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THE SUBVOLCANIC MAGMATIC ROCKS FROM THE NISTRU ZONE (GUTÎI MOUNTAINS)

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Abstract: The intrusive rock from Nistru zone represents the subvolcanic suite of the igneous activity from the southern part of the Gutâi Mountains. The subvolcanic magmatic rocks from Nistru zone follow, in succession, the phase of Sarmatian pyroxene andesites. They are spatially associated to the volcanic rocks, being distinguished by morphological and structural aspects, as well as by petrographic types. The relations between the main types of magmatic rocks emphasize their sequential emplacement: the first sequences form stocks of small sizes with irregular forms represented by the porphyry facies of the quartz-microdiorites with lateral transitions to andesitic facies and by porphyry quartz-micromonzodiorites. These stocks are accompanied by apophyses from which the ones of the quartz-micromonzodioritic outcrop on Nistru Valley; the second sequence of magmatic subvolcanic rocks is represented by dykes, apophyses and sills of a few meters size that pierce the stocks. These are represented by equigranular quartz-microdiorites under the form of a dyke that pierces the porphyry quartz-microdiorite stock, and porphyry microdiorites under the form of intrusive apophyses included in the porphyry quartz-microdioritic stock. The porphyry microgabbro forms a small sill occurring within the quartz-micromonzodioritic stock. The magma of the subvolcanic rocks suite from Nistru zone has an andesitic, calc-alkaline and metaluminous with low tendencies towards peraluminous character. The primary magma of the subvolcanic magmatic rocks suite was generated from the mixing of a mantle melt with the crustal material. Significant for crustal contamination, in its ascendant movement, is the high value of the Rb/Sr = 0.3 ratio. Under reducing environment various rock types were emplaced after the differentiation processes in the shallow chamber. The large ion lithofile elements (LILE): Rb, Cs, Ba, K, Sr/light rare earth elements (LREE):La, Ce, Nd, Pr, Ne, Sm and LILE/HFSE (high-field strengh elements: Ti, Y, Sc, Hf, Zr, U, Th, Ta, Nb, La, Lu ratios are characteristic for the contribution of the different mantle sources in generating the parental magma. The Rare Earth Elements (REE) patterns distribution within a Nistru intrusive subvolcanic rocks suite, evaluated by chondrite and N-MORB normalizing are characteristic of generated magmas in subduction conditions. The concentration of the large ion lithophile elements (LILE, Rb, Ba, Cs) and enrichments in light rare earth elements (LREE, La, Ce, Nd, Pr, Ne, Sm) indicate as important source for magma partial melting of ascending mantle wedge and fluid addition from dehydration of the subducting oceanic crust and associated sediments. The low content in Sr is related to the implication of the oceanic crust in the melting of the subducted plate. The heavy rare earth elements (HREE), Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y show abundances similar to those for N-MORB. The enrichment in the complete line of the elements from Ba $\rightarrow$ Hf, the strong fractioning of LREE, the Nb and Eu negative anomaly supports the fractional crystallization and the assimilation as predominant petrogenetic processes within the magma evolution and at the same time with the accumulation in upper magmatic chambers. Magma with subduction-related geochemical signatures can also be generated in syn-collisional tectonic setting.

Key-words: subvolcanic, magmatism, subduction, major elements, trace and rare earth elements, fractional crystallisation, assimilation.

1. INTRODUCTION

The Nistru zone represents the southern part of the Gutâi Mts (Fig. 1). The products of the Neogene volcanism with maximum development in the Nistru area are as follows: pyroclastic rocks with ignimbritic character, of Badenian age, pyroxene andesites of Sarmatian age and quartz andesites of Pannonian age, (Fig. 2). The subsequent intrusive magmatic activity generated a suite of magmatic rocks consolidated at a subvolcanic level.

The magma genesis and evolution in the subduction zone can be modified by some processes (crystal fractionation, magma mixing or crustal contamination), (Davidson, 1987, Reubi & Nicholls, 2004, Turner & Foden, 2001, Class et al., 2000, Harangi et al., 2007).

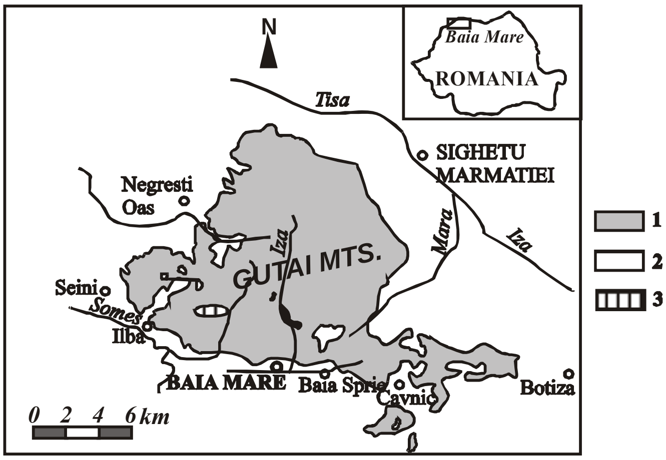


Figure 1. Localization of the study zone; 1.- Neogene igneous rocks; 2.- sedimentary rocks; 3.- Nistru zone.

The association of the volcanic rocks and the intrusive magmatic phase, from Nistru zone, represents the favourable environment for the convective circulation of the meteoric water which has penetrated through permeable areas at deep levels. The intrusive rocks from Nistru zone in subvolcanic facies are affected by hydrothermal alteration significant for their role in the metallogenetic activity, (Damian 2003). There is a strong relationship between the vein system development and the space-time distribution and compositional characteristics of magmatic formations from Nistru zone. The vein space from Nistru zone is emplaced in the volcanic rocks related with the subvolcanic magmatic bodies. The association between subvolcanic bodies, volcanic and volcaniclastic rocks in Nistru area has had a strong influence on the distribution of mineralization (the vertical zoning in the north-western part related with quartz-microdiorite and horizontal zoning of the mineralization around the quartz-micromonzodiorite stock in the NE-SE part of the Nistru area), (Damian 2000). The vein field in the Nistru zone, developed in volcanic rocks related to intrusive magmatism, indicates an association with a possible porphyry system that came before the epithermal system, (Mitchell 1992). Particularly meaningful for an association between a possible porphyry copper system and a vein system (base metal and gold) is the occurrence of the gold-chalcopyrite mineralogical complex within the quartz-micromonzodiorite stock, (Damian 1999).

2. GEOLOGICAL SETTING

The Nistru zone belongs to the southern part of the Gutîi Mts. The Gutîi Mts represent the NW of the median segment of the Neogene volcanic East-Carpathian chain (Romania). The Oaş-Gutîi volcanic area is situated in the Central Segment of the Carpathian Pannonian Neogene region, (Seghedi, et al., 2004). The Neogene magmatic activity in the Gutîi Mts has taken place in a long period of time, according to the radiometric data K-Ar, (13.4-9.0 Ma) (Edelstein et al., 1992), and 13.5-6.9 Ma, (Pécskay et al., 1995).

The Preneogene basement consists of crystalline rocks belonging to the Median Dacides and paleogene formations of the Transcarpathian Flysch (Săndulescu, 1984). The Neogene magmatism in the Oaş-Gutîi Mountains is related to the subduction roll back area from the southern part of the East European plate (Balintoni et al., 1997).

The Neogene magmatism was generated in stress conditions with compresive tendencies followed by extensional conditions, (Popescu, 1994). An important role in the tectonical evolution of the Neogene volcanic area have had two structural major elements, the Dragoş Vodă fracture E-W, (Popescu, 1986) and the Gutîi fracture NW-SE (Borcoş et al., 1979). The geochemical synthesis, geochronological geodinamic and tectonic evolution of the the Neogene-Quaternary magmatism in Carpathian-Pannonian region have been presented by (Seghedi et al., 2004, Konečy et al., 2002).

In this paper we describe the subvolcanic rocks suite from the Nistru zone. In the Nistru zone, the magmatic activity has been characterized by the extensive development of the volcanite represented by pyroxene andesites with subordinated participation of the quartz andesites. The products with an explosive character are represented by the rhyodacitic badenian formation which marks the beginning of the volcanic activity. The Badenian age of this formation has been established based on the biostratigraphical data. These are similar to the volcaniclastic deposits from Maramureş bazin, (Damian et al., 2007) and with those from North-Western Transylvania, (Seghedi et al., 2000). Within the rhyodacitic badenian formation there have been separated volcaniclastic complex and the sedimentary-volcanogene complex, (Borcoş et al., 1972a). The volcaniclastic complex is represented by pyroclastic rocks and the sedimentary-volcanogene complex consists of pyroclastic rocks with intercalations of terigene rocks (conglomerates, sandstones, marls and sometimes siltstones with contribution of pyroclastic material). The pyroxene andesites represent the general products of the volcanic activity during Sarmatian. The Sarmatian age of the pyroxenic andesites, has been confirmed by the K-Ar age determinations, 13.4-12.1Ma, (Edelstein et al.,1992, Pécskay et al., 1994). The pyroxene andesites are placed over the Badenian rhyodacitic pyroclastites and are intruded by the apophyses of the porphyry quartz-microdiorites and quartz-micromonzodiorites, (Fig. 2).

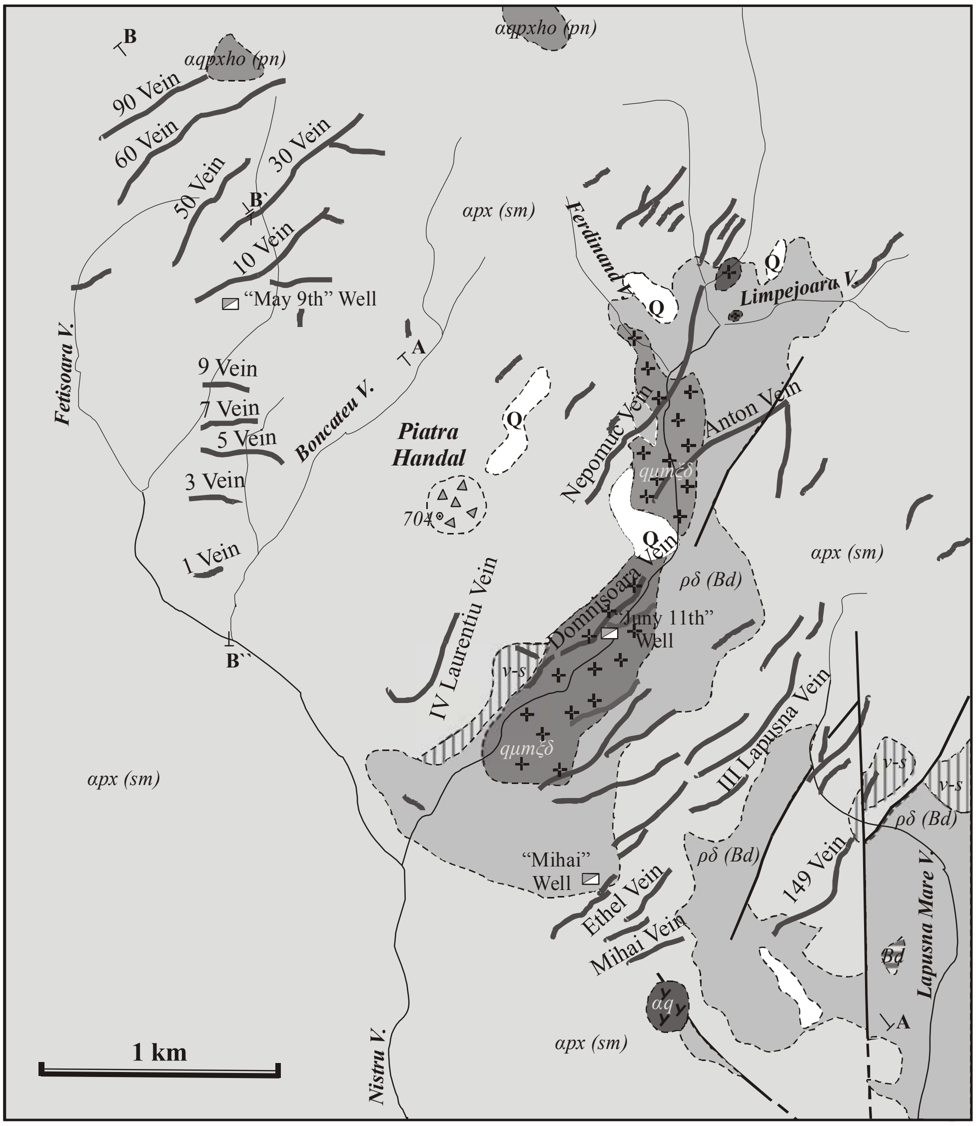


Figure 2. Geological map of the Nistru zone.

Legend

Sedimentary formations

QUATERNARY — alluvia, debris

BADENIAN — Bd — marl, mudstone, sandstone, conglomerate

Magmatic formations

PANNONIAN — αqpxho — quartz andesite

SARMATIAN — αpx — pyroxene andesite

BADENIAN a) ρδ — volcaniclastic rhyodacitic formation

b) v-s — volcano-sedimentary complex

Intrusive rocks

quartz andesite (dyke) *(αq)*

porphyry quartz-micromonzodiorite *(qμmξδ)*

Conventional signes

geological limit

vein

fault

well

The Pannonian quartz andesites appear in the northern part of the area as lava flows, disposed over the Sarmatian pyroxene andesites and in the SE part as an intrusion in the subvolcanic facies, which outcrops in the Galbena Hill, (Fig. 2).

3. THE IGNEOUS INTRUSIVE ROCKS

Geological and metallogenetic studies covering the mineralization in the Nistru area have been conducted by Borcoş et al., (1972b). According to these studies, the metallogenetic activity is controlled by the Piatra Handal volcanic edifice, with the groups of veins located on the north-western, southern and eastern sides of this structure.

Piatra Handal (+704.1 m) has been considered the point of origin for several andesitic intrusions (Borcoş et al., 1972b). Progress in the exploration and mining activity has allowed for an identification of various intrusive bodies, generated later than the Sarmatian andesitic lavas. The ore deposits are grouped around intrusive bodies and tend to become thinner as they advance in depth. By height, mineralization extend over approximately 800 m. Magmatic intrusions are located at about 200 m from the surface.

The igneous intrusive stage has created sequence of magmatic rocks of sub-volcanic character, which are associated in space to volcanic rocks, visibly different through their morphological and structural features, as well as through their petrographical types, (Tab. 1). The intrusive magmatic activity from the Nistru area followed, in succession, the stage of Sarmatian pyroxene andesites. They outcrop on the middle course of Nistru Valley, (Fig. 2) on the influents Ferdinand and Limpejoara, and they were intercepted in the depth of the mining galleries, (Fig. 3 and Fig. 4). The diferentiation processes were more intense than in the case of lava flows and lead to the individualization of a magmatic rocks suite consolidated on a subvolcanic level, sequentially emplaced.

The igneous intrusive rocks occur as irregular stocks, apophyses and dykes; they are represented by porphyry structural varieties and secondary, equigranular textural varieties were identified. They generate thermal metamorphism and hydrothermal alterations in sedimentary rocks and they are affected by extremely significant hydrothermal transformations.

The main intrusion is represented by the porphyry quartz-micromonzodiorites developed in the NE-SE part of the Nistru zone; its apophyses outcrop on the middle course of the Nistru Valley, over a length of about 2.5 km, (Fig. 2, Fig. 5). The general orientation of this intrusion is NNE-SSW. In depth, its maximum development is known down to the +25 m level, between the copper-bearing veins (Nepomuc and

Figure 5. Outcrop of the porphyry quartz-micromonzodiorite on Nistru Valley.

Domnişoara vein) on about 1000 m, and it appears as a stock (Fig. 3). In the north-eastern end, the quartz-micromonzodiorite stock is crossed by dikes of several meters represented by quartz-microdiorites and porphyry quartz-microdiorites. The intrusion in the south-eastern part is followed by an intrusive body of quartz andesites, representing the equivalent in subvolcanic facies of the lavas generated during the Pannonian age, (Fig. 3).

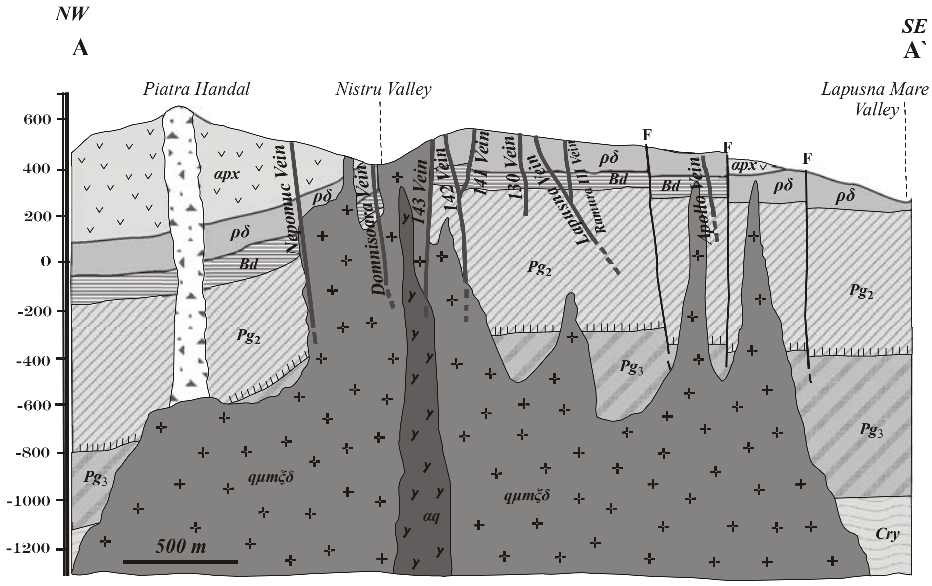
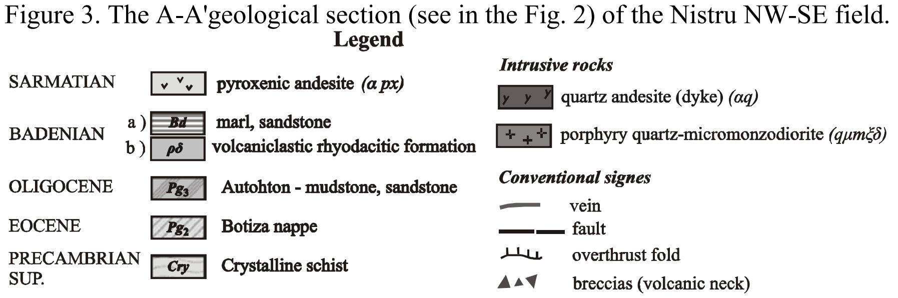


Figure 3. The A-A'geological section (see in the Fig. 2) of the Nistru NW-SE field.



In the north-western part of the Nistru zone, the intrusions are not visible at the surface and have only been found in mining galleries, as apophyses. In terms of composition, they are represented by porphyry quartz-microdiorites and porphyry microdiorites (Fig. 4). The porphyry microgabbro forms a small sill occuring within the porphyry quartz-micromonzodioritic stock. On the sedimentary protolith, the quartz-micromonzodiorite rocks generated the thermal metamorphism effects. The relations between the main types of magmatic rocks emphasize their sequential emplacement, (Damian 2000).

3.1. Mineralogy and petrography

Within the subvolcanic rocks suite from Nistru zone, the main petrographic types (Tab. 1) were identified under microscope and are characterised by the textural varieties, (porphyric and equigranular) with holocrystalline groundmass. The porphyry textural varieties are represented by quartz-microdiorite, and quartz-micromonzodiorite, (Plate I, Fig. a, b). The equigranular texture is identified subordinately in quartz-microdiorite (Plate I, Fig. c). The porphyric varieties with the microcristalline-cryptocrystalline groundmass are representative for microdiorites and quartz andesites in intrusive facies, (Plate I, Fig. e, f).

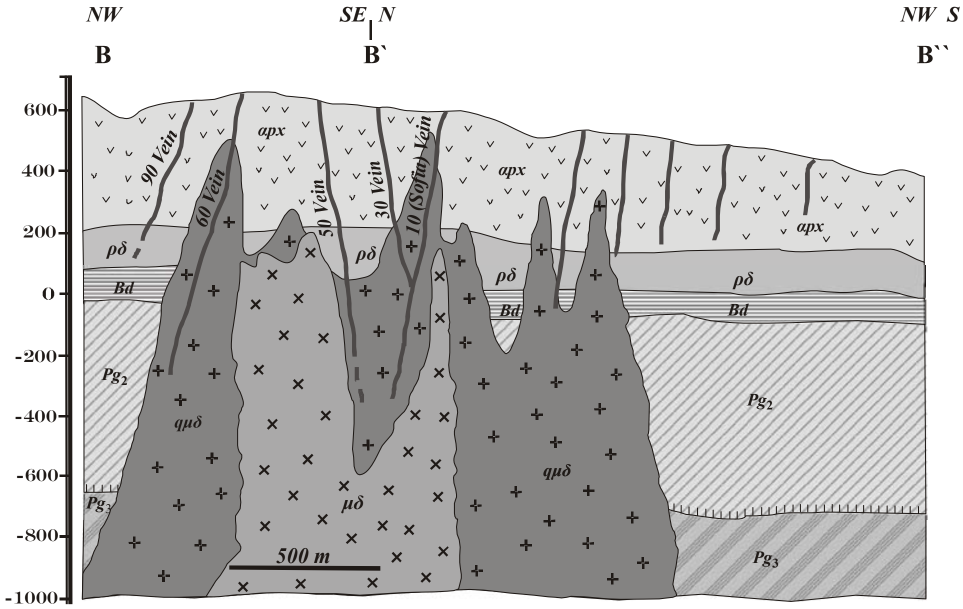
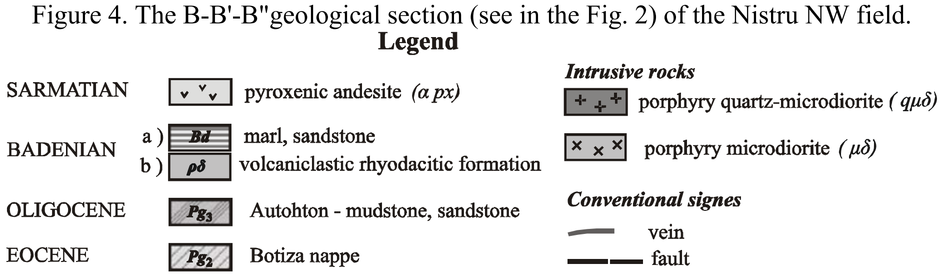


Figure 4. The B-B'-B"geological section (see in the Fig. 2) of the Nistru NW field.



Porphyry quartz-micromonzodiorites

The porphyry texture of quartz-micromonzodiorites resulting from the presence of a first generation of plagioclase feldspars, represented by andesine (An_{48-50}) with polysynthetically Albite, Pericline, and Karlsbad-Albite twinned. The second generation of plagioclase are zoned crystals (with the andesine core and the overgrowths consisting of basic oligoclase, or as crystals associated with K-feldspar. Spectacular myrmekite (antiperthite and perthite) are found around the second generation of plagioclase, (Plate I, Fig. d). The intergrowths of quartz and K-feldspar in quartz micromonzodiorites are of metasomatic origin. The mafic minerals are pyroxenes and amphiboles as phenocrysts, whereas typical accessories include crystals of apatite, rare zircon crystals, and magnetite. The groundmass is holocrystalline, (Plate I, Fig. b) and consists of plagioclase micro-crystals intergrown with quartz and K-feldspar, (Plate I Fig. d).

PLATE I

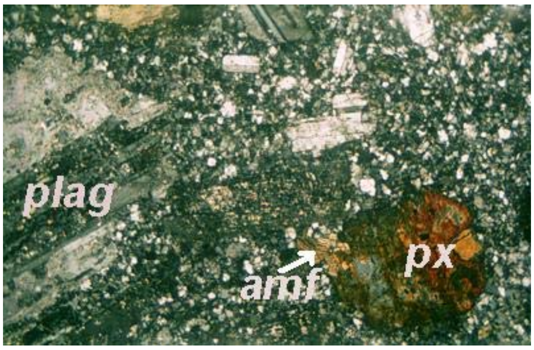


Figure a. Porphyry quartz-microdiorite N+, 66X

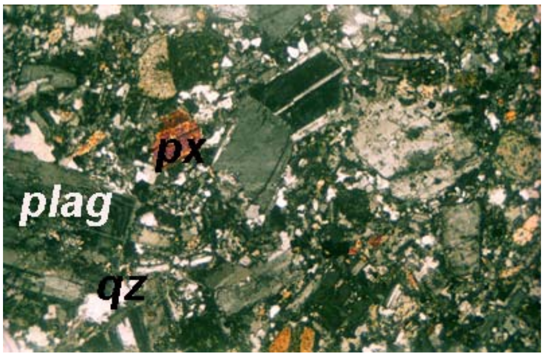


Figure b. Porphyry quartz micromonzodiorite, N+, 33X

Figure c. Echigranular quartz- microdiorite N+, 66X

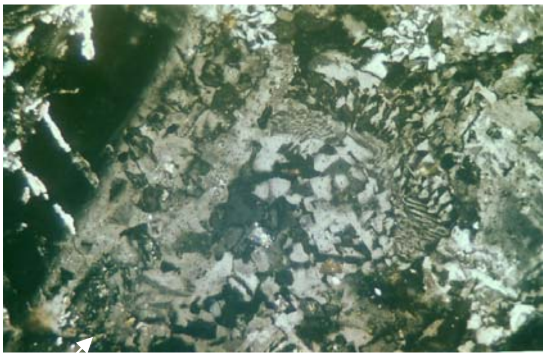


Figure d. Micro-intergrown in quartz-micromonzodiorite, N+, 130X

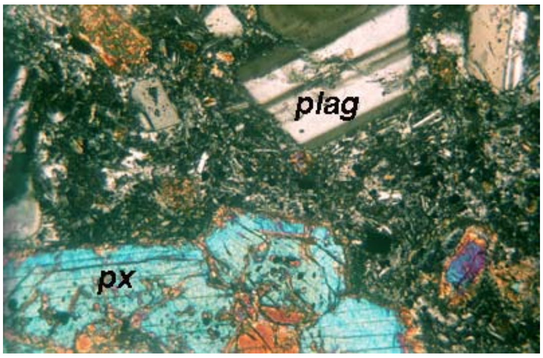


Figure e. Porphyry microdiorite, N+, 66X

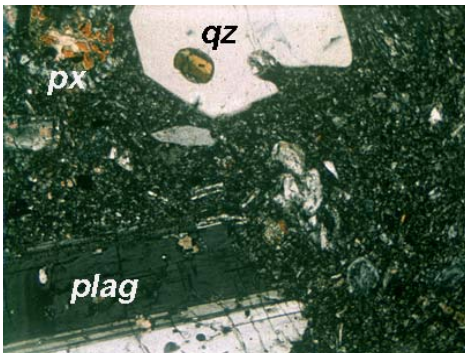


Figure f. Quartz andesite in intrusive facies N+, 66X

(px- pyroxene, plag-plagioclase, amf-amphibole, qz-quartz)

Porphyry quartz-microdiorites

The quartz-microdiorite rocks are represented mainly by the porphyry kind (Plate I, Fig. a) and secondary by the structural variety of equigranular holocrystalline, (Plate I, Fig. c). In the porphyry type the fine-grained aspect of the groundmass is given by euhedral, subhedral, and anhedral micro-crystals of plagioclase feldspars, inter-grown with granular quartz and rare micro-grains of chloritized pyroxenes, (Plate I, Fig. a). As secondary minerals, there are occurrences of anhedral magnetite, subhedral apatite and, less often, granular zirconium.

The equigranular holocrystalline structure results from the uniformity in size of the mineral components (feldspars, plagioclases, pyroxenes, and amphiboles) whose dimensions vary between 0.5-2 mm. (Plate I, Fig. c). The quartz in the groundmass of quartz-microdiorite rocks takes anhedral shapes, surrounded by over-growth areas and will sometimes take a skeletal aspect in the feldspar mass.

Porphyry microdiorites

This petrographic type is characterized by the presence of plagioclase and pyroxene phenocrysts in a groundmass made of plagioclase micro-crystals and microlites slightly oriented on a feldspar micro-crystalline base, largely associated with granular pyroxene micro-crystals forming agglomerates. (Plate I, Fig. e). The anorthite content of the plagioclase feldspars (An_{75}-An_{80} phenocrysts, An_{65} microliths) is reflected in the rocks petrochemical characteristics (SiO_2=54.58; Al_2O_3=18.54; CaO=7.42). The pyroxenes are represented by fresh clinopyroxenes, (clinohypersthene), prismatic euhedral crystals or twinned sections. There are frequent occurrences of intergrowths with orthopyroxenes entirely replaced by actinolite, chlorite and carbonates.

Quartz andesites in intrusive facies

These represent a distinct type of rock within the series of intrusive magmatic rocks whose texture and mineralogical composition reflect the magmatic crystallization at a subvolcanic level. The texture is massive; the microcrystalline groundmass is made of subhedral plagioclases, granular quartz, mafic and oxide minerals. The porphyry stage is represented by plagioclase feldspars, pyroxenes and amphiboles, (Plate I, Fig. f). The quartz, which is an essential component of these rocks, is strongly corroded, cracked, with sizes up to 6 mm. The plagioclase displays twinned crystals specific to Albite and Karlsbad - Albite. Their composition varies from An_{53} to An_{40}. The pyroxenes are represented by orthopyroxenes and clinopyroxenes in the shape of euhedral and subhedral crystals. At their ends they appear slightly opaque or are entirely replaced by chlorite and carbonates. The amphiboles are strongly pleochroic and they are represented by green hornblende. As accessory minerals, there are occurrences of zirconium and apatite, subordinated in the groundmass.

Porphyry microgabbro

The porphyry stage, represented by plagioclase feldspars and pyroxenes, covers a much less proportion than the groundmass. The anorthite content of the plagioclase varies between 53 and 83%, in phenocrysts and between 48 and 60% for the microlites in the groundmass. The clinopyroxenes in the shape of phenocrysts have a size of up to 1.5 mm, and in the shape of grains with sizes of up to 0.10 mm they are abundant in the groundmass. Orthopyroxenes occur in small amounts and only in the groundmass. The rock's groundmass has a high degree of crystallinity, resulting from the presence of plagioclase micro-crystals associated to pyroxene micro-grains and very small amounts of quartz (a percentage of 1.3%). These components are associated to opaque minerals represented by magnetite and ilmenite with granular shapes and a size below 0.05 mm.

3.2. The geochemistry of the intrusive magmatic rocks

3.2.1. Major elements and classification

Chemical analyses of major and trace elements have been made on the fresh samples of the petrographic types separated by microscopically analyses, (Plate I Fig. a-f). The chemical composition of the major petrographic type separated in the subvolcanic suite from Nistru zone is presented in table 1. For all the intrusive rock types, the variation limits for SiO_2 are quite large, between 50.48-63.69%. Within these rocks, quartz andesites are being emphasized with high values for SiO_2>60% and porphyry microgabbro with SiO_2 values of 50.48%. With a relatively high frequency, the porphyry quartz-micromonzodioritic rocks with a large variation of the SiO_2 content 54-59% are being distinguished. The porphyry quartz-microdiorites have content in SiO_2 of about 55-56% and the contents below this value, of approximately 51-54% represent the porphyry microdiorites rocks.

The Al_2O_3 content presents a restrained variation domain, between 16-18.5% with a maximum frequency for Al_2O_3 = 17.56%, which would be representative for the porphyry quartz-microdioritic and porphyry quartz-micromonzodioritic groups. In quartz andesites, the contents in Al_2O_3 have lower values 15-16.5%. Values of the Al_2O_3>20% characterize porphyry microgabbro and porphyry microdiorites. The contents in Fe_2O_3 and FeO vary from 5 to 10% with a maximum frequency of the value of 3.77%. The lowest contents correspond to the quartz andesites (5-6.5%), and the maximum to the porphyry microdiorites, microgabbro and partially porphyry quartz-micromonzodiorites. The MgO contents do not present important variations for the studied rock types, a maximum frequency of the 3.55% and 4.62% values being remarked. The low contents between 1.5-2.6% correspond to the quartz andesites. The CaO contents differentiate the types of magmatic rocks, separated mineralogically-petrographically. Thus, the highest contents in CaO = 6.56-7.42% are characteristic for the microgabbro and porphyry microdiorites.

The quartz andesites have CaO contents which vary within closer limits 4-5.5%, and in the case of porphyry quartz-micromonzodiorites and quartz-microdiorites the CaO content is between 3.7-5.7%. The restrained variation interval of the Na_2O with a maximum of frequency content between 2.32-2.61 characterizes the intrusive magmatic rocks suite. The K_2O content differentiates each petrographic type. The lowest values for K_2O correspond to the porphyry microgabbro and porphyry microdiorites, 0.82% and 1.37%. The relatively low contents in K_2O between 1.3-2.4% separate the quartz andesites group from the porphyry quartz-microdiorite group.

In contrast to these, the maximum value frequency from 2.48% corresponds to the porphyry quartz-micromonzodiorites. The MnO contents have in general low values; the highest frequency is specific for the values of 0.21%. For higher contents, a much lower frequency is being remarked and it would be representative for the porphyry microgabbro types.

Table 1. Major element data for intrusive magmatic rocks from Nistru zone (wt. %).

No. sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	CO_2	S	SO_3	H_2O^+	H_2O^-	petrographic type
264	59.42	18.0	2.89	3.74	0.12	2.74	3.71	2.80	2.37	0.75	0.15	0.26	0.16	0	2.02	0.38	1
323	57.37	16.28	1.78	5.97	0.14	3.80	4.27	1.75	2.12	0.75	0.13	0.66	0.14	0	4.16	0.36	1
585	55.50	16.67	3.87	3.74	0.20	3.25	5.32	2.33	2.65	0.75	0.11	0.74	0.79	0	3.36	0.56	1
686	59.46	18.92	2.70	5.32	0.21	2.84	2.73	2.50	2.50	0.75	0.14	0.32	0.14	0	2.74	0.40	1
793	58.79	16.55	3.61	4.10	0.14	3.40	5.69	2.92	2.10	0.52	0.13	0.57	00.5	0.03	0.94	0.42	1
823	53.96	16.45	5.23	5.81	0.51	3.77	4.19	2.92	1.92	0.69	0.11	1.16	0.15	0	2.30	0.47	1
552	55.62	16.87	3.86	2.63	0.11	3.86	4.57	3.25	2.20	0.79	0.14	1.22	1.35	0.03	3.13	0.80	1
344	56.70	17.60	4.56	2.95	0.14	4.00	6.56	3.20	1.37	0.70	0.14	0.50	0.41	0	0.60	0.24	2
324	50.48	20.66	3.65	5.90	0.40	3.22	7.42	2.50	0.80	0.75	0.15	0.74	0.16	0	2.44	0.26	3
165	54.58	18.54	4.00	3.81	0.16	4.90	7.42	2.32	1.02	0.82	0.11	0.57	0.16	0	1.15	0.18	4
180	51.18	21.52	4.62	3.60	0.22	2.46	7.14	2.12	1.42	0.67	0.15	1.01	0.40	0	2.87	0.32	4
130	55.35	16.79	4.22	4.23	0.18	4.87	5.96	2.27	2.82	0.42	0.11	0.66	0.08	0	1.60	0.24	4
222	54.19	16.19	3.63	4.85	0.19	5.14	6.93	2.40	2.32	0.46	0.13	1.14	0.01	0	2.02	0.18	4
1064	55.78	16.42	2.68	4.73	0.16	4.50	6.83	1.97	2.09	0.73	0.12	0.82	0.45	-	2.26	0.61	4
616	53.14	15.40	5.33	3.31	0.12	7.58	6.13	2.22	1.07	0.70	0.14	0.72	0.30	0	3.24	0.36	4
685	55.88	17.10	2.43	5.04	0.13	5.30	5.32	1.82	2.00	0.82	0.15	0.62	0.20	0	3.32	0.42	5
357	55.59	17.14	3.43	4.69	0.22	4.38	4.68	3.40	2.06	0.88	0.13	0.56	0.45	0	2.71	0.52	5
597	58.95	16.41	2.72	3.38	0.12	3.66	4.30	2.31	3.67	0.77	0.12	0.84	0.47	0.01	2.30	0.25	5
363	62.26	15.02	3.32	2.95	0.10	1.92	3.99	3.12	2.00	0.80	0.11	0.30	0.30	0	2.28	0.38	6
554	63.69	15.28	2.79	2.95	0.05	1.40	4.27	2.80	1.30	0.75	0.12	0.40	0.82	0	2.74	0.40	6
555	61.90	15.48	3.61	1.44	0.06	2.58	4.92	3.07	2.05	0.70	0.11	0.36	1.49	0	2.38	0.46	6
556	60.13	16.44	3.50	3.02	0.10	1.92	5.53	2.50	1.25	0.75	0.12	0.76	0.40	0	2.80	0.58	6

1 - porphyry quartz-micromonzodiorite, 2 - quartz-microdiorite equigranular, 3 - porphyry microgabbro, 4 - porphyry microdiorite, 5 - porphyry quartz-microdiorite, 6 - quartz andesite (dyke)

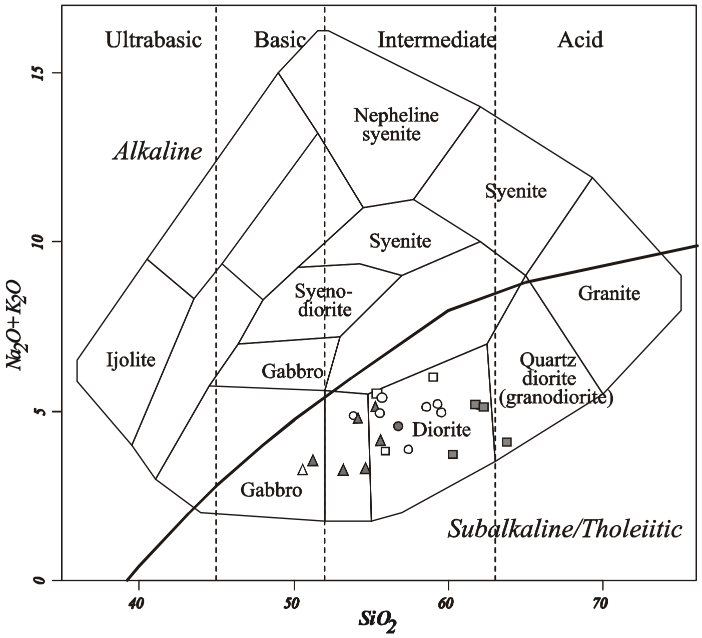


Figure 6. The Na_2O+K_2O-SiO_2 TAS diagram, (Cox et al., 1979).

Legend

- ○ q-micromonzodiorite
- ● q-microdiorite echigranular
- △ porphyry-microgabbro
- ▲ porphyry-microdiorite
- □ porphyry q-microdiorite
- ■ quartz-andesite

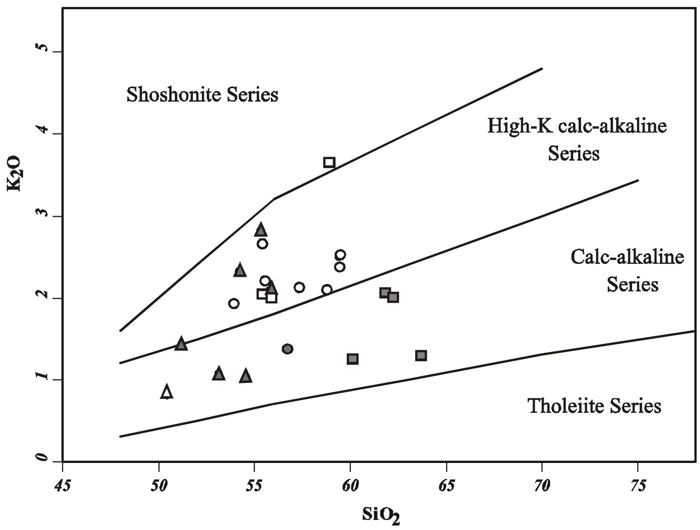


Figure 7. The K_2O-SiO_2 diagram, (Peccerillo-Taylor 1976). (See Legend Fig. 6).

The TiO_2 content has homogenous and sub-unitary values with a maximum frequency for the 0.765 content. In the case of P_2O_5, a variation of the contents between 0.1-0.2 percent is being remarked with a maximum of frequency for the 0.15% value. For the sulphur, the 0.27% value corresponds to the maximum frequency, and with a low frequency the values are slightly higher due to a beginning propylitisation. The presence of CO_2 is being remarked through quite restrained variations domains for sub-unitary values.

The petrographic types of rocks are differentiating by disposal in the non-alkaline domain, in the TAS diagram, (Fig. 6), (Cox et al., 1979). The samples are arranged in the diorite field at the limit with gabbro field and with the quartz-diorite field. The chemical character of magma which has generated the intrusive magmatic rocks from Nistru zone is predominant calc-alkaline with tendency high-K calc-alkaline, in the SiO_2-K_2O plot, (Peccerillo & Taylor 1976), (Fig. 7). The samples which are disposed in the high-K calc-alkaline field are represented by quartz-micromonzodiorite and subordinately by microdiorite type from the NE-SE part of the Nistru zone.

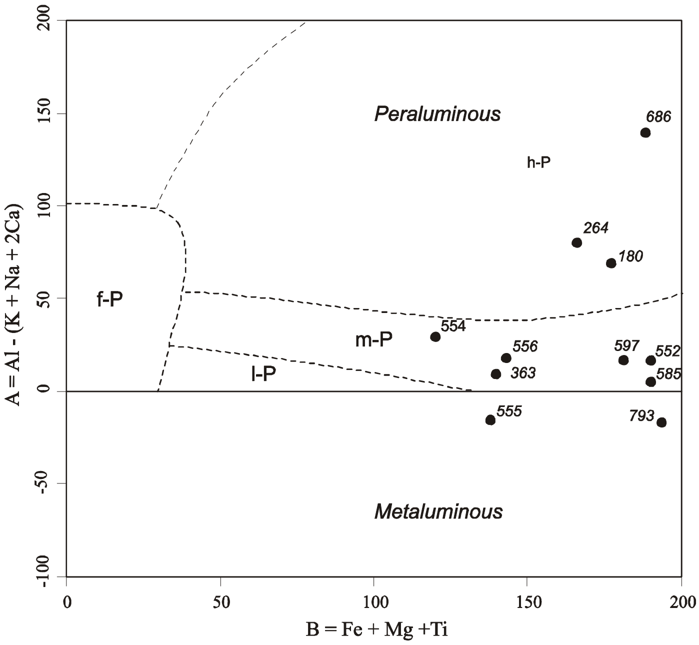


Figure 8. The diagram A=Al-(K+Na+2 Ca)-B=Fe+Mg+Ti (Villaseca et al., 1998).

The metaluminous with tendency to peraluminous character of the studied intrusive rocks is shown in the A = Al - (K + Na + 2 Ca) - B = Fe + Mg + Ti diagram, (Fig. 8), (Villaseca et al., 1998). The following fields are defined: l-P low peraluminous, m-P moderately peraluminous, h-P highly peraluminous, f-P felsic peraluminous, metaluminous.

3.2.2. Trace elements and petrogenetic processes

The geochemical spectrum of trace and rare elements characteristic to the Nistru subvolcanic zone is particularly significant for the processes specific to the evolution of the magmas that generated these subvolcanic rocks, (Hall 1996). The content of the trace and rare earth elements of the intrusive rocks in Nistru zone is shown in table 2.

The behaviour of the immobile trace elements (Rollinson, 1993) and that of the rare earth elements can offer us data regarding the petrogenetical processes specific to the rock groups. The geochemical spectrum characteristic for the Nistru zone presents high contents for K_2O, Rb, Ba, Th, Nb, Ce and values<1 for Ti, Tb, Lu, Tm, Ho.

The incompatible elements in the representative samples for the intrusive magmatic rocks from Nistru zone are normalized to primitive mantle (after Sun & McDonough, 1989), (Fig. 9). The large ionic lithofile elements (LILE=K, Rb, Cs) and light rare earth element (LREE) are enriched. The heavy rare earth element (HREE) and Y have a flat profile, show abundances similar to those for N-MORB, (Price et al., 1990). The low mobility of high-field-strength elements (HFSE) and the flat profiles of HREE in the MORB normalized diagram are significant for the magmas derived from a shallow mantle source, (Handley et al., 2007). The abundance of large ion lithophile (LIL) elements reflecting enrichment in the mantle wedge source and the melts derived from this mantle inherit that enrichment.

The abundance in high-field-strength (HFS) elements is lower in calc-alkaline magma. The concentrations of HFS elements are not affected by processes that cause mantle heterogeneity, (McCullough & Gamble 1991). The tendency of the Rb enrichment (Harangi et al., 1995) and variable depletion of Nb, (Seghedi et al., 2004) are characteristics of the rocks generated in the subduction conditions. The low grade of Sr might be explained through a reduced involvement of the oceanic crust in the melting of the subducted plate. The high ratio Rb/Sr=0.3 can be explained through processes of crustal contamination. Also, the high value of the Rb/Sr ratio could be due to the processes of fractioned crystallization in the course of evolution of the magma that generated these rocks.

Table 2 Trace and rare earth elements data of the intrusive rocks in Nistru zone.

Element	Sample									
	1076	**264**	**1064**	**357**	**1060**	**554**	**616**	**585**	**1073**	**556**
Ti	0.90	0.84	0.82	0.91	0.92	0.47	0.82	0.72	0.83	0.67
Rb	146.74	114.67	68.34	55.94	94.10	46.53	44.72	45.93	70.83	63.32
Sr	249.94	261.67	275.31	216.25	216.88	326.59	233.10	237.61	241.64	217.26
Y	33.61	27.31	23.99	29.15	27.75	17.84	28.67	30.86	26.71	16.55
Zr	186.42	182.38	128.71	146.47	132.88	106.10	152.99	178.26	145.45	117.76
Nb	17.97	182.38	9.28	9.98	11.30	9.05	9.51	10.83	9.42	10.36
Cs	3.90	8.70	7.61	15.97	27.01	2.01	3.81	8.79	11.27	9.53
Ba	251.10	304.36	598.02	235.43	542.46	311.63	280.57	539.15	644.97	440.56
La	24.04	16.87	15.33	16.05	16.98	20.60	16.18	24.94	16.87	17.28
Ce	50.36	35.45	33.00	34.71	37.34	37.17	35.51	47.65	35.20	32.62
Pr	6.22	4.17	4.14	4.46	4.88	4.13	4.55	5.93	4.70	3.78
Nd	25.72	17.02	17.47	18.91	20.80	15.22	18.34	25.08	18.91	13.91
Eu	1.25	0.88	0.86	1.07	1.15	0.77	0.98	1.03	0.99	0.77
Sm	5.26	3.67	3.73	4.38	4.49	2.78	4.12	5.05	4.20	2.73
Gd	5.69	4.02	3.86	4.60	4.78	2.81	4.27	5.18	4.49	2.83
Tb	0.87	0.63	0.59	0.73	0.74	0.41	0.75	0.88	0.75	0.44
Dy	5.71	4.47	4.11	5.18	5.03	2.86	4.65	5.51	4.64	2.82
Ho	1.11	0.85	0.79	0.96	0.94	0.57	0.92	1.13	0.97	0.57
Er	3.28	2.67	2.42	3.08	2.87	1.89	2.94	3.22	2.86	1.82
Tm	0.44	0.31	0.28	0.38	0.37	0.24	0.38	0.47	0.42	0.26
Yb	3.12	2.54	2.31	2.83	2.74	1.99	2.68	2.98	2.74	1.79
Lu	0.42	0.35	0.30	0.40	0.39	0.28	0.39	0.45	0.41	0.29
Hf	5.31	5.23	3.53	4.63	3.97	3.23	4.60	5.25	4.40	3.25
Ta	1.05	0.58	0.84	0.56	0.87	0.71	0.56	0.75	0.87	0.69
Th	5.96	6.83	4.28	4.90	4.38	7.88	5.40	8.66	5.31	6.99
U	1.68	2.88	1.30	1.65	1.28	2.34	1.70	2.10	1.75	2.18

Analysed at the Schenectady Geological Department, USA, dr. Marian Lupulescu

The enrichment in Th of the magma generated in the subduction processes, (Brown et al., 1984) can be realized through fractional assimilation-crystallization processes or through source variation processes. The variation of Nb involves various degrees of fractioned crystallization. The low contents of Nb, P, and Ti are related, according to Thompson (1984), to their being retained in the residues formed after the subducted crust became dehydrated and the mantle wedge above the subduction zone. Also the depletion in Ti is typical of subduction related magmas, (Harangi et al., 1995).

The negative anomaly of Nb and Ti are specific to the crustal contamination, (Rollinson 1993), and break-up in the early stages of the Fe-Ti oxides in calc-alkaline magmas, and reflect contamination of calc-alkaline magma by the continental crust depleted in Nb and in HFS elements (Ta, Ti), (Verma, 2001).

An enrichment of the rocks in the complete line of the elements from Ba to Sm is being remarked, comparative with N-MORB (Sun &McDonough, 1989), (Fig. 10) and also depletion in the Ti→Yb elements. Enrichment of light rare earth elements (LREE: La, Ce, Nd, Sm) and large ion lithophile elements (LILE: Cs, Rb, K, Ba) and the low ratio of HFSE (Sc, Y, Nb, Ta, Hf, Zr, U Th and La, Lu)/LILE are significant for the main processes which control the variation in the parental magma generated in the subductions.

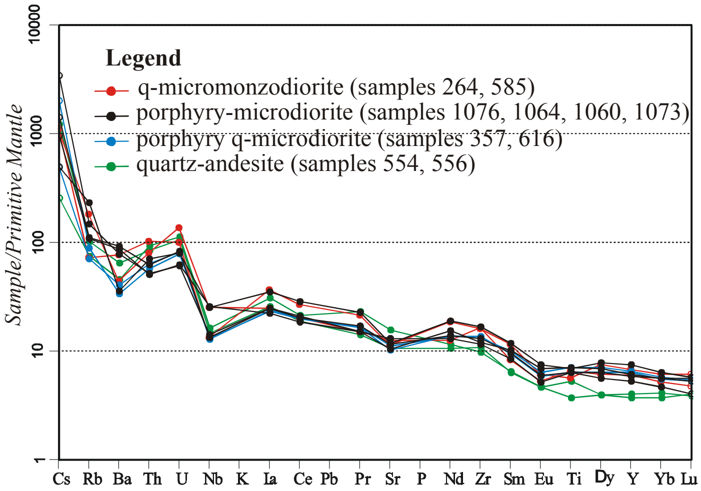


Figure 9. Primitive mantle normalized trace element variation diagram, (Sun &McDonough, 1989).

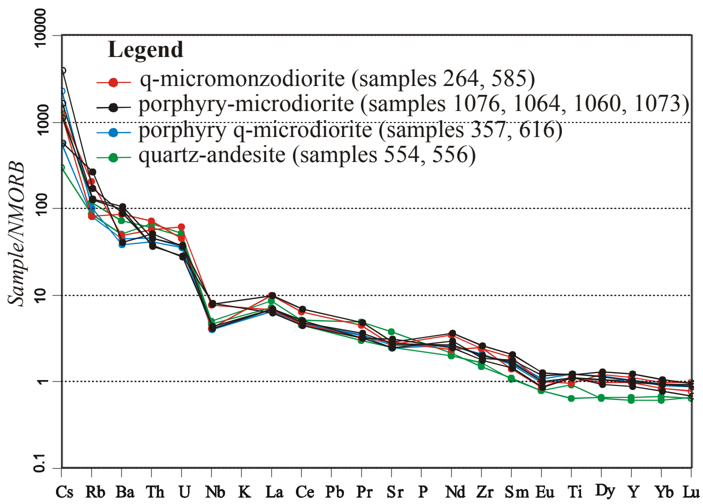


Figure 10. N-MORB normalized of the incompatible trace elements (Sun &McDonough, 1989).

The enrichment in LILE can be „inherited" from the subducted sediments, (Wilson 1989). Enrichment in the large ions lithophile elements (LILE) is related with metasomatized mantle wedge by the fluids released from the oceanic crust and subducted sediments, (Pearce 1983, Miskovic & Francis 2006). The crustal contamination could be due to addition of subducted sediments to the mantle and to assimilation of crustal material during ascent of mantle-derived magma, (Harangi, 2007).

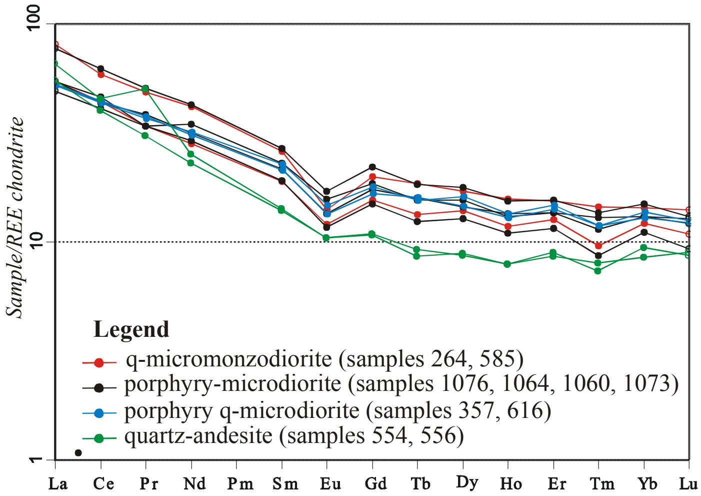


Figure 11. Chondrite normalized rare earth elements diagram, (Boynton, 1984).

The local enrichment in LREE (Fig. 11), of the upper mantle and the partial melting is characteristic for ascending mantle wedge above the subducting plate, (Sakuyama, 1983). The fluids resulting from the dehydration of the material in the subducted plate will react with that part of the mantle that is located above the subducted metasomatized plate. This creates favourable conditions for the melting of the material in the surrounding mantle and this material will participate as a source in creating magma. The HREE (heavy rare earth elements) remain relatively immobile in the chondrite normalized diagram, during slab dehydration (Tatsumi et al., 1986).

The Eu negative anomaly in chondrite normalized rare earth element, (Boynton, 1984), (Fig. 11) suggests the implication of the plagioclase fractional crystallization or the partial melting processes during the magma evolution en route to surface from the subvolcanic magma chamber, (Campbell et al., 1982, Rollison, 1993). The magnitude of this anomaly is inversely correlated with the oxidation fugacity, (McKay, 1989).

4. THE TECTONIC SETTING OF THE SUBVOLCANIC MAGMATIC ROCKS IN NISTRU ZONE

The tectonic setting specific to the formation of rocks in the subvolcanic part of Nistru zone has been outlined based on diagrams of the major elements variation, (Batchelor & Bowden, 1985), (Fig. 12), and of the minor chemical components variation, (Schandl & Gorton, 2002), (Fig. 13), (Pearce, 1984), (Fig. 14, and Fig. 15).

The tectonic discrimination diagram, which uses the major elements according with Batchelor & Bowden (1985), (Fig. 12) and suggests that the intrusive magmatic rocks from Nistru area can be generated in syn - collision tectonic setting.

The four diagrams suite for geotectonic environment discrimination of felsic volcanic rocks, proposed by Schandl & Gorton (2002) is based on a combination of four immobile trace elements (Ta, Yb, Th, and Hf), (Fig. 13). In Ta/Yb versus Th/Yb diagram, the Nistru rocks belong to the Active Continental Margins (ACM) at the Within-Plate Volcanic Zones (WPVZ) limit. Data of Ta vs. Th diagram show the tendency of Th enrichment with respect to Ta, of the studied rocks.

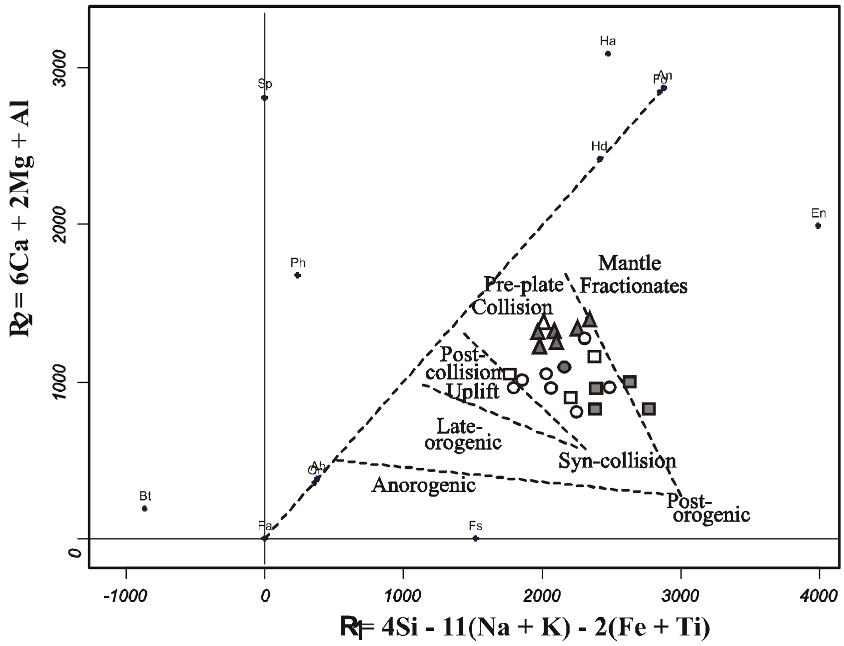


Figure 12. The geotectonic discrimination diagram based on major elements; R1=4Si-11(Na+K)-2(Fe+Ti) - R2 = 6Ca + 2Mg + Al, (Batchelor and Bowden 1985).

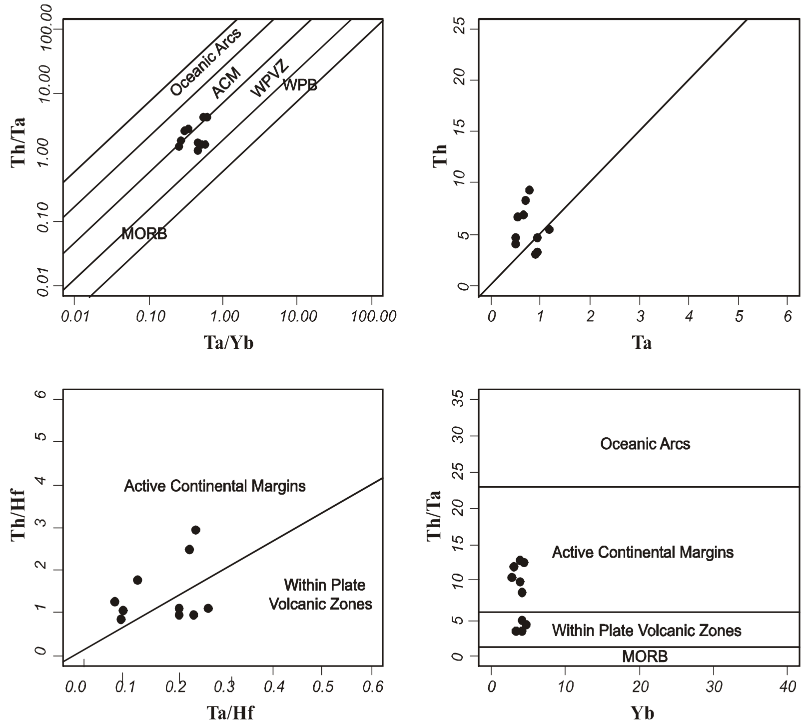


Figure 13. Diagrams for geotectonic environment discrimination based of immobile trace elements (Schandl & Gorton 2002).

This shows the influence of the rich in Th fluids in the subduction zone. The diagram of Ta/Hf vs Th/Hf ratios and Yb vs. Th/Ta shows the similar incompatibility between Th and Ta in two different tectonic environments: Active Continental Margins and Within-Plate Volcanic Zones. In these diagrams the Nistru intrusive rocks are predominantly related with the Active Continental Margins.

The trace analyses for Nb, Rb, Y, Ta for the Nistru subvolcanic bodies in the Rb-Y+Nb (Fig. 14); Rb-Yb+Ta (Fig. 15) diagrams, are grouped in the fields of volcanic arc granites syn-colisionale, (VAG) (Pearce et al., 1984).

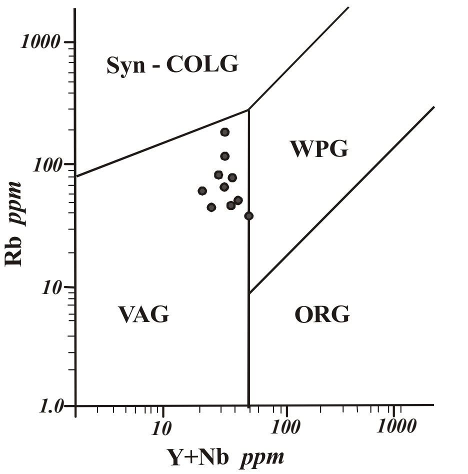


Fig. 14 Rb-Yb+Ta (after Pearce 1984. *(VAG)-volcanic arc granites, (Syn-COLG-syn-collisional granites (WPG)-within-plate granites, (ORG)-ocean-ridge granites*

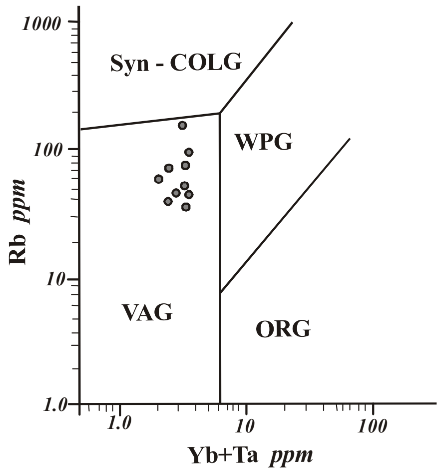


Fig. 15 Rb-Y+Nb (after Pearce 1984). *(VAG)-volcanic arc granites, (Syn-COLG-syn-collisional granites (WPG)-within-plate granites, (ORG)-ocean-ridge granites*

5. CONCLUSIONS

The manifestation mode of the magmatism, in a first explosive-effusive phase, has determined the forming of the volcanic structure, as a consequence of lava emission at surface. The subsequent intrusive magmatic activity has generated the magmatic rocks suite, consolidated at subvolcanic level. The subvolcanic magmatic bodies from Nistru zone, follow in succession the Sarmatian pyroxene andesites phase. The intense erosion of the volcanic structure emphasized the subvolcanic rocks consolidation level on the Nistru Valley and on their influents. They appear as small stocks, apophyses, dykes, sills. The first sequences of intrusive magmatic rocks form stocks of small sizes with irregular forms, represented by porphyric facies of quartz-microdiorites with lateral crossing to andesitic facies and by porphyry quartz-micromonzodiorites. The subvolcanic rocks suite in Nistru zone is the result of some specific placement mechanisms in the upper crustal magma chamber of a mixture between crustal and mantle derived magmas.

The relationships between the main intrusive rocks types emphasize their placement in a sequential place. In Nistru zone, the magmatic intrusive activity has evolved in two distinct magmatic chambers with particular evolutions: one in the NW part, of dioritic composition and one in the NE-SE of monzodioritic composition.

Between these two main stocks, the silicified breccia with pellicular film of hematite is developing, which would represent a specific neck for the prominence in Piatra Handal Hill, (Damian 1998). The porphyry textures with holocrystalline groundmass are predominant in the subvolcanic rocks suite. The fine holocrystalline or cryptocrystalline texture is specific outside the main stock. In a smaller amount, there are also occurrences of equigranular quartz-microdiorite rocks. The subvolcanic magmatic rocks from the Nistru area maintain the characteristics of the magma derived from the final melting of the upper mantle and of ascending mantle wedge above the dehydrating subducting slab, (Sakuyama 1983). In the N-MORB normalized trace elements patterns (Sun & McDonough, 1989) the enrichment of more mobile LIL elements (Cs, Sr, K, Rb, Ba) and LREE, and moderately immobile incompatible elements (HFS elements: Sc, Y, Th, Zr, Hf, Ti, Nb, P and HREE) has been observed, (Pearce 1983). The high to moderate mobile elements are relatively enriched in N-MORB. The LIL elements abundance and low HFSE/LILE ratio in the studied rocks are related with the normal calc-alkaline continental arc, (Brown et al., 1984). Enrichment of LILE and LREE can be attributed to the altered oceanic crust or sediment or both, (Handley et al., 2007). The heavy rare earth element (HREE) and Y are flat profiles, in the multi-element diagrams, (Sun & McDonough 1989, Thompson et al., 1982, Boynton, 1984) suggest that garnet is not an important residual mineral in the source region and that the magmas are derived largely from a shallow mantle source, above the garnet-spinel transition for wet peridotite, (Handley et al., 2007).

The geochemical composition of the magma, in its evolution in the two magma chambers, distinct at a subvolcanic level, has been significantly influenced by the crustal assimilation and fractioned crystallization. The effects of crustal assimilation and fractional crystallization are clearly visible in the low grade of Nb, the enrichment in Th and the high value of the Rb/Sr = 0.3 ratio. The high content of light rare earth elements (La, Ce, Nd, Pr, Ne, Sm) and of the large ion lithofile elements (Rb, Ba, Cs) is associated with Eu negative anomaly and with the low content of the high field strength elements (Ti, Y, Sc, Hf, Zr, U, Th, Ta, Nb), can be an indicator of the continental crustal contamination of magma, (Rollinson 1993).

The crustal contamination of the magma is also proven by the presence of Bi minerals in the whole of the mineralization (copper-gold mineralizations + bismuth sulphosalts) located inside the porphyry quartz-micromonzodiorite stock, (Damian, 1999).

The tectonic discrimination diagram, which uses the major elements according with Batchelor & Bowden (1985), suggests that the subvolcanic magmatic rocks suite from Nistru is related with the syn-collision processes. The magmatic intrusions have been accompanied by important metasomatic transformations, which include compositional changes and pervasive alterations, which have affected the adjacent sedimentary rocks and the intrusive eruptive ones. The thermal metamorphism is restrictive just in the zones adjacent to the intrusions, generated on sedimentary protolith. Post-magmatic fluids generate various types of hydrothermal alterations, (Damian 2003) whose composition, intensity and overlapping reflect the role of the intrusive magmatic phase (magma composition) and that of the lithological and structural control.

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