

## BIOTITE GEOCHEMISTRY OF THE VINȚA GRANITOID (APUSENI MTS.)

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### Abstract

Six biotite samples from the Vința granitoid were investigated in order to obtain informations regarding the geochemistry of their major and trace elements and to reveal the conditions of the magma from which their host rock consolidated.

The processing of the data revealed that all the samples represent Fe-biotite crystallized directly from the magma and that they are not affected by the subsequent subsolidus processes.

The biotite from pegmatite crystallized from moderately oxidized magma at lower temperatures than biotites from granitoids. The geochemistry of biotites from granitoids indicates a low degree of magma oxidation and higher temperatures. The distribution of octahedral cations in the bivariate diagrams suggest the presence of two batches of melts that led to the formation of different textural types of granitoids, massive and gneissic, a hypothesis supported also by the values of Mg# and by Fe/Fe+Mg ratio.

In the gneissic granitoids, biotites are accompanied by muscovite, while in the massive varieties biotites are unaccompanied by other ferromagnesian or aluminous minerals.

The study of the abundance of trace elements in biotites and in their host rocks indicates that over 50% of the total quantity of Zn, Cs, Nb and Ta and a large quantity of Rb, Sc, V, Ga and U from Vința granitoids are concentrated by the dark mica.

**Key words:** Vința granitoid, biotite, trace elements, gneissic, primary magmatic mineral

### Introduction

Biotite represents one of the most important ferromagnesian constituents of granitoid rocks, being in many cases the single dark mineral. Because of its complex crystal structure, this mineral may incorporate a large number of elements of different ionic sizes and charges, throughout a variety of isomorphic substitution; sometimes, it represents the

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main host of some trace components like Rb, Cs, Nb, Ta, Zn. Several studies pointed out that the geochemistry of biotite can reveal information about melting processes and thermodynamic conditions of the crystallization of the granitic melt.

### **Geological Setting**

The Vința granitoid represents a small irregularly shaped body intruded into the crystalline schists of the Baia de Arieș Series, which is part of the Apusenides. The age of intrusion is not well-known yet, being considered either pre-Variscan (486 Ma; Ianovici et al., 1976) or late-Variscan (261 Ma; Pană, 1998).

Two textural varieties of granitoids were recognized in the area, namely a massive and a gneissic one, along with a large number of metric bodies of pegmatite spread throughout the entire surface of the intrusion.

The main mineralogy of the granitic rocks is given by the presence of variable amounts of quartz, plagioclase, alkali-feldspar, biotite and muscovite. Among accessory minerals, zircon, titanite, apatite, tourmaline and garnet were identified (Pintilei et al., 2007).

Biotite is the only mica present in the massive granitoids and the most abundant mica in the gneissic varieties, where it is followed by muscovite. Under the microscope, biotite occurs as subhedral to anhedral phenocrysts, dark-brown to red-brown in colour, in most cases fresh; slightly affected by chloritization (sometimes penninic) crystals are also present. In the gneissic granitoids there are situations in which biotite is muscovitized. Inclusions of thin zircon needles with black pleochroic haloes in biotite are common.

### **Materials and methods/techniques**

Six representative samples of biotite (five from granitoids and one from pegmatites) were ground and sieved. The +0.2 -0.5mm (+65 -32 mesh/inch) fraction, previously freed by magnetic minerals using a hand magnet, was concentrated by multiple passes through a Frantz isodynamic separator and by handpicking under a binocular microscope. Almost pure resulting samples were ground into a fine powder and analyzed for major elements by means of the XRF technique and for trace elements by means of the ICP-MS spectrometer at the Institute of Geology and Mineralogy–University of Cologne; certified reference materials, namely MicaFe and MicaMg, were used. The Fe<sup>2+</sup> was determined by titration with KMnO<sub>4</sub> in the Geochemistry Lab of the Department of Geology –"Al. I. Cuza" University of Iași.

### **Results**

The chemical composition and structural formulae calculated on the basis of 22 positive charges (tab. 1) show that Si and Al cations p.f.u generally fill the tetrahedral sites. The octahedral sites display a slight variability between 2.505 and 2.633 cations p.f.u. and the 12-fold co-ordination ranges between 0.805 and 1.015 cations p.f.u. These values meet

the requirements imposed by Foster (1960):  $X=0.8-1.13$  and  $Y=2.5-3.15$  for an acceptable analysis of biotite.

Tab. 1 Chemical composition (%) and structural formulae (a.p.f.u.) of biotites from the Vința granitoid

Sample	Bi22	Bi27	Bi105	Bi108	Bi115	Bi120
Type	gneissic	massive	gneissic	massive	gneissic	pegmatite
SiO <sub>2</sub>	36.86	37.47	35.75	36.37	37.36	37.92
TiO <sub>2</sub>	2.45	3.05	2.81	2.85	2.88	3.20
Al <sub>2</sub> O <sub>3</sub>	17.64	17.63	17.64	17.82	17.53	19.19
Fe <sub>2</sub> O <sub>3</sub>	3.67	3.59	3.44	3.41	3.69	5.87
FeO	15.68	15.4	14.99	14.57	15.84	13.62
MnO	0.46	0.39	0.38	0.33	0.42	0.40
MgO	6.09	7.76	6.87	7.49	6.81	5.65
CaO	0.94	0.98	1.62	1.05	0.64	0.19
Na <sub>2</sub> O	0.74	0.63	0.75	0.69	0.67	0.37
K <sub>2</sub> O	6.50	8.84	5.52	7.88	7.92	7.81
P <sub>2</sub> O <sub>5</sub>	0.26	0.57	0.64	0.55	0.32	0.02
H <sub>2</sub> O	1.31	0.83	1.22	1.12	1.09	1.02
L.O.I.	3.56	2.85	4.82	2.23	3.02	4.12
Total	96.16	99.99	96.45	96.36	98.19	99.38
Number of ions on the basis of 22 positive charges						
Si	2.872	2.807	2.811	2.801	2.847	2.819
Al <sup>IV</sup>	1.128	1.193	1.189	1.199	1.153	1.181
Z	4.000	4.000	4.000	4.000	4.000	4.000
Al <sup>VI</sup>	0.492	0.364	0.446	0.419	0.421	0.501
Ti	0.144	0.172	0.166	0.165	0.165	0.179
Fe <sup>3+</sup>	0.215	0.202	0.204	0.198	0.212	0.328
Fe <sup>2+</sup>	1.022	0.965	0.986	0.938	1.009	0.847
Mn	0.030	0.025	0.025	0.022	0.027	0.025
Mg	0.707	0.867	0.805	0.860	0.774	0.626
Y	2.610	2.594	2.633	2.601	2.608	2.505
Ca	0.078	0.079	0.136	0.087	0.052	0.015
Na	0.112	0.092	0.114	0.103	0.099	0.053
K	0.646	0.845	0.554	0.774	0.770	0.741
X	0.836	1.015	0.805	0.964	0.921	0.809
Fe/Fe+Mg	0.636	0.574	0.596	0.569	0.612	0.652
Al <sub>t</sub>	1.620	1.557	1.635	1.618	1.574	1.682
Mg#	40.89	47.33	44.95	47.83	43.41	42.50
Fe <sup>3+</sup> /Fe <sup>2+</sup> +Fe <sup>3+</sup>	0.17	0.17	0.17	0.17	0.17	0.28

Biotite represents a solid solution with annite, phlogopite, syderophyllite and eastonite as end members (Deer, 1992; Rieder et al., 1998). In the same time, Forster (1960) shows

that biotite can be classified according to the abundance of 6-fold co-ordinate cations from octahedral sites. The diagram  $R^{3+}(Al^{VI}+Fe^{3+}+Ti) : Mg : (Fe^{2+}+Mn)$  of Figure 1 reveals that all biotites from granitoids plot in the field of Fe-biotite and the biotite from pegmatite plots close to this field.

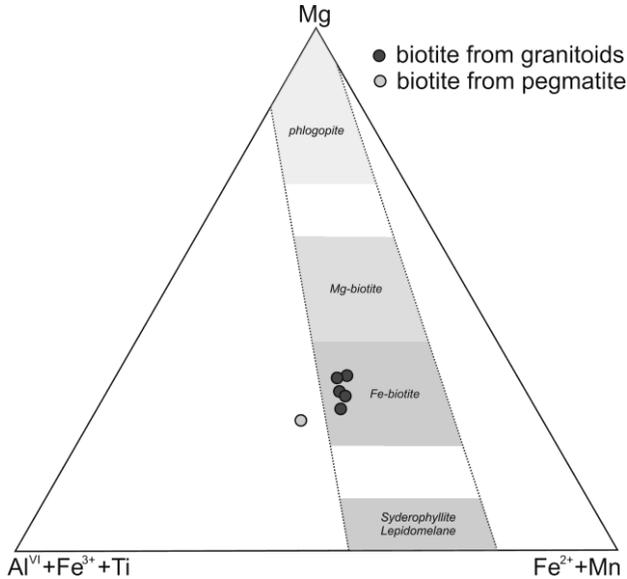


Fig. 1 Plot of biotite samples in the octahedral ion diagram of Foster (1960)

The chemical composition of biotites depends on various factors (P, T,  $f_{O_2}$ ,  $f_{H_2O}$ ) and it is considered that this reflects the conditions of the melt from which their host rocks were generated. Mg-rich biotites are stable at high temperatures, while Fe-rich varieties are stable at relative lower temperatures, which means that Mg# ( $Mg \cdot 100 / (Mg + Fe^{2+})$ ) ratio decrease with the cooling of the melt (Oba et al., 1984). The abundance of Al from the octahedral sites is also increasing with decreasing of Mg and it is positive correlated with the abundance of  $Fe^{2+}$ . A possible explanation can be the very common substitutions of the  $Mg \rightleftharpoons Fe^{2+}$  (phlogopite-annite substitution) and  $3M^{2+VI} \rightleftharpoons 2Al^{VI} + \square^{VI}$  types, identified in biotites from peraluminous magmas by Stussi and Cuney (1996).

The values of the Mg# and  $Fe/(Fe+Mg)$  ratio presented in Table 1 suggest that samples Bi27 and Bi108 (which represent biotites from massive granitoids) crystallized at higher temperature than samples Bi22, Bi105 and Bi115 (which represent biotites from gneissic granitoids) and sample Bi120 (biotite from pegmatite).

In the bivariate diagrams presented in Figure 2a-d, one can see that the substitutions mentioned above may be responsible for the abundance of the cations in the octahedral sites of biotites from the Vința granitoid. The distribution of the samples in this diagrams also

shows that biotite from pegmatite crystallized under different conditions over the biotite from granitoids. The substitution of Al for Mg and  $\text{Fe}^{2+}$  in biotites from granitoids (fig. 2a and 2b) shows a slightly different trend in the case of biotites of the massive type, compared to biotites of the gneissic type, which could suggest different conditions of magma evolution.

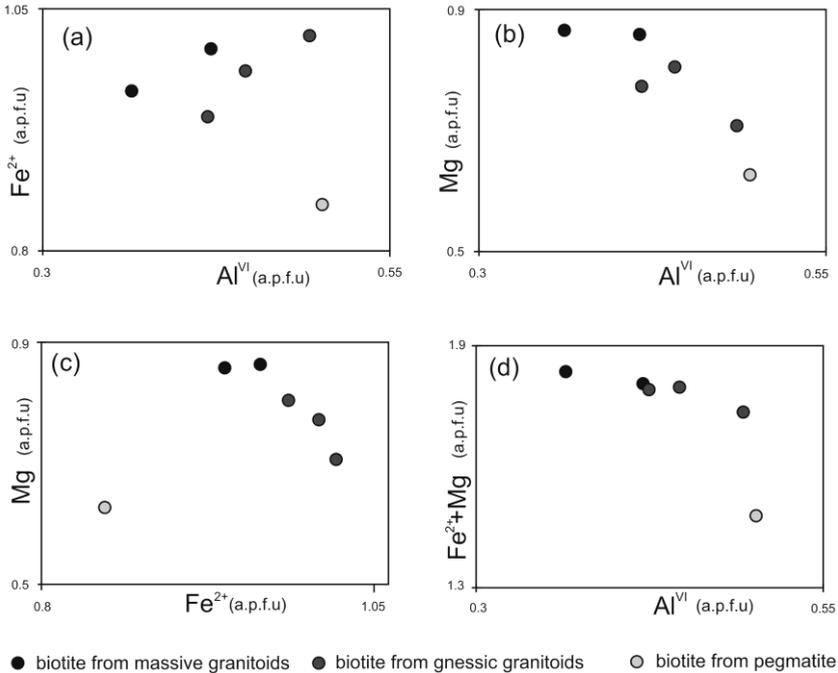


Fig. 2 Bivariate diagrams between  $\text{Fe}^{2+}$ , Mg and Al from octahedral sites of biotites

Previous studies carried out by Wones and Eugster (1965) showed that abundance of Mg,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the octahedral sites of biotite could offer a relative estimation of the oxidation degree of the magma from which it crystallized. The plot of the biotite samples from the Vința granitoid in the diagram  $\text{Fe}^{3+} : \text{Fe}^{2+} : \text{Mg}$  of Wones and Eugster (fig. 3) indicates an oxygen fugacity ranging between hematite-magnetite and Ni-NiO buffers; the sample of biotite from pegmatite shows a higher degree of magma oxidation. At the same time values of the  $\text{Fe}^{3+}/\text{Fe}^{2+}+\text{Fe}^{3+}$  ratio (tab. 1) for biotites from granitoids ( $\text{Fe}^{3+}/\text{Fe}^{2+}+\text{Fe}^{3+}=0.17$ ) and from pegmatite ( $\text{Fe}^{3+}/\text{Fe}^{2+}+\text{Fe}^{3+}=0.28$ ) are thought to indicate a low and intermediate degree of oxidation, respectively, as Buda et al. (2004) stated in a study of biotites from Variscan granitoids of Central Europe. It is also interesting to note that the plots of biotite from granitoids follow a linear trend which is parallel to those for

the buffer equilibria, suggesting that biotite crystallized at the relatively constant oxygen fugacity.

The MgO, FeO<sub>t</sub> and Al<sub>2</sub>O<sub>3</sub> contents of biotites from calc-alkali igneous rocks reflect the mineral associations present in the host rock (Nockolds, 1947).

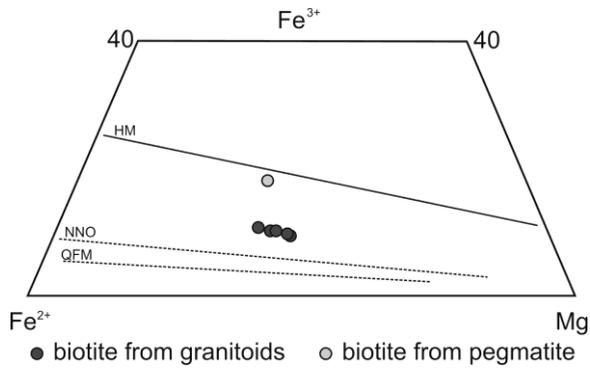


Fig. 3 Fe<sup>3+</sup> : Fe<sup>2+</sup> : Mg variation diagram (Wones and Eugster, 1965) for biotites from the Vința granitoid

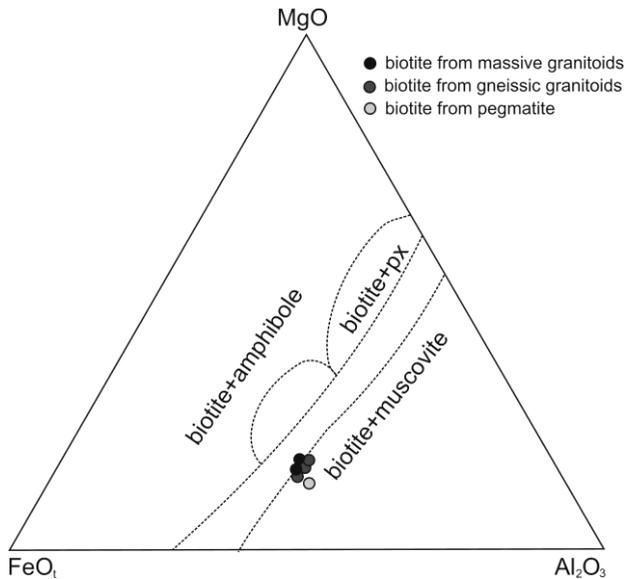


Fig. 4 MgO : FeO<sub>t</sub> : Al<sub>2</sub>O<sub>3</sub> variation diagram (Nockolds, 1947) for biotites from the Vința granitoid

The plot of biotite samples in the diagram  $MgO : FeO_t : Al_2O_3$  (fig. 4) points out that in the gneissic varieties of granitoids, this mineral is accompanied by other aluminous phases like muscovite and/or garnet, while in the massive varieties biotite is rather unaccompanied by other ferromagnesian or aluminous minerals. This hypothesis is well sustained by the microscopic observations of the rocks from which biotites were separated.

All the interpretations of this study are based on the assumption that biotites are primary magmatic minerals, that their chemical composition is unaffected by late- or post-magmatic fluids or by subsolidus re-equilibrations and that it reflects the magmatic conditions. In order to test this hypothesis, the biotite samples were plotted in the  $10TiO_2 : FeO+MnO : MgO$  ternary diagram of Nachit et al. (2005) (fig. 5).

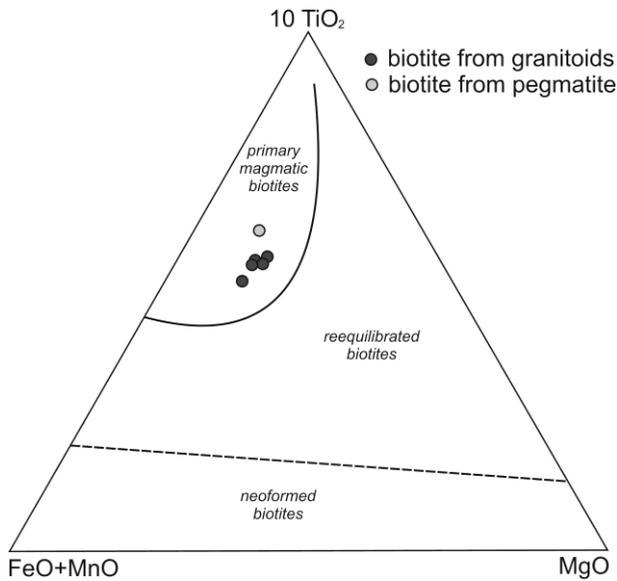


Fig. 5  $10TiO_2 : FeO+MnO : MgO$  variation diagram (Nachit et al., 2005) for biotites from the Vința granitoid

The diagram of Figure 5 reveals that all the biotite samples used in the present study are indeed primary magmatic minerals and that they are unaffected by subsequent processes.

Several studies (Rankama and Sahama, 1970; Liakhovich, 1972; Murariu, 2001) pointed out that biotite represents the main host mineral for trace elements like Rb, Zn, Nb, Cs, Ta in the calc-alkali igneous rocks.

The abundance of some trace elements in biotites, along with their content in the host rocks and the normative participation of biotite in corresponding rocks, were used in order to determine how much of these elements are concentrated in biotite.

The normative participation of biotite in three rock samples of the Vința granitoid is 4.95% in V22, 8.28% in V27 and 6.01% in V115 (Pintilei, unpublished work). The amount of trace elements in the biotite, as well as in its host rock and the percentage of each element concentrated by the biotite are presented in Table 2.

Tab. 2 Trace elements in biotite, in its host rock and the percentage of each element concentrated by this mineral

	Biotite content (ppm)			Host rock content (ppm)			Concentrated %		
	Bi22	Bi27	Bi115	V22*	V27*	V115*	Bi22	Bi27	Bi115
V	100,00	152,00	123,00	24,00	42,00	n.a.	20,63	29,97	-
Zn	521,00	385,00	451,00	48,00	52,00	47,00	53,73	61,30	57,67
Ga	48,00	44,00	44,00	19,00	17,00	19,00	12,51	21,43	13,92
Sc	24,01	31,48	28,75	4,05	5,49	4,72	29,35	47,51	36,58
Rb	763,51	669,67	729,08	149,40	116,24	103,49	25,30	47,70	42,34
Sr	25,75	16,05	25,75	149,20	213,84	177,84	0,85	0,62	0,87
Nb	83,00	73,94	98,98	9,48	11,64	11,07	43,33	52,62	53,76
Cs	125,75	57,76	53,78	13,05	9,02	5,46	47,69	53,03	59,10
Ba	131,71	275,42	222,12	218,24	255,73	239,61	2,99	8,92	5,57
Ta	11,30	16,91	9,38	1,23	2,93	1,02	45,39	47,85	55,18
Pb	19,83	7,41	14,14	30,63	22,80	26,88	3,20	2,69	3,16
U	22,06	3,82	6,76	4,55	1,59	2,00	23,98	19,85	20,34

\*Pintilei (unpublished work)

Data presented in Table 2 shows that more than half of entire amount of Zn, Cs, Nb and Ta from granitoid rocks is concentrated in biotite. One also can see that biotite from the Vința granitoid contains an important quantity of Rb, Sc, V, Ga and U and represents a key mineral in respect of the amount of these elements in the entire host rock. These aspects reveal the important role of biotite in the distribution of some incompatible trace elements in the Vința granitoid.

## Conclusions

This paper presents, for the first time, the chemical composition of some biotites from the Vința granitoid. The processing of the data revealed that all the samples represent Fe-biotite terms which crystallized directly from the magma and which are unaffected by subsequent processes; this aspect made them valuable tools in the petrogenetic approach.

The biotite from pegmatite crystallized from a moderately oxidized magma at lower temperatures than those of biotites from granitoids. At the same time, the geochemical features of biotites from granitoids indicate a low degree of magma oxidation that remains constant over the consolidation process; also, there is the possibility of the presence of two batches of melts where phlogopite-annite and  $3M^{2+VI} \rightleftharpoons 2Al^{VI} + \square^{VI}$  substitutions acted slightly different, leading to the formation of two different textural types of granitoids, a massive and a gneissic one, respectively.

In the gneissic granitoids, biotites are accompanied by other aluminous minerals, which are represented by muscovite and possibly garnet, while in the massive varieties biotites seem to be unaccompanied by other ferromagnesian or aluminous mineral phases.

The study of the abundance of trace elements in biotites and in their host rocks indicate that over 50% of the total quantity of Zn, Cs, Nb and Ta and a large quantity of Rb, Sc, V, Ga and U from Vința granitoids are concentrated by the dark mica.

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