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THE GEOCHEMICAL ROLE OF THE ALKALINITY OF CRYSTALLIZATION ENVIRONMENT IN THE GENESIS OF PEGMATITES FROM THE CARPATHIAN PROVINCE, ROMANIA

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Abstract

The genesis of pegmatites is the result of a complex geochemical evolution of the pegmatitic fluids, under the alkaline conditions of a crystallization environment. In each stage of genetic processes, there are specific minerals that crystallize, some of which are significant for the stage in progress; the pegmatite crystallization can come to an end no matter the stage in progress is, generating thus totally banded, partially banded or massive pegmatite bodies.

Thus, the main stages developing during the evolution of pegmatite genetic processes are: the calc-alkaline stage (Ca, Na) which is presented in every type of pegmatite; the alkaline stage 1: potassic stage (K) and/or sodic stage (Na); the alkaline stage 2: the potassic stage (K); the hydrolysis stage (H_2O); the alkaline stage 3: the sodic stage (Na); the acidic stage (silicatic - Si).

Keywords: crystallization, genesis of pegmatites, genetic stage, pegmatites.

Introduction

The genesis of pegmatites is considered by scientists as a complex geochemical evolution of the pegmatitic fluids, under the alkaline conditions of a crystallization environment. The first attempt to explain the genesis of pegmatites can be found out in

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Fersman's paper work (1931), who stressed the changes of the chemical elements' role over the process of pegmatite building up.

In the same time, the importance of metasomatic processes in the formation of some pegmatite-forming minerals was recognized by scientists (Jahns, 1955, 1982; Solodov, 1971; Černý, 1982 a, b, 1992; London, 1992 etc.).

The evolution of the chemistry of pegmatitic solutions in the genesis of minerals was explained by Ginsburg (1960), Ginsburg and Rodionov (1960), Vlasov (1961) in their paper works; these authors revealed the role of alkalis in the geochemical evolution of the pegmatitic process.

Subsequent studies stressed that the chemical changes during the formation processes of pegmatites is much more complex.

Starting from the changes of mineralogical associations formed in the succeeding stages, changes of the nature of the pegmatitic fluids in pegmatite-forming processes have been supposed; the pegmatitic fluids change from alkaline to neutral (rich in water and mineralizers), than to acid (rich in silica) and again to alkaline, neutral and acid (Rodionov and Davidenko, 1964; Şmakin, 1965; Kocinev et al., 1977; Murariu, 2001 etc.).

Results and Discussion

The field and laboratory researches, as well as other data from scientific papers (Rodionov and Davidenko, 1964; Şmakin, 1965; Kocinev et al., 1977; Murariu, 2001 etc.), put in evidence, in pegmatite bodies from Carpathian Province, the presence of some successive stages of the geochemical evolution in pegmatitic process (fig. 1).

In each stage of genetic processes, there are specific minerals that crystallize, some of which are significant for the stage in progress; the pegmatite crystallization can come to an end no matter the stage in progress is, generating thus totally banded, partially banded or massive pegmatite bodies.

I. The calc-alkaline stage (Ca, Na) is present in every type of pegmatite. In massive pegmatite bodies and in the boundary zone of the banded pegmatites, the calco-sodic stage generates an enrichment of plagioclases in anorthite molecule and the enrichment of garnets in andradite (± grossular) molecules as a result of an important supply of calcium from micas and from the surrounding paragneisses.

In this stage, the boundary band of the pegmatite bodies was formed, where the microgranular structure prevails.

The chloritization of biotite is confirmed by the increased oxidation level of Fe (f_0). In this stage, the alkalinity of oligoclase shows smaller values relative to the microcline and albite alkalinities from the inner zones of the pegmatite bodies (tab.1)

In the contact zone of the pegmatite bodies with the metamorphic rocks, some Fe-Mg minerals (biotite, tourmaline) was formed; their genesis follows different patterns, such as metasomatic or anatectic processes. The products of this stage are plagioclase-rich pegmatites of upper temperature.

II. The alkaline stage 1: potassic stage (K) and/or sodic stage (Na). The presence of this stage in banded pegmatite bodies is proved by an important feature of pegmatites: the graphic structures; in such cases, the crystallization process is interrupted by the increase of alkalinity up to the limit where quartz becomes soluble. In the pegmatite bodies from Romania, the presence of graphic structures is highly variable.

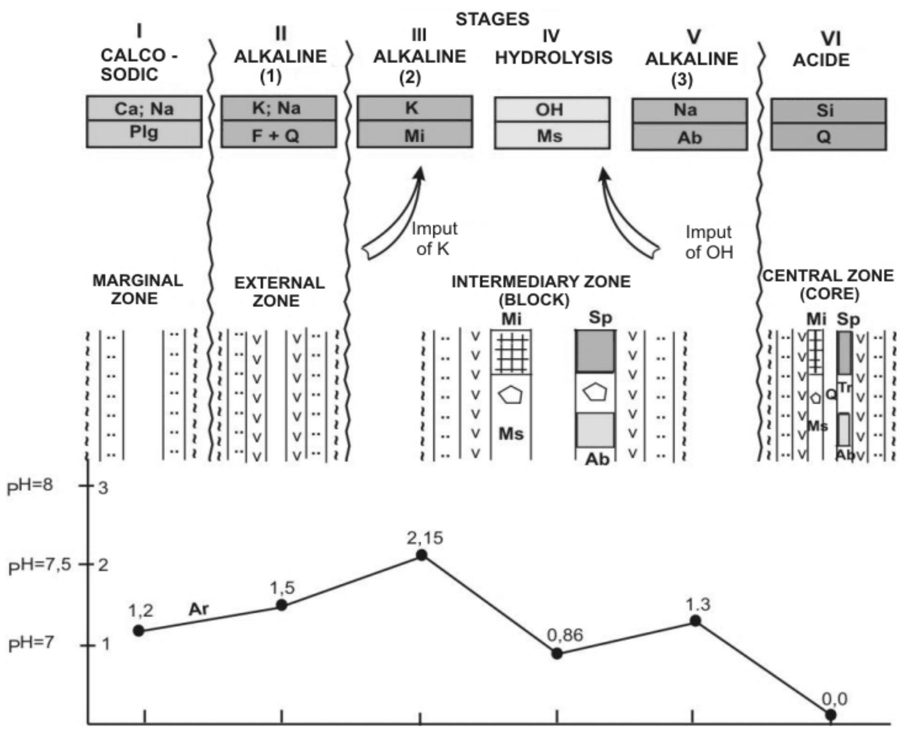

Fig. 1 The alkaline crystallization stages

The graphic structure is specific to feldspar-rich pegmatites, being rare in muscovite-rich pegmatites and in those with rare metals. The alkalinity of this stage is determined by the feldspar type that participates to the structure formation; thus, the graphic structure with microcline have a higher alkalinity then those rich in plagioclase (tab. 1).

III. The alkaline stage 2: the potassic stage (K) is characterized by a high participation of alkalis that leads to the crystallization of a monomineral band consisting of massive microcline (block microcline).

This stage is found out in all type of pegmatites, especially in feldspar-rich (potassic) ones: Cataracte – Lotru Mts., Teregova – Semenic Mts., Crişeni – Gilău Massive, Scărişoara –Rodnei Mts. etc.). In the pegmatite bodies of Carpathian Province this stage does not generate rare-metals mineralizations.

IV. The hydrolysis stage (H_2O). The development degree of the hydrolysis is higher in banded pegmatite bodies and depends on the amount of H_2O and of some volatile compounds (B, F, Cl, etc). This stage is responsible of the muscovitization of potassic feldspar and biotite, as well as the crystallization of some minerals with rare metals: Li, Be, Nb (Teregova – Semenic Mts.; Haneş, Pietrele Albe – Lotru Mts.; Voislova – Poiana Ruscă Mts.). The hydrolysis of potassic feldspar and the formation of the muscovite take place following the reaction:

$$\underset{\text{potassic feldspar}}{3KAlSi_3O_8} + H_2O = \underset{\text{muscovite}}{KAl_2AlSi_3O_{10}(OH)_2} + \underset{\text{quartz}}{6SiO_2} + K_2O$$

The quartz+muscovite complex formed throughout the hydrolysis of the potassic feldspar represents 10-20% of the pegmatite bodies; it is made up of 30% muscovite and 60-65% quartz. In the hydrolysis stage, the muscovitization of the biotite takes place as well:

$$\underset{\text{biotite}}{K(Mg,Fe)_3AlSi_3O_{10}(OH)_2} + Al_2O_3 = \underset{\text{muscovite}}{KAl_2AlSi_3O_{10}(OH)_2} + 3(Mg, Fe)O$$

This mineral transformation undergoes many steps, and sometimes the muscovite flakes have fine inclusions of hematite on their cleavage planes. The magnesium and the iron have an important contribution in tourmaline and garnets crystallization. The muscovite has a higher alkalinity relative to that of tourmaline and garnets.

V. The alkaline stage 3: the sodic stage (Na). Represents a stage in the albitization process:

$$KAlSi_3O_8 + Na^+ = Na\ AlSi_3O_8 + K^+$$

This stage produces the pertite structure of feldspars associations in all type of pegmatites and the appearance of cleavelandite, spodumene and of other lithium minerals (ambligonite – montebrasite; triphylite - lithiophylite, tavorite) in the pegmatite bodies from Conțu field, Cibin Mts. (the Getic pegmatitic Subprovince).

As about rare metal-bearing pegmatites, the alkaline stage 3 leads to the crystallization of beryl, columbite+tantalite and cassiterite. The albite alkalinity is higher then that of spodumene (tab. 1).

Tab. 1 The relative alkalinity (RA) of pegmatites from Carpathian Province

Rock, minerals (%)	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	a_{Mg}	CaO	a_{Ca}	Na_2O	a_{Na}	K_2O	a_K	RA
Pegmatite													
Albite (13)	67.65	20.24	0.06	-	-	-	1.06	0.04	10.43	1.46	0.39	0.07	1.57
Oligoclase (8)	65.76	21.35	0.13	-	-	-	2.83	0.11	9.10	1.27	0.80	0.15	1.53
Microcline (8)	64.96	19.16	0.09	-	-	-	0.51	0.02	1.87	0.26	13.21	2.51	2.79
Muscovite (32)	45.37	36.00	0.97	1.04	0.53	0.01	0.49	0.02	0.70	0.09	9.65	1.83	1.95
Biotite (20)	36.65	19.65	4.69	7.56	6.97	0.21	0.96	0.04	0.29	0.04	8.06	1.53	1.82
Garnet (15)	37.72	18.71	3.26	26.35	1.08	0.03	2.02	0.11	-	-	-	-	0.14
Tourmaline (17)	37.03	35.17	4.03	7.55	3.26	0.09	1.11	0.04	0.41	0.06	0.91	0.17	0.36
Spodumene (9)*	63.47	28.37	1.08	0.41	0.05	0.01	0.18	0.07	0.26	0.03	0.21	0.04	0.63
Quartz (1)	99.88	-	0.01	-	-	-	-	-	-	-	-	-	0.00
K-pegmatite (69)	72.26	15.76	0.32	0.24	0.53	0.01	0.77	0.03	2.71	0.38	6.59	1.25	1.67
Na-pegmatite (60)	73.00	16.22	0.49	0.27	0.93	0.02	1.30	0.05	5.31	0.74	1.91	0.36	1.17
Li-pegmatite (8)	73.27	19.39	0.67	-	-	-	-	-	2.19	0.31	1.15	0.22	0.72
Micas pegmatite (15)	76.30	15.17	0.44	0.23	0.29	0.08	1.11	0.04	2.98	0.40	2.19	0.41	0.86
Graphic pegmatite (K)	70.72	16.00	0.10	0.36	0.35	0.01	0.70	0.03	1.40	0.19	10.20	1.93	2.15
Graphic pegmatite (Na)	74.65	16.80	0.37	-	-	-	0.78	0.03	5.83	0.82	1.20	0.23	1.08

- undetermined; * Li_2O = 6.16 %; ( ) number of analyses

VI. The acid stage (silicatic – Si). The increasing of acidity leads to the crystallization of massive quartz associated with microcline in the intermediate bands of pegmatite bodies, as well as to the crystallization of the quartz-bearing nucleus; in the pegmatite body, nucleus geodes of quartz and sulfides develop sometimes (Rebra valley).

The mineralogical products of this stage are present in the pegmatite bodies with banded structure. The central nucleus of quartz was reported in pegmatite bodies from Teregova (Semenic Mts.), Măru stream (Țarcu Mts.–Muntele Mic), Rebra valley (Rodnei Mts.) etc.

After Rodionov (1964), the presence of block structures, consisting of microcline and quartz, is the result of the successive crystallization of these minerals.

By the end of this stage, all band units of the pegmatite bodies crystallize, the subsequent products replacing partially, sometimes entirely, the former mineral associations.

The changes of the mineral associations, specific to pegmatite bodies from Carpathian Province, in different stages of the pegmatitic processes evolution allowed to identify the periodicity of changes of fluid nature, from alkaline (the calco-sodic stage, first potassic/sodic stage, second potassic stage, sodic stage), to neutral (hydrolysis stage) and to acid (the first and the second silicic stages). These aspects show the changes in the crystallization environment, from alkaline, to neutral and finally to acidic, reflecting thus the cyclicity of the geochemical conditions in the evolution of the pegmatite genetic processes in Carpathian Province.

This evolution of processes is confirmed by the pH values of the paste and of the mineral suspensions which crystallized in different stages of the pegmatite genesis (tab. 2).

Data of table 2 show that the paste and the microcline suspensions have the highest values of alkalinity. On the other hand, the muscovite belongs to the mineral group having paste and suspensions pH corresponding to the neutral solutions.

Some changes of the pH of paste and mineral suspensions can be caused by the composition of fluid inclusions in minerals.

Tab. 2 pH of paste and mineral suspension in the genesis of pegmatites from the Carpathian Province

Minerals	Band	Stage	pH of paste and suspension	Nature of crystallization environment
Microcline	Intermediate	III (K)	7.7 – 7.8	Alkaline
Albite	Intermediate	V (Na)	7.1 – 7.3	Alkaline
Muscovite	Intermediate	IV (H_2O)	7.0	Neutral
Apatite	Intermediate	V (Na)	7.1	Low alkaline
Beryl	Intermediate	V (Na)	6.7	Low acidic
Quartz	Medium	VI (Si)	6.3	Acidic

The pH of fluids from pegmatitic quartz inclusions is 6.8-6.9, and the most important cation from these fluids is Na^+, followed by K^+, Li^+, Ca^{2+} and Mg^{2+}.

The geochemical evolution of the pegmatite genetic processes, in pegmatites from the Carpathian Province, is reflected throughout the modification of the alkalis role.

The importance of the alkalis during the succession of stages in the genesis of pegmatites is confirmed by the relative alkalinity (RA) data concerning the pegmatites and the pegmatite-forming minerals, estimated after Rodionov (1964) method.

Table 1 shows that the highest alkalinity is specific to feldspar-bearing pegmatites: 1.67 – K-pegmatites and 1.17 – Na-pegmatites.

As about the alkalinity of pegmatites showing a graphic structure, this is much higher in the case of quartz+potassium feldspar mineralogical associations. The alkalinity of pegmatite-forming minerals decreases as follows: microcline (2.79) > muscovite (1.95) > biotite (1.82) > albite (1.57) > oligoclase (1.53) > spodumene (0.63) > tourmaline (0.36) > garnet (0.14).

The relative alkalinity was calculated using the formula:

$$Ar = n_1k_1 + n_2k_2 + n_3k_3 + ...+ n_mk_m \; ; \; k = A\bullet p/M \bullet v; \; a = 1/v$$

Where:

k – relative alkalinity corresponding to 1% oxide
A – atomic weight of the element
M – molecular weight of the oxide
V – ionization potential of the element
a – relative alkalinity of the cation
n – amount of each cation in mineral or rock
p – coefficient depending on the oxide type.

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