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THE SPODUMENE FROM CONŢU-NEGOVANU PEGMATITES (LOTRU-CIBIN MTS.)

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1. Introduction

The spodumene pegmatites from the Conţu-Negovanu field were discovered in 1963 and have raised a particular interest ever since, due to their special and complex rare-metal mineralization. The spodumene found in this area represents the largest occurence of the kind in Romania, having associated some other Li-minerals (phosphates belonging to the triphylite-lithiophilite series) or Li-rich ones (biotite, garnet, muscovite, feldspars), which commonly display also differentiated Rb, Cs, Ba, Sr enrichments.

2. Geological setting

Conţu-Negovanu pegmatite field is located within the northern part of the Lotru Mts., on the slopes of Conţu river, a tributary to Sadu river. The pegmatite bodies are hosted by mesometamorphic rocks belonging to Sebeş-Lotru Group, which is the most extended litostratigraphic entity of the Getic Realm. The Sebeş-Lotru sequence represents a crustal fragment of Cadomian-Caledonian age, part of an active continental margin or an island arc near a continent. Possibly, arround 430 M.a., this terrain collided with an ahead block, being consequently involved in a subduction process (Balintoni *et al*., 2004). The lithology of Sebeş-Lotru Group is roughly represented by a lower migmatitic complex and upper kyanite–staurolite-bearing micaschists alternating with biotite paragneisses; metaultramafites are also present (Berza *et al*., 1994). The entire region has polycyclic metamorphic features, the best known being those related to the last metamorphic event, developed in the amphibolite facies, within the kyanite-staurolite zone (Hârtopanu, 1978; 1986; 1988). The genesis of the Conţu-Negovanu pegmatites is considered to be metamorphic, as they seem to have originated mainly, if not entirely, as a result of segregation within a fluid under preanatectic conditions (Săbău *et al*., 1987). The tabular and lens-shaped pegmatite bodies display a large scale inhomogeneity leading to an incomplete zoning, of which the best represented are the aplite and the intermediate zone. The latter shows no differentiation of the quartz core (Maieru *et al*., 1968) and the mineral replacement relationships make evidence of a complex evolution. Beside the spodumene pegmatites (or lithian pegmatites - LPs), in the Conțu-Negovanu field are also present common feldspar-mica pegmatites (FPs). For each of them, the mineralogical composition, as well as the bulk chemistry features and geochemical signatures suggest the affiliation to two distinct pegmatite classes, according to Černý`s (1992) systematic classification of pegmatites: (i) rare-element class and (ii) muscovite class, respectively (Murariu, 2001). More specifically, the FPs are of *ceramic and mica-bearing type*, being barren or poorly mineralised (Li, Be, Ti, Nb, Ta, U, Th, Y, REE) and the LPs are assigned to one of the five subdivision types of the rare-element class: the *albite–spodumene type*, characterised by minor to extensive mineralisation (Li, Rb, Cs, Be, Ga, Y, REE, Sn, Ti, U, Th, Hf, Nb, Ta), with typical substantial Li and variable rare-alkali fractionation (Černý, 1992). The former consist of Qtz + K-feld, Plg + Ms ± Bt ± Tur ± Grt and small amounts of staurolite, apatite, ilmenite, rutile *etc.*, whereas the latter present the typical mineral assemblage: Ab (cleavelandite) + Sp + Qtz + Ms and contain also subordinate amounts of microcline, biotite, garnet, apatite, kyanite, triphylite-lithiophilite, heterosite-purpurite, amblygonite-montebrasite, uraniferous magnocolumbite, huréaulite, tavorite *etc*. (Pomîrleanu *et al.,* 1967; Aurelia Movileanu *et al*., 1972; Hann, 1987; Săbău *et al*., 1987; Murariu, 2001).

The spodumene occurs as a main mineral in the LPs from Conțu-Negovanu field, and is associated especially with albite (including its lamelar variety, the cleavelandite), quartz and greenish Li-rich muscovite. Frequently, in this assemblage phosphates may be also associated, some times just within the spodumene aggregates (photo 1.).

Spodumene is present as large, massive crystalls and aggregates, with prismatic or tabular habit, of several tens of centimeters in length (photo 2.). Its colour is light green or greenish-white and the more advanced the weathering is, the more its luster and general aspect turns porcelanous to earthy. Usually, the spodumene is fissured lengthwise and/or widthwise (photo 3.) and the fissures are often filled with quartz or feldspars.

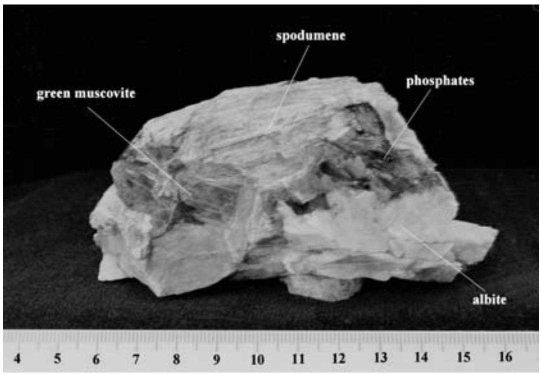

Photo 1. Spodumene, green muscovite, albite and
Li, Mn, Fe phosphates, in Li-pegmatite.

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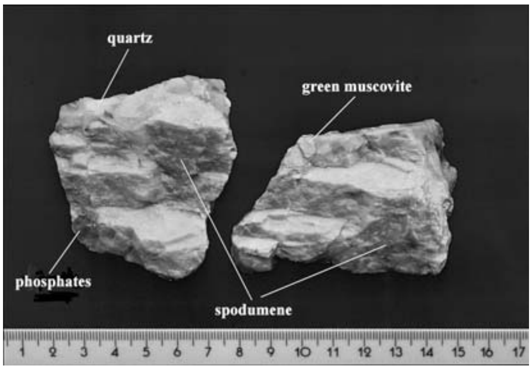

Photo 2. Massive spodumene aggregates, associated with
quartz, green muscovite and Li, Mn, Fe phosphates.

3. Samples and analythical method

Five spodumene samples have been separated under binocular lenses and turned into fine grained powders, in order to be investigated by *X*-ray fluorescence and ICP-MS techniques. Another four samples have been prepared in thin slides for EMPA investigations.

In *X*-ray fluorescence technique, bulk analyses were performed with a Philips PW 2400 *X*-ray spectrometer, using the analytical procedure called „oxiquant”. Seventytwo natural rocks and clays were used to determine the calibration curves of the pertinent elements.

EMPA were carried out with a JEOL JXA-8900 instrument, using an operating current of 20 nA and accelerating voltage of 20 kV. *X*-ray intensities of the alkalis, the minor (Ti and Mn) and the major elements were counted for 5s, 40s and 60s, respectively. In order to minimize losses of Na and K, the beam diameter was expanded to 10 mm. Components were standardised using natural minerals, glasses of natural rocks (Jochum *et al*., 2000) and synthetic oxide compounds. The results were corrected using the ZAF procedure (Reed, 1996).

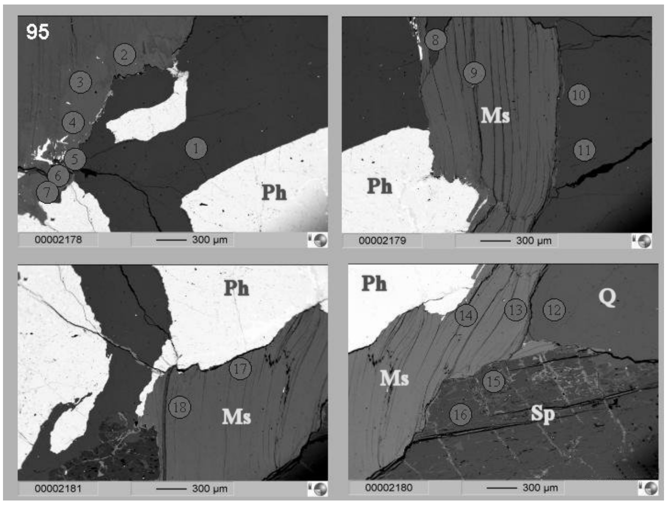

Photo 3. Electron microprobe image (Sp – spodumene; Ms – muscovite; Q – quartz; Ph – Li, Mn, Fe phosphates).

The ICP-MS investigations were performed with a Perkin Elmer/Sciex ELAN 6000 ICP-MS (quadrupole mass spectometer). Measurements of element concentrations were performed using as internal standards Ru-Re (10 ng/ml) to minimize drift effects and two calibration solutions (high purity chemical reagents). A batch of 5-7 samples was bracketed by two calibrations procedures. Accuracy and precision of determinations were checked with certified reference materials (CRM) (Govindaraju, 1994; Dulski, 2000). All the quantitative investigations were performed in the laboratories of the Geological Institute of the „Albertus Magnus” University of Köln, Germany.

4. Results and discussion

The chemical composition and the structural formulae of the investigated samples are listed in Table1 and the minor element distribution data in Table 2.

Table 1. Chemical composition (wt.%) and unit formulae (a.p.f.u.) of spodumene

Oxides wt (%)	Samples										
	Sp 101[1]	Sp 103[1]	Sp 104[1]	Sp 951[2]	Sp 952[2]	Sp 961[2]	Sp 962[2]	Sp 21[3]	Sp 23[3]	Sp T	Sp G
SiO_2	62,90	63,16	63,04	65,71	65,15	65,47	64,689	62,57	62,86	63,45	64,31
TiO_2	0,003	0,003	0,005	0,00	0,013	0,005	0,007	-	-	-	-
Al_2O_3	24,84	26,34	26,68	28,04	27,92	28,03	28,118	28,47	27,83	27,40	26,73
Fe_2O_3	0,78*	0,67*	0,54*	-	-	-	-	1,32	1,52	0,05	0,34
FeO	-	-	-	0,481*	0,538*	0,308*	0,336*	0,31	0,60	-	0,32
MgO	0,00	0,00	0,00	0,00	0,00	0,00	0,006	0,05	0,05	0,01	0,02
MnO	0,17	0,07	0,07	0,036	0,054	0,069	0,064	0,24	0,12	-	0,08
CaO	0,17	0,11	0,10	0,002	0,015	0,036	0,006	0,33	0,25	0,16	0,04
Li_2O	5,14	5,42	5,53	-	-	-	-	6,66	6,41	7,87	7,10
Na_2O	1,76	0,84	0,40	0,129	0,143	1,254	0,173	0,02	0,06	0,11	0,24
K_2O	0,53	0,23	0,14	0,016	0,01	0,00	0,006	0,06	0,29	0,03	0,12
P_2O_5	0,34	0,07	0,03	0,027	0,00	0,00	0,00	-	-	-	-
H_2O^+	-	-	-	-	-	-	-	0,16	0,16	0,30	0,25
Unit formulae on the basis of 6 oxygens (a.p.f.u.)											
Si	2,062	2,044	2,040	-	-	-	-	1,962	1,977	1,977	2,009
Al	0,960	1,004	1,017	-	-	-	-	1,052	1,031	1,006	0,984
Fe^{3+}	-	-	-	-	-	-	-	0,031	0,036	0,001	0,008
Fe^{2+}	0,019	0,016	0,013	-	-	-	-	0,008	0,015	-	0,008
Mg	0,00	0,00	0,00	-	-	-	-	0,002	0,002	0,057	0,031
Mn	0,005	0,002	0,002	-	-	-	-	0,006	0,003	-	0,002
Ca	0,006	0,004	0,003	-	-	-	-	0,011	0,008	0,005	0,001
Li	0,678	0,705	0,720	-	-	-	-	0,839	0,811	0,986	0,892
Na	0,112	0,053	0,025	-	-	-	-	0,010	0,004	0,007	0,015
K	0,022	0,009	0,006	-	-	-	-	0,002	0,012	0,002	0,005
M	0,842	0,789	0,769					0,869	0,855	1,058	0,962

[1]- XRF analysis; [2]- EMPA; [3]- chemical analysis; *- total iron analysed as FeO or Fe_2O_3; (Sp-101)-(Sp-103)-(Sp-104) – spodumene associated with albite, muscovite and quartz; (Sp-951)-(Sp-952)-(Sp-961)-(Sp-962) – spodumene associated with albite, microcline, muscovite, phosphates; (Sp-21) – large spodumene associated with cleavelandite, microcline, quartz and muscovite (Murariu, 1992-1993a); (Sp-23) – spodumene associated with greenish muscovite, cleavelandite and quartz (Murariu, 1992-1993a); (Sp-T) – spodumene from Tanco pegmatite (Canada) (Černý and Ferguson, 1972); (Sp-G) – spodumene from Glavnîi pegmatite (Siberia) (Zagorski and Kuznețova, 1990).

Table 2. Minor elements ($\mu g \cdot g^{-1}$) in spodumene.

Minor elements ($\mu g \cdot g^{-1}$)	Samples				
	Sp-101	Sp-103	Sp-104	Sp-111	Sp-112
Li	23880	25223	25697	34522	31086
Sc	0,00	0,1	0,1	1,581	1,43
V	3,8	1,5	0,00	-	-
Cr	19,7	6,8	2,5	-	-
Co	2,1	6,1	0,1	-	-
Ni	0,00	0,00	0,00	-	-
Zn	17,3	16,3	0,00	-	-
Rb	70	28	20	251	52
Sr	7	13	11	73	30
Y	0,00	0,00	0,00	0,084	0,188
Zr	1	1	1	5,296	2,958
Nb	18	3	3	2,181	1,838
Cs	58	9	51	47	40
Ba	21	9	4	40	15,202
La	0,038	0,067	0,030	0,137	0,177
Ce	0,068	0,065	0,056	0,184	0,393
Pr	0,006	0,011	0,008	0,019	0,055
Nd	0,030	0,089	0,047	0,135	0,319
Sm	0,002	0,016	0,011	0,029	0,095
Eu	0,002	0,003	0,001	0,003	0,02
Gd	0,003	0,005	0,004	0,013	0,091
Tb	0,001	0,003	0,001	0,001	0,012
Dy	0,006	0,011	0,009	0,016	0,049
Ho	0,00	0,004	0,002	0,002	0,008
Er	0,003	0,004	0,004	0,005	0,014
Tm	0,001	0,002	0,001	0,00	0,002
Yb	0,003	0,005	0,004	0,007	0,01
Lu	0,001	0,002	0,001	0,001	0,002
Hf	0,1	0,3	0,2	0,932	0,548
Ta	2,5	1,4	0,8	2,327	1,328
Pb	33	3.6	2,3	14	12,023
Th	0,00	0,14	0,11	0,314	0,193
U	0,31	0,92	6,77	1,528	2,752
$(La/Yb)_N$	8,54	9,03	5,06	13,19	11,93
$(Ce/Yb)_N$	5,86	3,36	3,62	6,80	10,17
$(La/Sm)_N$	12,95	2,63	1,72	2,97	1,17
$(Gd/Yb)_N$	0,81	0,81	0,81	1,50	7,34
Eu/Eu*	2,50	1,03	0,46	0,47	0,66

The bulk chemistry data generally show a constant participation of the main oxides. Li oxide presents relatively low contents: 5,14–5,53% Li_2O for the XRF + ICP-MS investigated samples and 6,41–6,66% Li_2O for the samples investigated by chemical analysis, as compared to other spodumene samples in the world, such as the Tanco (Manitoba) spodumene: 7,87% Li_2O (Černý and Ferguson, 1972) or the Glavnîi (Siberia) spodumene: 7,10% Li_2O (Zagorski and Kuznețova, 1990, from Murariu, 2001). The structural formulae show a small Si excess in the XRF analysed samples (0,04–0,062 a.p.f.u.), whereas the other samples are characterized by a small deficit (1,962–1,984 a.p.f.u.). According to Deer *et al.* (1992), the Si excess may represent small amounts of SiO_2 which existed in the spodumene solid solution. On the other hand, this excess may be also due to albite and muscovite inclusions, frequently present in the spodumene mass. The *M* site occupation is also deficitary because of the low participation of Li, which is to some extent substituted for by Na, K, Ca, Mn, especially during the albitization stages. The minor element distribution data show a rather low participation, of some interest being the rubidium (70–251 $\mu g \cdot g^{-1}$Rb), strontium (30–73 $\mu g \cdot g^{-1}$Sr), caesium (40–47 $\mu g \cdot g^{-1}$Cs) and barium (21–40 $\mu g \cdot g^{-1}$Ba) contents. These values are probably due to the feldspar and muscovite inclusions, characterized themselves by important Rb, Cs, Sr and Ba substitutions. Another reason to support this idea is given by the relatively important contents of lead (12–33 $\mu g \cdot g^{-1}$Pb), which is also known to substitute for K in pegmatite feldspars and muscovite. The REE distribution within the investigated samples is scarce, especially because the spodumene does not have structural sites of greater coordination than 6-fold and moreover, its two octahedral sites are occupied by small radius cations, such as Li^+ and Al^{3+}. Also, the REE's incompatibility with the spodumene crystalline lattice leads to a variable fractionation, depending on the crystallisation stage and on the inclusions type. The chondrite normalized REE pattern shows a LREE concentration trend and a high degree of fractionation clearly manifested only in one sample (Sp–112) (fig.1.).

A positive Eu^{2+} anomaly is displayed by the sample (Sp–101), which is consistent with the highest Ca content of all samples. In the other samples a low degree of REE fractionation may be observed and also highly irregular concentration patterns, ressembling the zig-zag pattern of the REE abundance vs. atomic number plot, only more irregular. Therefore, it is very likely that the spodumene late crystallisation would have also comprized some REE minerals (*e.g.* REE phosphates), crystallized from the residual fluid and present as minute inclusions in spodumene. Their geochemical signature seems to be very complex, as it almost elimitates the chondrite normalization effect.

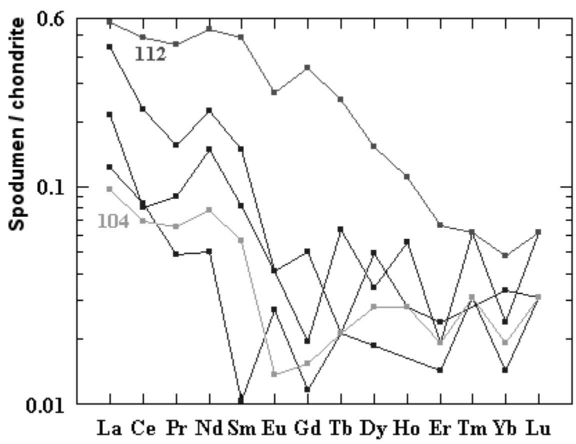

Fig. 1. Chondrite normalized REE pattern in spodumene samples

The presence of spodumene in the Conțu-Negovanu pegmatites, as well as the wider Li, Rb and Cs enrichment required a more specific assignment, as far as the pegmatite classification is concerned. Therefore, the thorough examination of their physical, chemical and geochemical characteristics showed that they match those of the *albite–spodumene* type, according to Černý's pegmatite classification (1992). The specific features of this pegmatite type belonging to the rare-element pegmatite class are:

- a composition which displays albite and quartz dominance over spodumene and K-feldspar;
- homogeneous, nearly uniform internal structure;
- mineralization restricted to substantial Li, which locally may reach more than 2 wt.% Li_2O;
- widely variable rare-alkali fractionation;
- rather obscure parent melt origin and crystallization conditions.

Considering that all these conditions are roughly reached, the Conțu-Negovanu lithian pegmatites may be regarded as belonging to the *albite-spodumene* pegmatite type.

5. Conclusions

- The spodumene occurs as a main mineral in the lithian pegmatites from Conțu-Negovanu field, being associated with albite (including the cleavelandite variety), quartz, greenish muscovite and sometimes Li, Mn, Fe phosphates.
- The spodumene characteristics as well as those of the whole lithian pegmatites assign them to the *albite-spodumene* pegmatite type belonging to the rare-element pegmatite class.

- The extraordinary large spodumene aggregates indicates the Conțu-Negovanu occurence as the greatest of the kind in Romania.

- The Li_2O contents are rather low (5,14-5,53 % Li_2O), as compared to other occurences in the world.

- The minor elements have a rather low participation (70-251 $\mu g \cdot g^{-1}$ Rb; 30-73 $\mu g \cdot g^{-1}$ Sr; 40-47 $\mu g \cdot g^{-1}$ Cs; $\mu g \cdot g^{-1}$ Ba) which probably reflects the presence of the feldspar and muscovite inclusions in the spodumene mass.

- The REE contents are very low and the chondrite normalized REE pattern is highly irregular, suggesting the presence of some REE-rich mineral inclusions, such as Li, Mn, Fe phosphates, presumably belonging to the triphylite-lithiophilite series.

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