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GEOCHEMICAL ASPECTS OF THE DISTRIBUTION OF MAJOR ELEMENTS IN THE VINȚA GRANITOID (APUSENI MTS.)

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Abstract

The different textural types of granitoids within the Vința intrusion were recognized by previous studies.

The aim of this paper is to test if there is any geochemical link between textural and geochemical aspects of the granitoid rocks.

The abundances of major components illustrate the presence of significant differences between massive varieties and gneissic varieties of granitoids, especially regarding the content of elements that are normally included in the mafic minerals (TiO_2, FeO, MgO, CaO, P_2O_5). The correlations between these elements are strongly positive, indicating that biotite, the main mafic mineral in the intrusion, together with apatite and calcic plagioclase, play an important role in their distribution.

The bivariate diagrams show that the extremes of the composition could be discriminated, the felsic varieties and the mafic varieties being plotted in the opposite corners.

Cluster analysis indicated the presence of two subzones within each of the massive and gneissic varieties. The resulting four subzones could also be separated bases on the TiO_2+FeO+MgO+CaO+P_2O_5 sum, which is different for each of them.

Areal distribution of the data suggests a gradual transition from mafic to felsic types, but a reverse crystallization that could be attained taking into account either one batch of melt or two batches of melt.

Key words: Vința granitoid, massive, gneissic, correlation coefficient, cluster analyses, areal distribution, mafic, felsic

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Introduction

Previous petrographical studies of the Vința granitoid indicate that two textural types of granitic rocks are present in the area: a massive one and a gneissic one, but an extension of each of them is not given. At the same time, geochemical data regarding granitoid rocks from the Vința intrusion is scarce and has no precise spatial indication. The aim of this study is to test, on the basis of 26 analyses of major elements, both from massive and gneissic varieties of granitoids, if there is any geochemical variation within the Vința pluton.

Geological Setting

The Vința granitoid represents the only small body intruded into the mesometamorphic rocks of the Baia de Arieş Series, North Apuseni Mountains. The granitic rocks crop out south of the Arieş River, near the Vința village, being limited by Șesei Valley to the west and the Hermăneasa Valley to the east.

The different textural characteristics of the granitoid rocks that outcrop in the area were recognized for the first time by Ștefan et al. (1967) and later confirmed by Ianovici et al (1969, 1976), who remarked that gneissic granitoids are the dominat rock type.

Both massive and gneissic types of granitoids are medium-grained porphyritic hypidiomorphic-granular rocks, the texture of the later being imprinted by oriented layout of the micas.

The main mineralogy is given by the presence of variable amounts of quartz, plagioclase, alkali-feldspar and micas. In the massive varieties, the only mica present is biotite, while in the gneissic varieties muscovite appears besides biotite, but never as dominant mica.

During the field trips conducted in the area over the past years, we noticed that the truly gneissic type of granitoids outcrops in the east of the intrusion, in the Hermăneasa Valley, while the truly massive type outcrops in the southern part, in the Mică Valley (the main affluent of the Șesei Valley). Between these two regions there seems to be a continuous textural transition that sometimes made it impossible to distinguish between massive and gneissic varieties. The microscopic study reveals, however, significant differences between these two types of granitoids regarding the presence of late- and/or post-magmatic processes that affected them. Thus, a relatively well-developed alkaline metasomatism (potassic and calcic) observed in the gneissic varieties almost lack in the massive varieties.

The source of late-/post-magmatic fluids are probably genetically related of those that generated the large number of small bodies of pegmatites that are distributed throughout the intrusion. The main effect of the potassic metasomatism was the generation of a secondary microcline, while calcic metasomatism led to the formation of myrmekite on account of alkali-feldspar under the influence of fluids which previously had contact with carbonate lenses that are widespread in the area.

The other important differences between textural types of granitoids are given by the abundance of mafic minerals, having been noticed that this is higher in the massive varieties.

Several samples were collected from the entire surface of the intrusion, the location of those used in this study being presented in Figure 1.

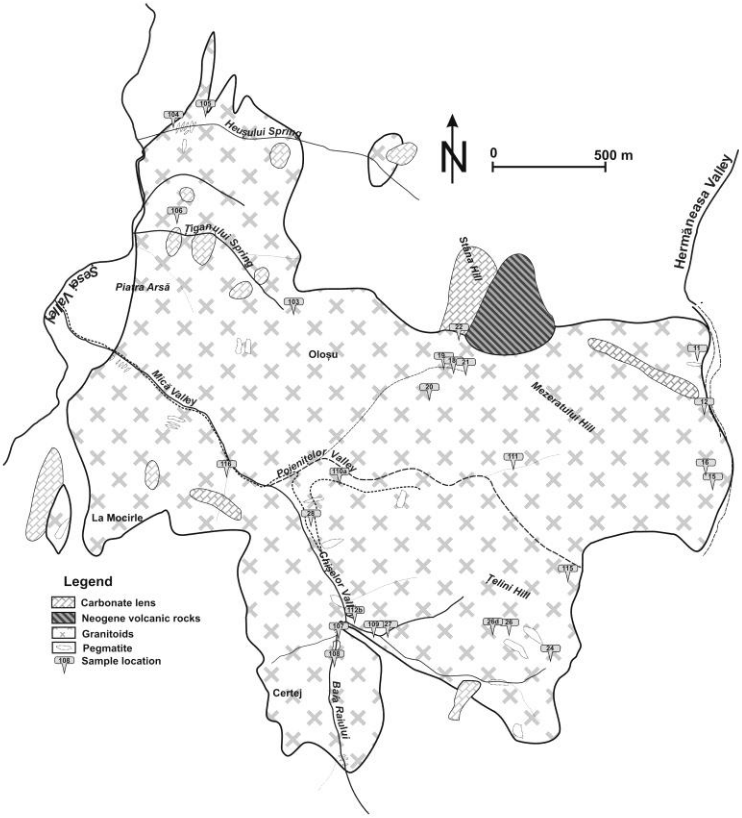

Fig. 1 Geological Map of the Vința granitoid and location of samples

Materials and methods/techniques

Twenty six representative samples were crushed into cm -size chips, and then altered parts were removed. The chips were further crushed into a coarse powder with an alligator and after that into a fine powder with an automatic agate mortar. Analyses of major elements were carried out by means of a Philips PW 2400 WD-XRF spectrometer at the Institute of Geology and Mineralogy–University of Cologne, using as certified reference materials AC-E, GS-N and MA-N. The Fe^{2+} was determined by titration with $KMnO_4$ in the Geochemistry Lab of the Department of Geology –"Al.I.Cuza" University of Iași.

Results

The contents of major elements in the granitic rocks form the Vința intrusion are listed in Table 1, with the specification that MG represent massive granitoids and GS represent gneissic granitoids. The separation into massive and gneissic types was made based on the macroscopical and microscopical study of samples.

Tab. 1 Contents of major elements in the granitic rocks from the Vința intrusion

Sample	V24	V26	V26D	V27	V28	V103	V104	V106	V107
Rock type	MG	MG	MG	MG	MG	MG	MG	MG	MG
SiO_2	67.70	69.50	69.50	67.40	67.60	67.97	71.67	66.83	69.06
TiO_2	0.43	0.39	0.37	0.44	0.47	0.41	0.33	0.45	0.31
Al_2O_3	16.40	16.00	15.90	16.70	16.4	15.96	14.9	15.92	15.69
Fe_2O_3	0.72	0.55	0.65	0.65	0.72	0.84	0.58	0.77	0.33
FeO	1.52	1.76	1.56	1.96	2.02	1.57	1.54	1.82	1.50
MnO	0.05	0.05	0.05	0.06	0.06	0.05	0.05	0.06	0.05
MgO	0.93	0.90	0.87	1.11	1.17	0.98	0.83	1.09	0.69
CaO	2.42	2.74	2.81	3.10	3.22	2.87	2.33	2.54	2.62
Na_2O	3.87	4.48	3.88	4.05	4.10	3.97	3.57	3.87	4.07
K_2O	2.59	1.65	2.52	2.72	2.30	2.32	1.71	2.76	2.50
P_2O_5	0.17	0.16	0.15	0.17	0.20	0.17	0.06	0.19	0.13
H_2O^-	0.22	0.13	0.07	0.07	0.11	0.19	0.18	0.31	0.11
L.O.I.	1.19	0.81	0.91	0.87	0.74	1.31	1.78	2.05	0.61
Total	98.21	99.12	99.24	99.30	99.11	98.61	99.53	98.66	97.67

Tab. 1 (continued-1)

Sample	V108	V109	V112b	V11	V12	V15	V16	V18	V19
Rock type	MG	MG	MG	GS	GS	GS	GS	GS	GS
SiO_2	67.75	70.34	66.44	73.30	72.80	72.80	74.20	70.80	73.00
TiO_2	0.48	0.41	0.53	0.13	0.14	0.17	0.09	0.24	0.14
Al_2O_3	16.51	15.82	16.47	15.20	14.90	14.90	14.90	15.60	14.60
Fe_2O_3	0.68	0.49	0.72	0.56	0.66	0.52	0.26	0.69	0.32
FeO	2.04	1.48	2.43	0.39	0.36	0.57	0.18	0.96	0.61
MnO	0.05	0.04	0.06	0.02	0.03	0.04	0.02	0.05	0.02
MgO	1.14	0.80	1.16	0.24	0.21	0.26	0.15	0.49	0.30
CaO	3.22	2.84	3.13	1.17	1.28	1.33	1.07	1.94	1.95
Na_2O	4.08	4.27	4.17	3.75	3.77	4.00	4.17	3.87	3.85
K_2O	1.86	1.35	1.82	3.28	3.85	3.40	2.99	3.14	3.08
P_2O_5	0.20	0.13	0.22	0.12	0.11	0.13	0.10	0.14	0.08
H_2O^-	0.16	0.20	0.11	0.14	0.08	0.11	0.15	0.08	0.15
L.O.I.	0.73	0.76	0.79	1.05	0.87	0.85	0.93	0.83	0.71
Total	98.90	98.93	98.05	99.35	99.06	99.08	99.21	98.83	98.81

Tab. 1 (continued-2)

Sample	V20	V21	V22	V105	V110a	V111	V115	V116
Rock type	GS	GS	GS	GS	GS	GS	GS	GS
SiO_2	69.20	70.50	71.20	71.30	71.04	70.23	70.06	70.02
TiO_2	0.3	0.25	0.26	0.26	0.35	0.24	0.34	0.31
Al_2O_3	15.40	15.40	15.20	14.91	15.22	15.37	15.61	15.29
Fe_2O_3	0.51	0.86	0.35	0.48	0.47	0.45	0.44	0.54
FeO	1.37	0.83	1.30	1.13	1.46	1.11	1.50	1.52
MnO	0.05	0.04	0.05	0.04	0.04	0.05	0.05	0.04
MgO	0.62	0.51	0.55	0.61	0.68	0.53	0.72	0.71
CaO	2.44	1.95	1.93	1.90	2.32	2.07	2.07	2.30
Na_2O	3.95	3.58	3.82	3.90	3.72	3.62	3.69	3.85
K_2O	2.95	3.49	3.34	2.78	2.73	3.61	2.96	2.86
P_2O_5	0.14	0.13	0.14	0.10	0.17	0.14	0.11	0.15
H_2O^-	0.11	0.22	0.06	0.29	0.11	0.07	0.14	0.28
L.O.I.	0.66	1.11	0.83	0.88	0.81	0.65	0.89	0.80
Total	97.70	98.87	99.03	98.58	99.12	98.14	98.58	98.67

At first sight, the data from Table 1 point out important differences regarding the abundances of some elements. One can notice that the contents of elements that are normally included in mafic minerals (TiO_2, FeO, MgO, CaO, P_2O_5) are higher in the massive varieties of granitoids than in the gneissic varieties, while content of SiO_2 and K_2O have a contrary distribution. Abundances of Fe_2O_3, MnO and Na_2O generally exhibit slight variations, regardless of the textural type. These are supporting mineralogical observations which attest the variable participation of mafic minerals within Vința granitic rocks and the presence of metasomatism, but the latter seems to affect other minerals rather than sodic plagioclase.

The link between major elements could be established using the matrix of correlation coefficients (tab. 2). The data presented in Table 2 reveal strong negative correlations between SiO_2 and the TiO_2 (r=-0.92), Al_2O_3 (r=-0.89), FeO (r=-0.90), MnO (r=-0.86), MgO (r=-0.92) and P_2O_5 (r=-0.81), but also strong positive values of correlation coefficient between the latter components, indicating the important role of the mafic minerals (mainly of biotite, apatite and calcic plagioclase) in their distribution.

One can also notice also generally poor correlations of Fe_2O_3 and Na_2O with the other components.

One of the problem that result from the XRF analysis is that the sum of the components usually deviates in some degree from a perfect 100%, leading to a more difficult comparison between different sets of data. One way to eliminate these difficulties is to use a ratio of elements instead of their direct content.

Tab. 2 The matrix of correlation coefficients for major elements of granitoids from the Vința intrusion

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
SiO_2	1.00	**-0.92**	**-0.89**	-0.58	**-0.90**	**-0.86**	**-0.92**	**-0.87**	-0.29	0.48	**-0.81**
TiO_2	**-0.92**	1.00	**0.86**	0.52	**0.96**	**0.82**	**0.98**	**0.93**	0.35	-0.72	0.75
Al_2O_3	**-0.89**	**0.86**	1.00	0.55	**0.80**	0.73	**0.86**	**0.82**	0.45	-0.53	**0.82**
Fe_2O_3	-0.58	0.52	0.55	1.00	0.38	0.46	0.52	0.41	-0.07	-0.15	0.54
FeO	**-0.90**	**0.96**	**0.80**	0.38	1.00	**0.85**	**0.96**	**0.93**	0.33	-0.69	0.70
MnO	**-0.86**	**0.82**	0.73	0.46	**0.85**	1.00	**0.83**	0.76	0.15	-0.40	0.63
MgO	**-0.92**	**0.98**	**0.86**	0.52	**0.96**	**0.83**	1.00	**0.94**	0.32	-0.70	0.72
CaO	**-0.87**	**0.93**	**0.82**	0.41	**0.93**	0.76	**0.94**	1.00	0.41	-0.73	0.67
Na_2O	-0.29	0.35	0.45	-0.07	0.33	0.15	0.32	0.41	1.00	-0.59	0.40
K_2O	0.48	-0.72	-0.53	-0.15	-0.69	-0.40	-0.70	-0.73	-0.59	1.00	-0.31
P_2O_5	**-0.81**	0.75	**0.82**	0.54	0.70	0.63	0.72	0.67	0.40	-0.31	1.00

In our case, the best component that we could use for dividing seems to be SiO_2 , considering its high correlation with the majority of the other components.

If one compare the values of correlation coefficients from Table 2 with those from Table 3, which represents the matrix of correlation coefficients of major elements divided by content of $SiO_{2,}$ one may remark that those from the latter are higher for the majority of the components, except K_2O.

Tab. 3 The matrix of correlation coefficients for major elements divided by SiO_2 content of granitoids from the Vința intrusion

	TiO_2/ SiO_2	Al_2O_3/ SiO_2	Fe_2O_3/ SiO_2	FeO/ SiO_2	MnO/ SiO_2	MgO/ SiO_2	CaO/ SiO_2	Na_2O/ SiO_2	K_2O/ SiO_2	P_2O_5/ SiO_2
TiO_2/SiO_2	1.00	**0.93**	0.59	**0.97**	**0.82**	**0.98**	**0.94**	0.69	-0.62	**0.80**
Al_2O_3/SiO_2	**0.93**	1.00	0.65	**0.88**	0.73	**0.92**	**0.89**	0.73	-0.42	**0.87**
Fe_2O_3/SiO_2	0.59	0.65	1.00	0.47	0.46	0.60	0.50	-0.26	-0.12	0.61
FeO/ SiO_2	**0.97**	**0.88**	0.47	1.00	**0.85**	**0.97**	**0.94**	0.66	-0.60	0.76
MnO/ SiO_2	**0.82**	0.73	0.46	**0.85**	1.00	**0.83**	0.76	0.15	-0.40	0.63
MgO/ SiO_2	**0.98**	**0.92**	0.60	**0.97**	**0.83**	1.00	**0.95**	0.67	-0.60	0.77
CaO/ SiO_2	**0.94**	**0.89**	0.50	**0.94**	0.76	**0.95**	1.00	0.71	-0.64	0.73
Na_2O/ SiO	0.69	0.73	-0.26	0.66	0.15	0.71	0.41	1.00	-0.63	0.68
K_2O/ SiO_2	-0.62	-0.42	-0.12	-0.60	-0.40	-0.64	-0.73	-0.63	1.00	-0.25
P_2O_5/ SiO_2	**0.80**	**0.87**	0.61	0.76	0.63	0.73	0.67	0.68	-0.25	1.00

At this point, one can proceed to verify if there is any geochemical variation within the Vința pluton.

The bivariate diagrams presented in Figures 2 and 3 point out that a geochemical zoning is possible, and this is very clear for the samples collected from the Hermăneasa Valley and the southern zone of the intrusion, that we assumed to represent the true types of gneissic and massive granitoids. In all the diagrams from Figures 2 and 3, these samples plots at the opposite corners. Moreover, in the diagram CaO/SiO_2:MgO/SiO_2 from Figure 2b, an advanced zoning is present, but this fact is hard to attain in the others diagrams.

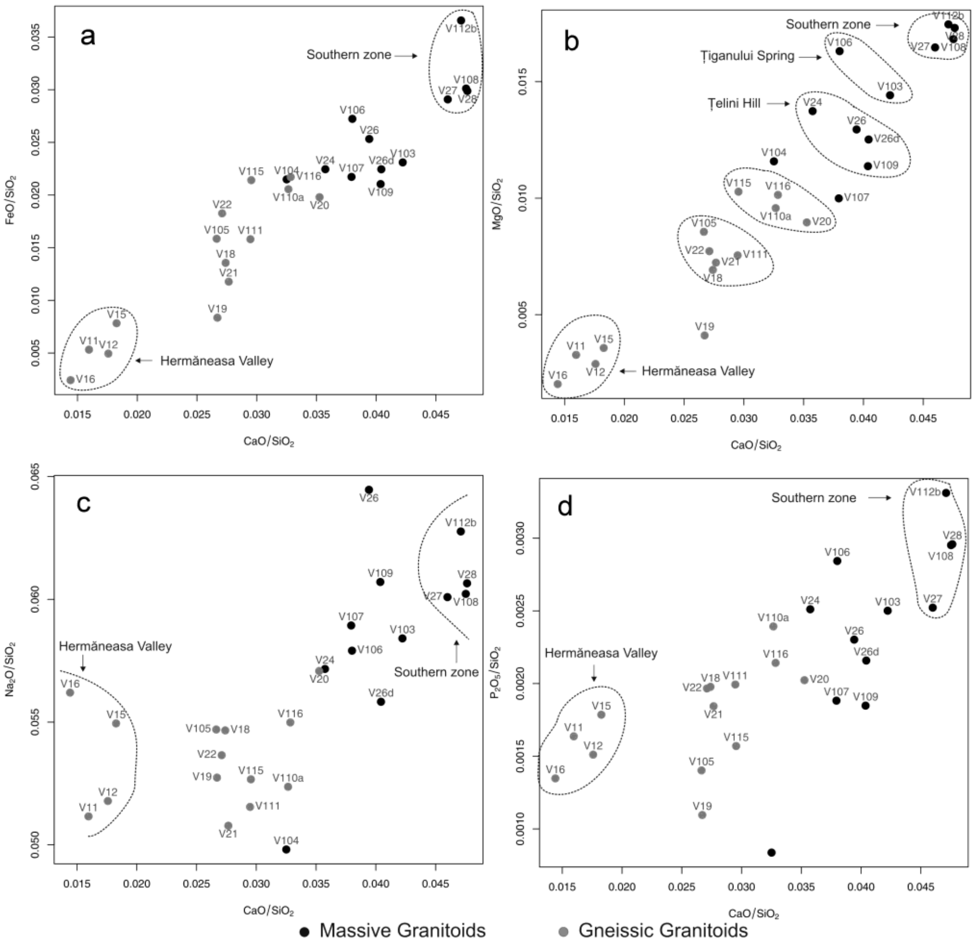

Fig. 2 Bivariate diagrams of CaO/SiO_2, MgO/SiO_2, FeO/SiO_2, P_2O_5/SiO_2 and Na_2O/SiO_2 ratios of granitic rocks from theVința intrusion

What is remarkabe is the fact that in almost all the diagrams presented there is a good discrimination between the massive and gneissic granitoids. The only sample that seems not to respect the mentioned distribution is sample V104, collected from the northern part of the intrusion, on Heuşului Spring. Even if from a mineralogical point of view, this sample is one of massive texture, from the geochemical point of view it is closer to gneissic varieties.

The diagrams from Figure 3a-d also show that, in relation to the values of MgO/SiO_2, FeO/SiO_2 and P_2O_5 ratios, two more samples, one of the massive type and the other of the gneissic type, are added to the groups previously marked.

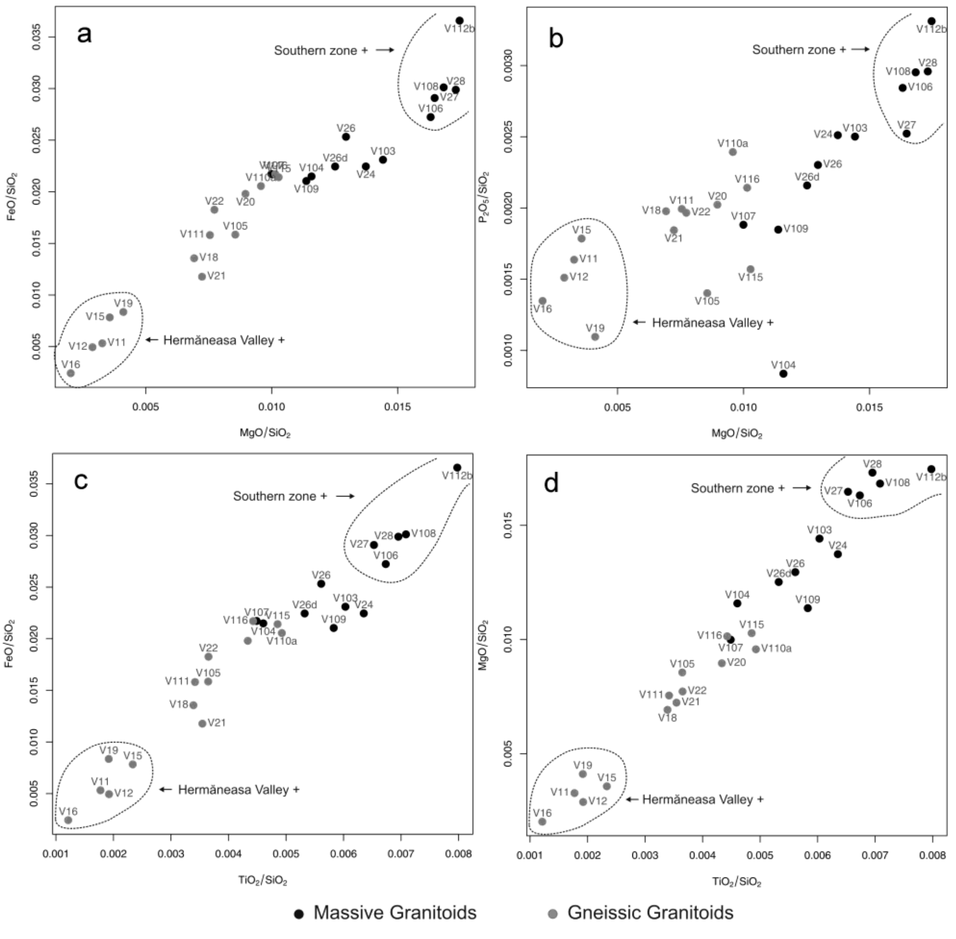

Fig. 3 Bivariate diagrams of TiO_2/SiO_2, MgO/SiO_2, FeO/SiO_2 and P_2O_5/SiO_2 ratios of granitic rocks from the Vința intrusion

The above graphic representations do not manage to make an effective discrimination between textural types of granitoids, which means that additional methods are needed.

One of this approaches could be the cluster analysis of the values resulted after dividing by SiO_2 content.

The dendrogram made up based on the cluster analysis (fig. 4) show that different textural samples could be reasonably discriminated using this method. Moreover, two subgroups could be separated within each textural type based on geochemistry. The four groups may also be separated on the basis of the TiO_2+FeO+MgO+CaO+P_2O_5 sum, observing that its values are 6.78-7.48 for the group **1a**, 5.25-6.09 for the group **1b**, 3.67-4.99 for the group **2a** and 1.59-3.08 for the group **2b**, the group 1a represent the most mafic type, while the group 2b represents the most felsic type.

Is was also noticed that sample V104 is closer to the group 2a of intermediate felsic composition, having the value of the sum mentioned above equal with 5.09.

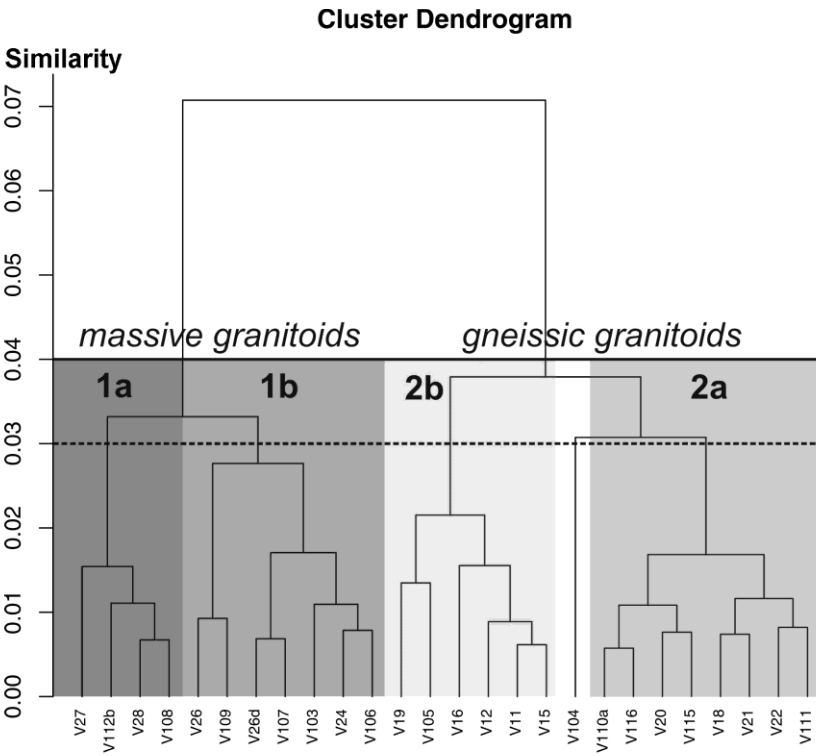

Fig.4 The Cluster dendrogram for granic rocks of the Vința intrusion

By resuming up all the data and the interpretations presented above on the map of the Vința intrusion, on gets to the representation from Figure 5. One can see that there is a geochemical zoning within the Vința granitoid. The massive granitoids outcrop in the central part of the intrusion along a NNW-SSE oriented strip, with the most mafic varieties on the southern half, upstream of the Mică Valley. The gneissic granitoids surrounding the massive varieties mainly in the east, north and west. Within the intrusion there seems to be a gradual transition between different textural types.

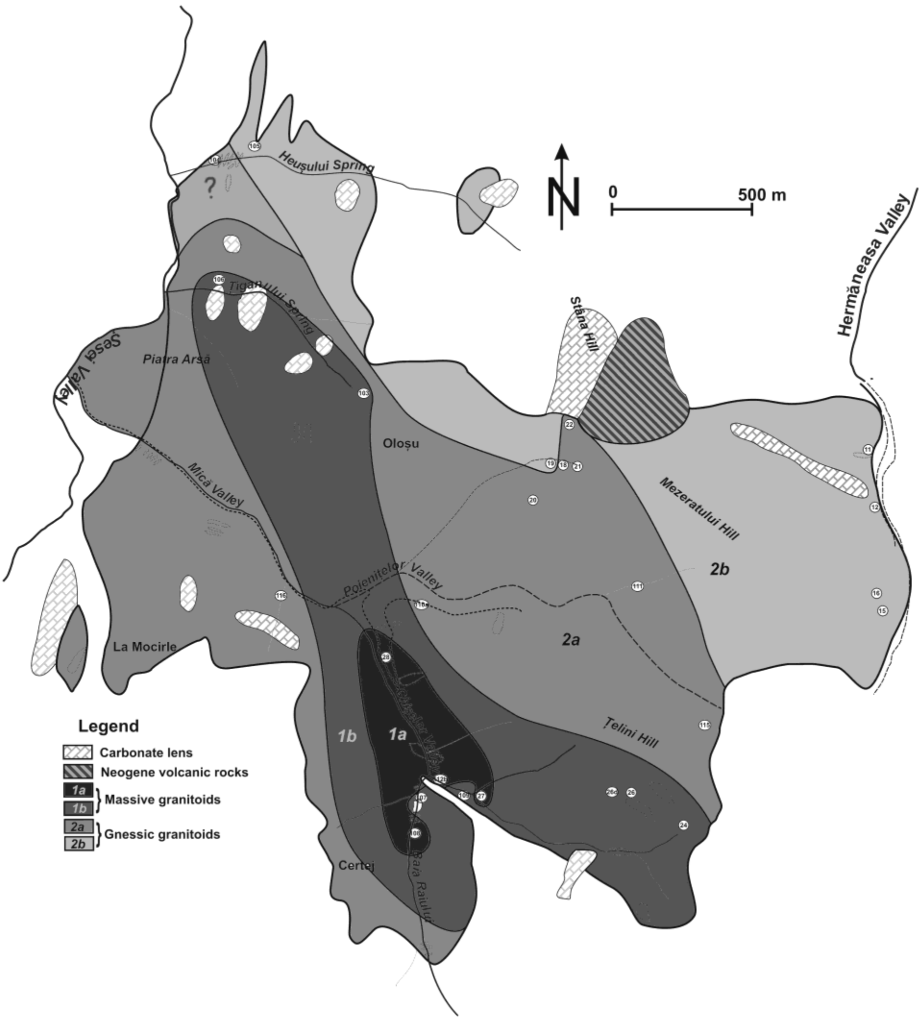

Fig. 5 Map with area distribution of the textural varieties within the Vința granitoid

The arrangement of mafic varieties in the center of the intrusion and of felsic varieties toward its edge suggests a reverse crystallization if a single batch of magma is taken into account (Clarke, 1992; Cobbing, 2004).

At the same time, two batches of magma emplaced at different times could be taken into account, trace element distribution and biotite geochemistry supporting this hypothesis (Pintilei et al., 2007, Pintilei, 2009).

Conclusions

Major elements of 26 granitoid samples were investigated in order to test if there is any geochemical zoning within the Vința granitoid.

The abundances of major components show the presence of significant differences between massive varieties and gneissic varieties of granitoids, especially regarding the content of elements that are normally included in the mafic minerals (TiO_2, FeO, MgO, CaO, P_2O_5). The correlations between these elements are strongly positive, indicating that biotite, the main mafic mineral in the intrusion, together with apatite and calcic plagioclase, plays an important role in their distribution.

The bivariate diagrams made up after reducing inconveniences given by deviations of the sum from the perfect value show that the extremes of the composition could be discriminated in this way, the most felsic varieties (those from the Hermăneasa Valley) and the most mafic varieties (those from the southern zone) being plotted in the opposite corners.

Further discriminations made with the help of cluster analysis indicated the presence of two subzones within each of the massive and gneissic varieties. The resulting four subzones could also separated bases on of TiO_2+FeO+MgO+CaO+P_2O_5 sum, which is different for each of them.

Areal distribution of the interpreted data suggests a gradual transition from mafic to felsic types, but a reverse crystallization that could be attained taking into account either one batch of melt or two batches of melt.

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