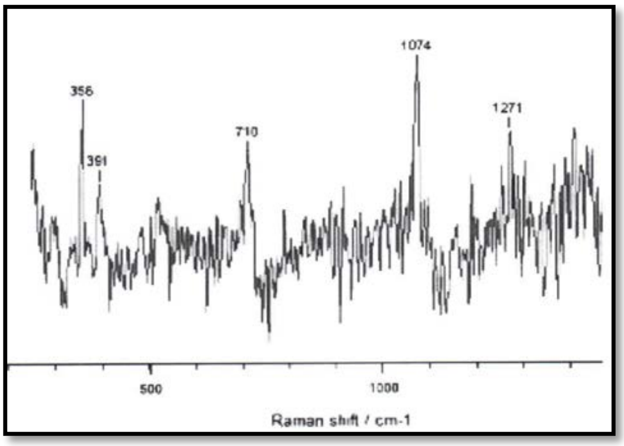

Figure 7. Raman spectra for a sample of spodumene, from Conțu lithium pegmatites.

4.2.1. X-ray powder diffraction (XRD)

Several X-ray diffractions analyzes were performed, of which one sample recorded beryl. The powder X-ray diffractogram was indexed by comparison with ICDD sheet 01-078-2222 of beryl, in which the mineral crystallizes in the hexagonal system, space group P6/mcc (192). The data from the aforementioned sheet a = 9.267 Å, b = 9.187 Å, V (A^3) = 683.23; were chosen as starting values. The values obtained by calculating the diffractogram can be traced in (Table 4), values that correspond to the data from the literature. The representative diffractogram can be seen in (Figure 8), in which beryl is associated with albite and quartz.

Table 3 b. Chemical formulas for 4 samples of spodumene, from Conțu pegmatites

Sample	Chemical formulas for spodumene
21/c10	$Li_{0.99}(Al_{1.06}Fe_{0.01})_{1.07}Si_{2.19}O_6$
169/c1	$Li_{0.97}(Al_{1.08}Fe_{0.01})_{1.09}Si_{2.17}O_6$
170/c1	$Li_{0.97}(Al_{1.09}Fe_{0.01})_{1.10}Si_{2.17}O_6$
173/c1	$Li_{0.99}(Al_{1.08}Fe_{0.01})_{1.09}Si_{2.17}O_6$

4.2. BERYL ($Be_3Al_2(SiO_3)_6$)

Beryl was indicated in the pegmatites from Conțu macroscopically, but also by powder X-ray diffraction and infrared transmittance spectroscopy. Macroscopically, it has a greasy luster, colors in light green to dark green tones, (the emerald variety), in the mass of quartz and albite (Figure 5).

4.2.2. Infrared transmittance spectroscopy (ITS)

By infrared transmittance spectroscopy, the presence of beryl was confirmed. BeO_4 vibrates at frequencies around 900 cm^{-1} and 1000 cm^{-1}, Farmer, (1974), which we can see on the spectra of the mineral sample: N118 with valence vibrations at 1094 cm^{-1}, 1039 cm^{-1}, 957 cm^{-1}.

The representative spectra for a sample of beryl from the Conțu pegmatites can be seen in (Figure 9).

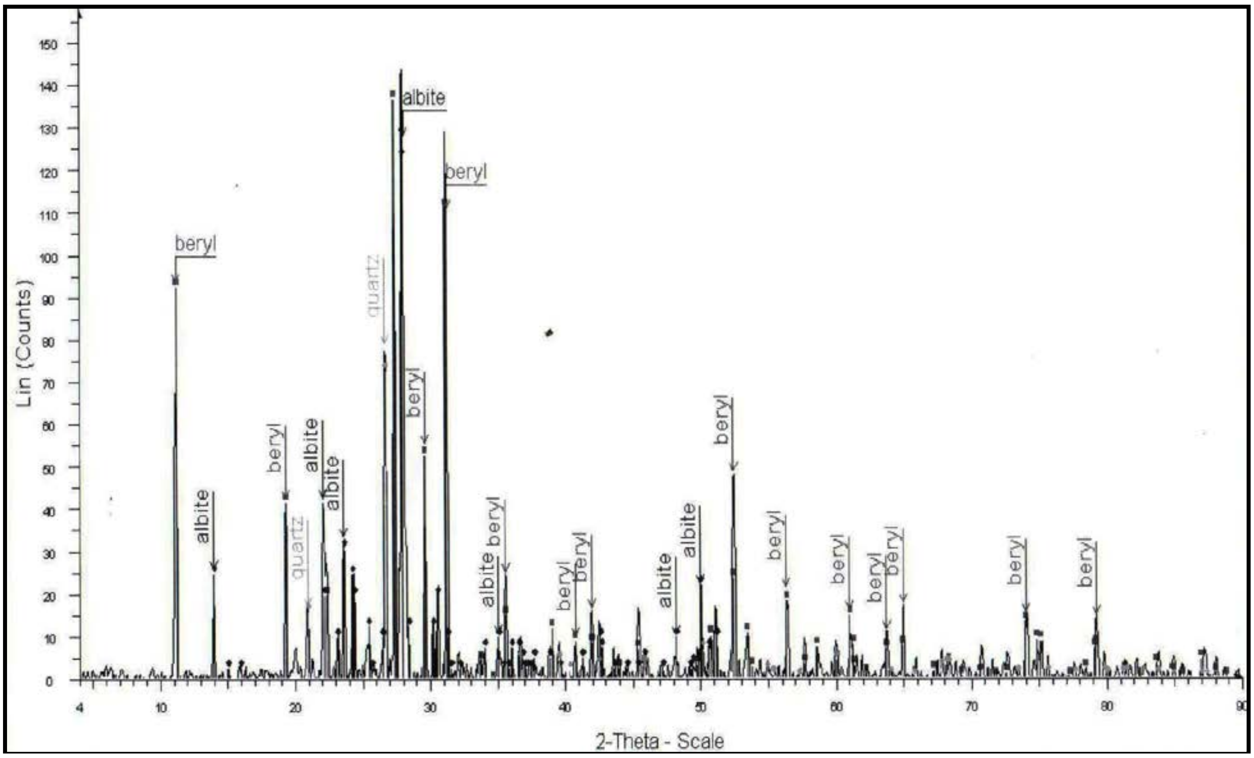

Figure 8. Powder X-ray diffractogram for a sample of beryl associated with albite and quartz.

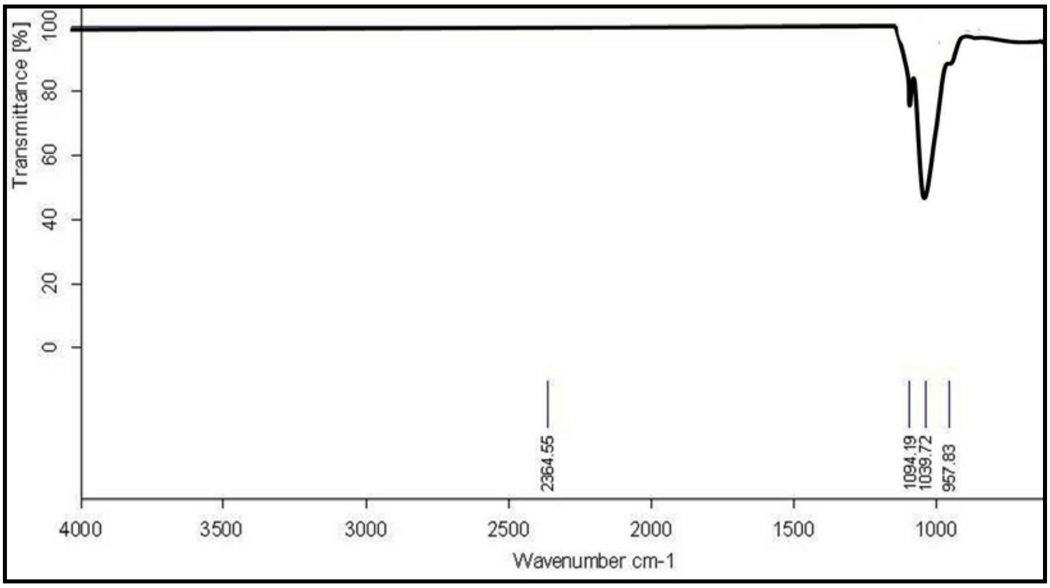

Figure 9. Infrared transmittance spectra for a sample of beryl from the Conțu lithium pegmatites.

Table 4. Values of elementary cell parameters for a sample of beryl from Conțu lithium pegmatites

Sample	a(Å)	c(Å)	V (A^3)
Ce. 48 F	9.258(8)	9.204(5)	683.22(1)
Brown, & Mills (1986)	9.2527(3)	9.1971(3)	681.89(4)
Aurisicchio, et al., (1988)	9.2209(3)	9.2214(6)	679.01(4)

4.2.3. Genesis

Beryl was born in the third stage of crystallization. The mineral crystallizes alongside albite, quartz, spodumene, muscovite, heterosite–purpurite, spessartine, tavorite, blende, cassiterite, magno-columbite, hureaulite and alluaudite, Săbău, (1995).

The high frequency and content of elements characteristic of hydrothermal phases (Cu, Pb, Zn, Li), as well as the regional zonation of minor elements (Li, Be, Sn), cassiterite occurs in cleavelandite mass (Figure 5), support the genesis of pegmatites from residual granitic magmas. The idea of the genesis of pegmatites from residual magmas differentiated and consolidated in several stages, related to different phases of magmatism, has certain implications on the reserve fund for this, which increases at least several times.

Beryl was born in evolved granitic magmas, Charoy, (1999).

5. DISCUSSIONS

Beryl and spodumene, indicated in the Conțu pegmatites study area, probably represent some of the minerals with a substantial economic impact.

We can say with certainly that the two minerals are present in the Conțu pegmatitic fields, because analytical methods indicated them; methods that complement each other (at least three methods for highlighting a mineral). Probably due to the exotic character of these pegmatites, regular intergrowths of quartz with microcline, we can say that they formed from a magmatic protolith, but at considerable distances from it. The concentration for some minor elements suggests the idea of a complex preparation of the pegmatites, through which, in addition to the main components (potassium, sodium, mica, and quartz substance) could be concentrated as by-products, and some of the rare and dispersed elements found (Rb, Cs, Li, Be). Spodumene can provide a source for battery manufacturing, for the electrification of all devices used in everyday life.

6. CONCLUSIONS:

Lithium pegmatites appear within the Getic units, at the base of mica schist with kyanite porphyroblasts. The main lithium pegmatitic bodies are known as Conţu Inferior and Conţu Superior. Possibly their concentration was achieved following the movement of a fluid over long distances from the magmatic protolith, the migration path of the pegmatitic fluid is probably due to the faults present in the area. The mineral composition of pegmatites is complex. Among the main minerals, we highlight albite, spodumene, quartz, and muscovite. Subordinate minerals are represented by microcline and oligoclase. Accessory minerals are represented by phosphates of the isomorphic series triphylite – ferrisicklerite – heterosite, wolfeite, maricite, ’’ferrogatehouseite’’, monazite, vivianite, hydroxylapatite, fluorapatite; of oxides: cassiterite, uraninite; silicates: garnets, sillimanite, beryl, petalite, titanite (sphene). These minerals were continuously transformed until the emplacement of lithium pegmatites. The large dimensions of the minerals (spodumene 25 cm – Călin, et al., 2020b), 70 cm - Androne, (2005a) indicate an input of water from the hydrothermal fluid and/or from the neighboring pelitic rocks that present large amounts of minerals such as muscovite and biotite; phyllosilicates which, through tectonic deformations, yielded water to both muscovite and lithium pegmatites.

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