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Geochemistry of orthogneisses from the northern part of the Central Rhodope, Bulgaria

Zlatka Cherneva[1], Elena Stancheva[2], Lilan-Anna Daieva[2], Emilia Voynova[3]

[1] *Sofia University "St. Kliment Ohridski", 1504 Sofia; cherneva@gea.uni-sofia.bg*
[2] *Geological Institute, Bulgarian Academy of Sciences, 1113 София*
[3] *Research Institute "Geology and Geophysics" Corporation, 1505 Sofia*

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З. Чернева, Е. Станчева, Л.-А Даиева, Е. Войнова – Геохимия ортогнейсов в северной части Центральных Родоп. Позднеюрские магматические протолиты двуслюдяных и лептитовидных гнейсов Центральнородопской Асеницской единицы соответствуют такой последовательности составов, которая начинается метаалюминиевым гранодиоритом и кончается широко распространенным пералюминиевым лейкогранитом. Распределение главных элементов и элементов-следов в магматических протолитах сохранено в значительной степени несмотря на наложенный метаморфизм амфиболитовой фации. Систематические геохимические изменения соответствуют тренду магмического фракционирования. Самым ярким доказательством этого являются: увеличение отношения Rb/Sr с 0.1 до 22, уменешение значения Eu/Eu* с 0.8 до 1.0 и уменьшение Zr/Hf отношения с 40 до 11 от менее кислых к самым кислым ортогнейсам. Вся ортогнейсовая серия отличается высокими значениями отношения LILE/HFSE, которые подтверждют преимуществено коровый магматический источник пород.

Abstract. The late Jurassic igneous protoliths of the two-mica and leptitoid gneisses in the Central Rhodope Asenitsa unit correspond to a range of metaluminous granodiorite to wide-spread peraluminous leucogranite compositions. Despite the amphibolite facies metamorphic overprint, the major and trace elements distribution of the igneous protoliths are preserved to a significant extent. Systematic geochemical variations display magma fractionation trends The most indicative of the latter are increasing Rb/Sr ratios from 0.1 to 22, decreasing Eu/Eu* values from 0.8 to 0.1, and decreasing Zr/Hf ratios from 40 to 11 towards the most felsic orthogneisses. The whole orthogneiss suite is distinguished by high LILE/HFSE ratios that support crustal dominated and evolved magma source.

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Key words: felsic orthogneiss, geochemistry, magma fractionation, Central Rhodope, Bulgaria.

Introduction

The orthometamorphic rocks geochemistry is important for better understanding the protoliths origin and the premetamorphic geodynamic settings. Metamorphozed igneous rocks are common in the Rhodope massif. Recent geological mapping (Sarov et al., 2006) has outlined an orthogneiss sub-unit within the framework of the Asenitsa unit (Ivanov, 1988) in the northern part of the Central Rhodope (Fig. 1). A new isotope U-Pb zircon study has proved the igneous origin and ascertained late Jurassic protoliths age (150 Ma) of the orthogneisses and late Paleocene metamorphism at 56 Ma (von Quadt et

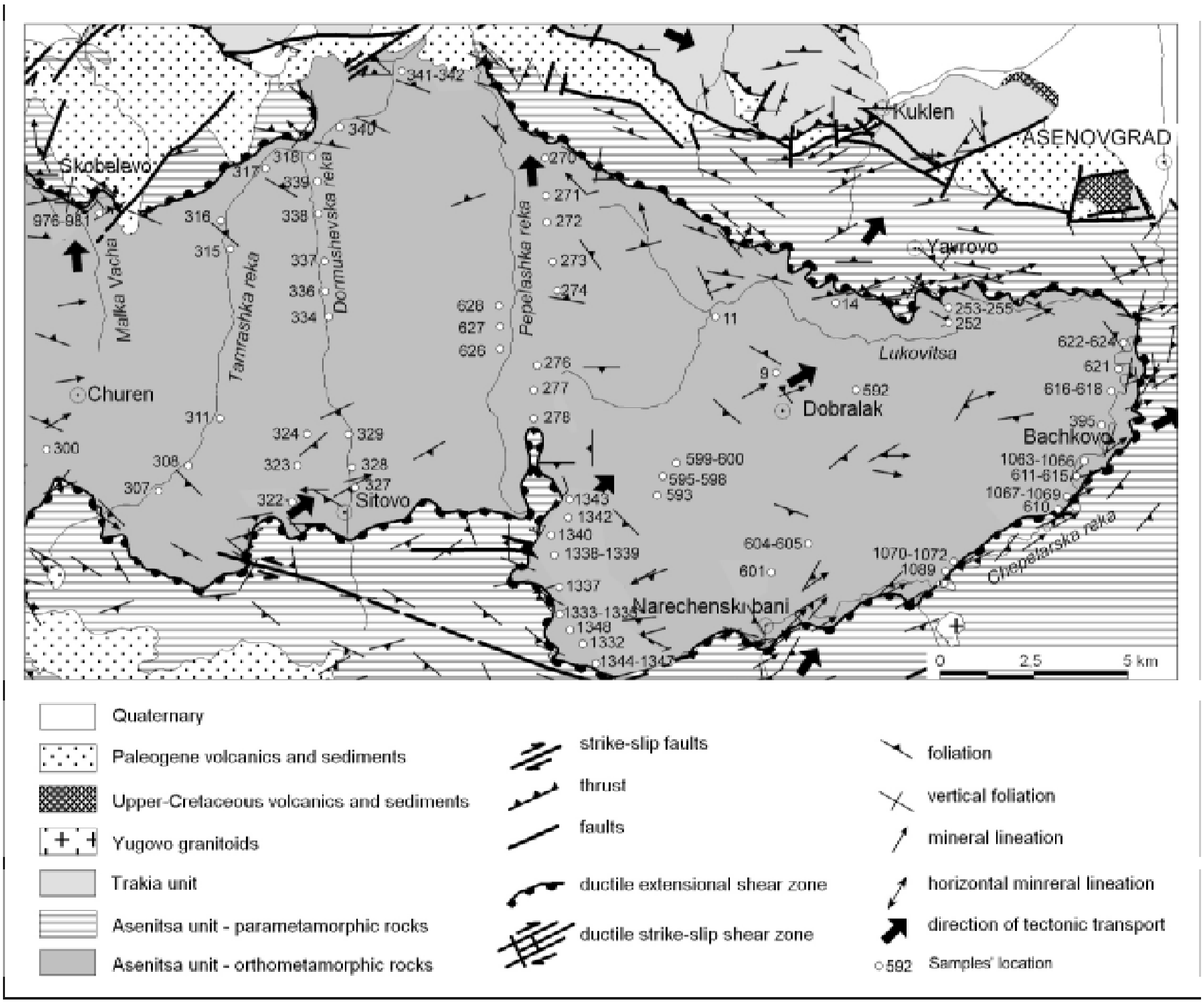

Fig. 1. Simplified geological map of the Asenitsa unit (Naydenov et al., 2006) with points of samples locations

al., 2006). We present whole rock geochemistry data on the same orthogneiss sub-unit that support the igneous protoliths origin and enable further geodynamic interpretations.

The Asenitsa tectonic unit (Ivanov, 1988; Burg et al., 1990) is the uppermost thrust sheet of the Central Rhodopian Dome (a metamorphic core complex in the Central Rhodope, Ivanov et al., 2000). The regional metamorphic peak in the Asenitsa unit is 550°C / 1.3 GPa as estimated in pelitic schists of the parametamorphic part of the unit in the area of Biala Cherkva resort (Guiraud et al., 1992). The orthogneiss sub-unit is dominated by two-mica and leptitoid (leptite-like) gneisses known as Dobralak and Bachkovo formations (Ivanov et al., 1984) or Boikovo and Bachkovo formations (Kozhoukharov, 1984) from the lithostratigraphic subdivisions of the Central Rhodope metamorphic rocks. The origin of the leptitoid gneiss protoliths has been a matter of discussions summarized in Kozhoukharova and Kozhoukharov (1962), whose consideration argues against the suggestion of syn-metamorphic metasomatic origin (Vergilov, 1960) and gives preference for arkoses to felsic pyroclastic rocks. Subsequent studies focused attention on rocks geochemistry. Zagorchev, Moorbath (1986) emphasized high Rb contents and strongly variable Rb/Sr ratios of the leptitoid gneisses. The distribution of Rb, Sr and Ba in whole rocks and K-feldspars from two-mica and leptitoid gneisses was interpreted to be consistent with magma fractionation trend and referred to igneous protoliths origin (Arnaudova et al., 1990). Average geochemical features of the leptitoid gneisses supported the idea of crustal igneous protolith (Stancheva, Cherneva, 1992). Meanwhile Kolcheva (1987) reported petrographic data and major elements geochemistry on isolated metagranitoid bodies (Dobralak metagranites) hosted by two-mica gneisses of the orthometamorphic subunit. Geochemical data mentioned above are used for comparison here as well as data on basic orthometamorphic rocks (Daieva, Kozhoukharova, 1987; Kozhoukharova, Daieva, 1990) that crop out within the Asenitsa unit.

Materials and methods

The whole rock geochemistry is based on 118 samples of biotite, two-mica, and leptitoid gneisses representing the most widespread rocks in the orthogneiss sub-unit (Fig. 1). The rock-forming mineral assemblages comprise plagioclase, K-feldspar and quartz, and different proportions of biotite, muscovite and minor epidote. The most common accessory minerals are zircon, apatite, allanite, garnet and magnetite. Detailed petrographic description is available in Kozhoukharova, Kozhoukharov (1962), Kolcheva (1987) and Sarov et al. (2006). Samples of decimeter to meter-scale layers and lenses of aplitoid gneisses hosted by two-mica and leptitoid ones are added to the dataset. These are free of micas and display strongly variable proportions of K-feldspar and plagioclase that enable a separate consideration of aplitic plagiogneisses.

The whole-rock samples (1 to 5 kg) were crushed and coned to 150 g that were pulverized in an agate mill. Routine XRF and AAS analytical techniques were used to determine the major and trace elements (Rb, Sr, Ba, Zr, Y, V, Cr, Cu, Zn, Pb, Ni, Co and Li), and INAA technique for REE, Th, U, Hf, Ta, Cs, and Sc (Appendix, Table 1 and 2). All analyses were performed in the Geological Institute of the Bulgarian Academy of Sciences through different scientific projects during the last 25 years.

Geochemistry

The orthogneisses have calc-alkaline affinity. They plot in the fields of tonalite, granodiorite, and granite with aplitic plagiogneisses falling in the trondhjemite field according to the CIPW normative ratios of the Ab-Or-An system (Fig. 2a). Negative linear trends of Ti, Al, Fe, Mn, Mg, Ca and P oxides versus SiO_2 (60–77 %) on the Harker variation diagrams (not shown) reflect a magma differentiation pattern. Similarly, the ratios between mafic phases' components (Fe, Mg, and Ti), plagioclase (Ca, Na) and K-feldspar display a continuous systematic change corroborating a protoliths genetic connection for the most widespread rocks except for the aplitic plagiogneisses (Fig. 2b). The whole suit ranges from metaluminous to peraluminous (A/CNK 0.86–1.4) with increasing A/CNK and decreasing A/NK ratios towards the most felsic compositions. The majority of the later (leptitoid and aplitic ones) is peraluminous, however part of the samples plot close to the metaluminous-peralkaline boundary (Fig. 2c). More than 90% of the compositions form a compact group of points in the Syn-Collision granite field with a cluster of leptitoid and aplitic gneisses along the Anorogenic granite field boundary (Fig. 2d). Some biotite gneisses together with the Dobralak metagranites plot in the Pre-Plate Collision field. Aplitic plagiogneisses distribute in Syn-Collision and Mantle Fractionates granite fields.

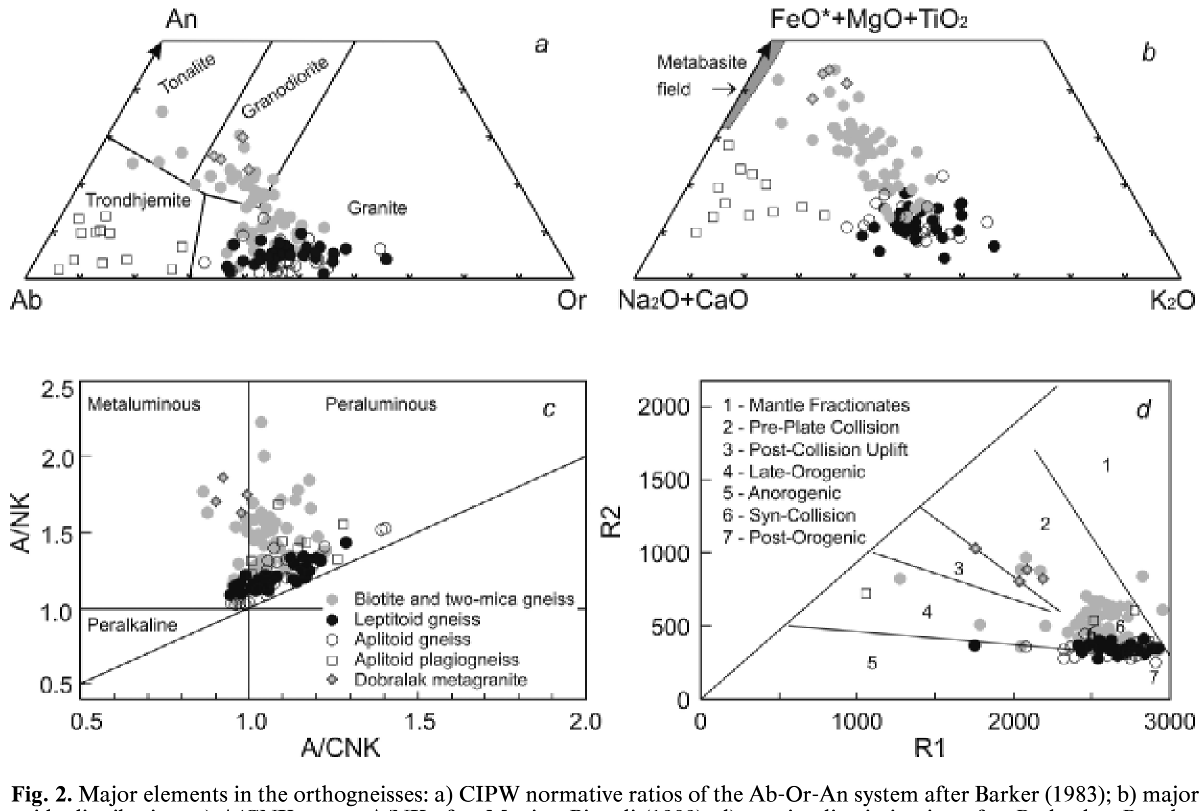

Fig. 2. Major elements in the orthogneisses: a) CIPW normative ratios of the Ab-Or-An system after Barker (1983); b) major oxide distribution; c) A/CNK versus A/NK after Maniar, Piccoli (1989); d) granite discrimination after Bathcelor, Bowden (1985). Dobralak metagranite data from Kolcheva (1987); metabasites field data after Daieva, Kozhoukharova, (1987) and Kozhoukharova, Daieva (1987)

The major elements geochemistry supports an assumption of genetically related igneous protoliths dominated by felsic rocks. The differentiation trend ranges from granodiorite to leucogranite compositions with the Dobralak metagranites at the offset. The K-feldspar bearing aplitic gneisses show close similarity with the leptitoid ones that is supported by almost identical average major oxides contents (Tabl. 1). The aplitic plagiogneisses deviate from the whole suite, suggesting a different origin.

The compatible trace elements occurring as trace constituents in mafic minerals (Cr, Ni, Co, V, Sc, Zn, Tabl. 1) are depleted by an average factor of 0.1 when compared with the continental crust contents (Rudnik, Gao, 2003). Some of them (Co, V, Sc, Zn) as well as Li show negative correlation with SiO_2 corresponding to micas decrease in the most felsic orthogneisses.

The LIL elements (Rb, Ba and Sr; Tabl. 1) occurring as trace constituents in alkali feldspar and plagioclase show a variation that reflects a protolith differentiation trend: a negative correlation of SiO_2 with Sr (20–600 ppm) and Ba/Rb (0.08–10); a positive correlation with Rb (80–540 ppm) and the Rb/Sr ratio (0.1–22). The whole suite forms a continuous steady trend, whose most fractionated part is represented by the richest in Rb felsic gneisses. In the leptitoid gneisses most frequent Rb/Sr values are in the range of 1 to 10 (Fig 3a). The persistent increase of Rb as compared to Ba and Sr in the K-feldspars of the studied rocks supports the conclusion of magma differentiation (Arnaudova et al., 1990). The LILE variation in K-feldspar-bearing aplitic gneiss covers the whole evolutionary trend suggesting discrete magma portions and release of fractionated melt. The aplitic plagiogneisses keep lower LILE contents and deviate from the common group together with some plagioclase enriched biotite gneisses indicating possible connection with more basic magma source (Fig. 3 b).

Crude positive correlations of Pb with K_2O and Rb in the whole orthogneiss suite suggest a dominant role of alkali feldspar in lead distribution. Nevertheless some particular variations (Tabl. 1), the contents of Pb maintain high values in all rock types with considerable enrichment in the leptitoid gneisses (average 54 ppm).

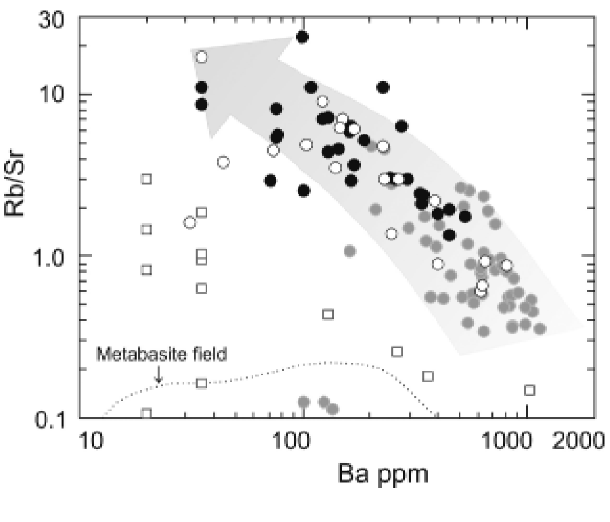

Fig. 3. LIL elements distribution with a fractionation trend of igneous protoliths formation. The symbols are as on Fig. 2

The total REE contents vary from 100 to 220 ppm in biotite and two-mica gneisses and from 40 to 100 ppm (rarely 150 ppm) in the leptitoid ones (Fig. 4 a-c; Tabl. 2). The former have higher LREE contents and La_N/Yb_N ratios (4–11) with variable negative Eu-anomalies (Eu/Eu* 0.3–0.8). The leptitoid gneisses exhibit uniform chondrite-normalized distribution patterns with lower La_N/Yb_N (1–6) and strong negative Eu-anomaly (0.1–0.3 usually). The latter indicate that the most felsic protoliths formed from magmas that had already crystallized substantial amounts of plagioclase. The Eu-anomaly values show negative correlation with Rb/Sr ratios, so that the strongest Eu-deficiency associates with the highest Rb contents in the most fractionated leptitoid and aplitoid othogneisses. The whole orthogneiss suit is distinguished by low LREE/HREE ratio that suggests negligible role or absence of HREE-rich residual phases (like garnet and pyroxene) during magma generation.

HFS elements (Zr, Hf, Nb, Ta, Th) occurring as essential components in accessory phases or as trace constituents in mafic minerals are supposed to reflect the primary protolith geochemistry to a satisfactory extent. The HFSE contents are higher or close to the bulk continental crust ones (Fig. 4 d-f). The Zr contents decrease from biotite and two-mica (80–250 ppm) towards leptitoid and apitoid gneisses (40–110 ppm). Negative correlation of Zr with SiO_2 is compatible with zircon fractionation. Limited data on Hf, Nb and Ta (Tabl. 2) show increased concentration of Ta and Hf in the most felsic rocks. The Zr/Hf ratios decrease from 23–40 (biotite and two-mica) to 11–30 (leptitoid gneisses). The highest Hf concentrations (Zr/Hf 11–15) associate with the lowest Eu/Eu* values corroborating magma fractionation mechanism. The Nb/Ta ratios keep very low values (1–5) like typical Syn-collision peraluminous leucogranites, however Ocean Ridge Granite normalized patterns (not shown) display small negative Nb-anomaly reminiscent of Volcanic Arc Granites (Harris et al., 1986). The area of study is well known with high Th and U-contents (Ancirev et al., 1983). Data available display enrichment of Th by factors from 2 to 10 when compared with the continental crust and considerable variation in U concentrations (Fig. 4 d-f) that is responsible for large Th/U variation (1–16) as well.

The continental crust normalized patterns (Fig. 4 d-f) display a typical incompatible trace element association (Rb, Pb, Th, U, Ta, Hf, HREE) whose enrichment is assisted additionally by the process of magma fractionation. The aplitic plagiogneisses, nevertheless deviating with lower LILE contents, show strongly fractionated incompatible trace elements, which patterns almost coincide with the K-feldspar-bearing ones.

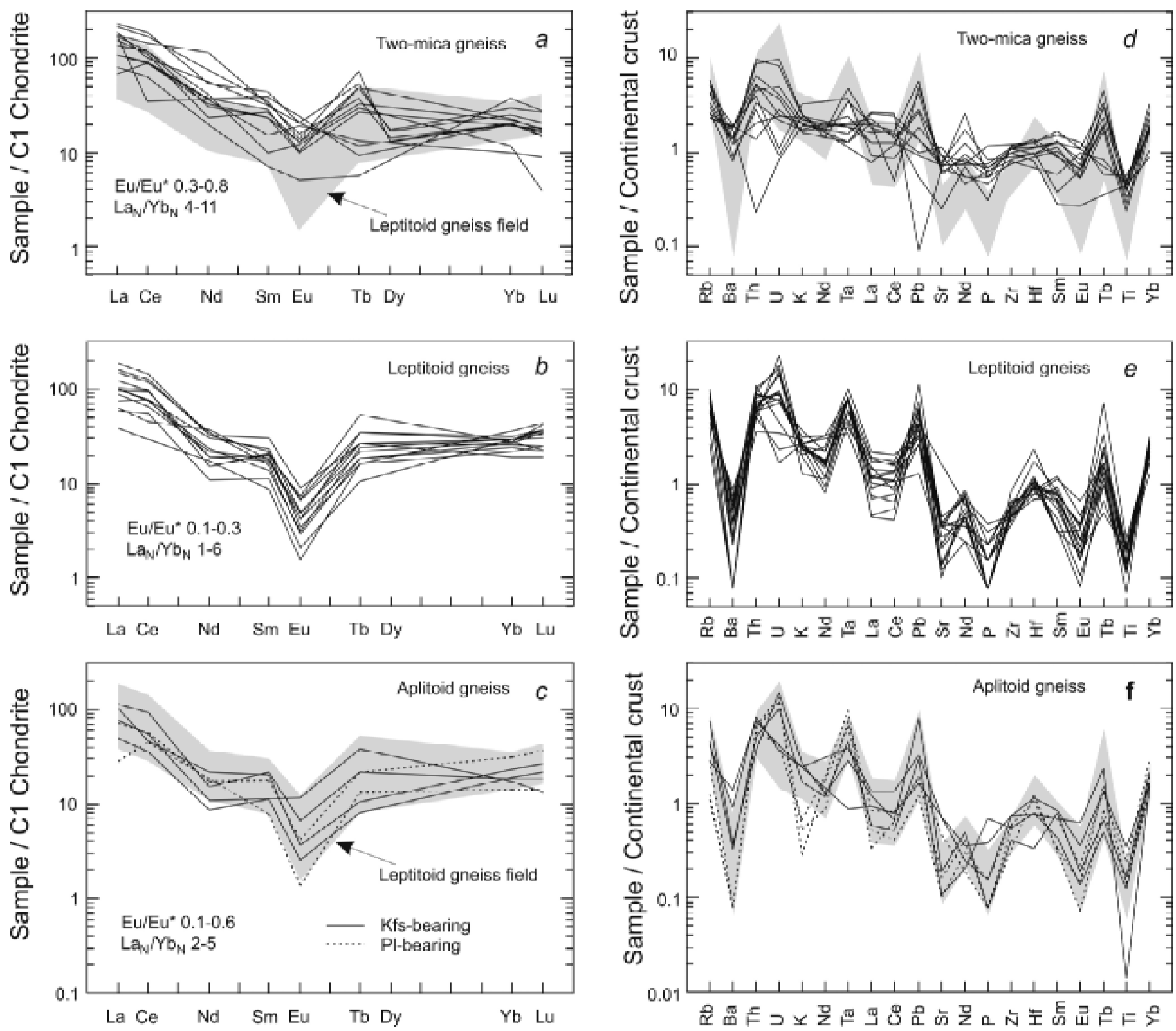

Fig. 4. Chondrite normalized REE patterns (a-c) and continental crust normalized spider diagrams (d-f)

Discussion

The whole orthogneiss suite is distinguished by high LILE/HFSE ratios that support crustal dominated, and evolved magma sources. On the SiO_2 versus Rb/Zr diagram after Harris et al. (1986) most of the biotite and two-mica gneisses plot in the Volcanic-arc and Late or post-collision calc-alkaline granite field (Fig. 5a). The Rb/Zr ratios increase systematically with the silica contents and the leptitoid gneisses plot above the discrimination line in the field of the Syn-collision peraluminous leucogranites. The Hf-Ta-Rb ratios (Fig. 5b) support a close resemblance with collision granites. The zircon saturation temperatures calculated after Watson, Harrison (1983) are in the range 750–800°C for biotite and two-mica orthogneisses, and 700–750°C for leptitoid and aplitoid ones. Low zircon-saturation temperatures refer to a "cold" granite type (Miller et al., 2003) and are consistent with the presence of zircon grains with an older lead component and more pronounced crustal affinity (εHf<0, von Quadt et al., 2006).

Pb-isotope data on K-feldspars from the orthogneisses (Arnaudov et al., 1992) provide additional information on the crustal sources of the former igneous suite. The K-feldspars Pb-Pb model ages (110–140 Ma) approach to recently obtained U-Pb zircon age (150 Ma, von Quadt et al., 2006). The Pb-isotope ratios values approach the young upper crust characteristics according to the Pb-isotope evolution model of Kramers, Tolstikhin (1997). Most of them are in the range $^{206}Pb/^{204}Pb$ 18.571–18.844; $^{207}Pb/^{204}Pb$ 15.638–15.693; $^{208}Pb/^{204}Pb$ 38.610–38.781. The Rb-Sr isotope data available also support crustal magma source as follows from calculated initial $^{87}Sr/^{86}Sr$ ratio (0.714 at 118 Ma, Zagorchev, Moorbath, 1986).

The positive εHf_i isotope values of dated zircons (+0.24 to +4.55 at 150 Ma) demonstrate that young crustal and/or lithospheric mantle material played an important role during magma generation (von

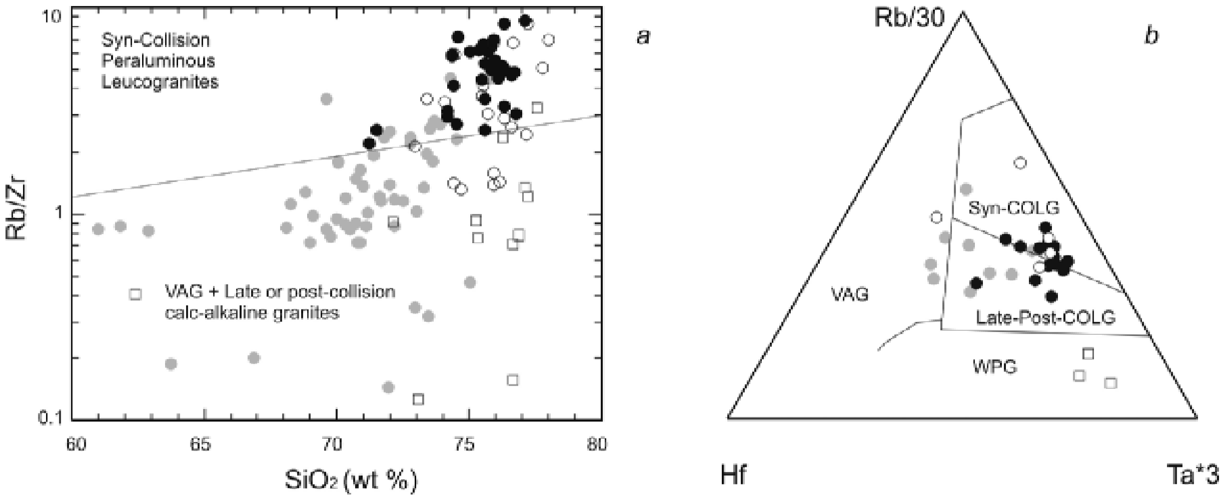

Fig. 5. LILE-HFSE granitoids discrimination diagrams after Harris et al. (1986). The symbols are as on Fig. 2

Quadt et al., 2006). Ovtcharova (2005) reported similar positive εHf signatures and general geochemical characteristics about biotite metagranites of 150 Ma protolith age in the Eastern periphery of the Central Rhodopian Dome (Startsevo and Borovitsa units, Sarov et al., 2004). Data on 150 Ma old zircon (εHf_i +0.3 to +4.7) in migmatites from the Chepinska river valley in the Western Rhodope argue for late Jurassic granitoid protolith of mixed crustal-mantle origin as well (Cherneva et al., 2006). Hence late Jurassic igneous protoliths of granitoid compositions are wide spread among the high-grade Rhodope metamorphic rocks. Yet limited isotope signatures available suggest young crust or lithospheric mantle input to dominantly crustal magma sources.

The majority of data on the Asenitsa orthogneisses indicate the important role of magma differentiation that produced protoliths with a range from granodiorite to leucogranite compositions. Fractionation of plagioclase and allanite in the earlier stages of magmatic evolution should explain the highly evolved signatures of the most felsic orthogneisses. The aplitic plagiogneisses, although strongly fractionated deviate from the above trend, suggesting different magma source. Some geochemical characteristics focus attention on probable genetic relations with more basic igneous protoliths (Fig. 2b, Fig. 3), probably with metabasites that crop out in the Asenitsa unit as well. Yet missing isotope data on the latter preclude from discussing such an idea.

Conclusions

The late Jurassic igneous protoliths of the two-mica and leptitoid gneisses in the Central Rhodope Asenitsa unit correspond to a range of granodiorite to leucogranite compositions. Despite the Alpine metamorphic overprint, the major and trace elements compositions of the igneous protoliths are preserved to a significant extent. These correspond to collision granite geochemistry and continental crust dominated magma source.

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З. Чернева, Е. Станчева, Л.-А. Даиева, Е. Войнова — Геохимия на ортогнайси от северната част на Централните Родопи. Горноюрските магмени протолити на двуслюдените и лептитоидни гнайси от Централнородопската единица Асеница съответстват на поредица от металуминиеви, гранодиоритови до широкоразпространени, пералуминиеви, левкогранитови състави. Въпреки наложения метаморфизъм в амфиболитов фациес, разпределението на главните елементи и елементите следи се е запазило в значителна степен. Закономерните геохимични вариации съответстват на трендове на фракционна магмена кристализация. Най-показателни сред тях са нарастващо Rb/Sr отношение от 0,1 до 22, намаляващи Eu/Eu* стойностис от 0,8 до 0,1 и Zr/Hf отношения от 40 до 11 към най-фелзичните ортогнайси. Всички ортогнайси се отличават с високи LILE/HFSE отношения, което подкрепя интерпретацията за корово доминиран и еволюирал магмен източник.

Table 1
XRF and AAS whole-rock analysis of majoroxides (wt %) and trace elements (ppm) in orthogneisses from the Asenitsa unit, Central Rhodope

Sample	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^t$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Ba	Rb	Sr	Zr	Cr	V	Ni	Co	Cu	Pb	Zn	Li
Biotite and two-mica gneisses																								
9	69.79	0.41	15.43	2.87	0.10	1.04	2.05	3.41	3.41	0.10	1.41	100.02	790	114	235	146	32	58	7	10	5	54	29	14
11	69.61	0.35	15.14	2.82	0.08	1.32	2.93	3.62	3.06	0.09	1.00	100.02	855	112	300	132	<20	51	2	9	7	31	31	6
14	71.80	0.32	14.73	1.86	0.06	0.20	1.64	3.61	4.24	0.06	1.25	99.77	545	254	212	108	<20	38	1	5	1	46	16	12
252a	72.00	0.25	14.00	1.91	0.05	0.49	1.97	3.57	4.59	0.07	0.85	99.75	641	255	243	102	<20	21	2	2	9	45	27	15
254b	69.10	0.36	14.80	3.11	0.07	0.98	2.00	3.59	3.47	0.11	1.90	99.49	632	134	182	138	<20	45	2	1	9	31	40	11
270b	73.50	0.24	13.60	1.49	0.06	0.52	1.52	3.60	4.34	0.08	0.81	99.76	403	289	185	111	<20	21	5	2	8	62	25	5
271	72.80	0.26	13.50	1.69	0.04	0.55	1.52	3.49	5.19	0.08	0.70	99.82	766	261	269	111	<20	<20	3	1	5	36	24	6
272c	72.51	0.27	14.19	2.11	0.07	0.14	1.99	3.46	3.98	0.07	1.00	99.79	625	165	197	143	<20	<20	5	2	4	29	30	11
274	73.00	0.27	13.72	1.89	0.05	0.60	1.45	3.68	4.19	0.07	0.72	99.64	676	156	164	153	<20	<20	2	1	5	50	27	8
276a	70.35	0.36	14.56	2.81	0.11	1.22	2.86	3.56	3.38	0.07	0.80	100.08	1140	107	301	90	<20	26	4	4	6	55	29	6
300c	70.71	0.40	15.74	2.35	0.04	0.84	2.71	3.26	3.20	0.09	0.74	100.08	521	259	128	175	<20	20	2	2	1	14	34	36
307a	70.07	0.41	14.22	2.84	0.11	1.07	3.06	3.13	3.79	0.09	1.30	100.09	813	206	255	116	<20	40	4	4	9	15	27	21
308a	61.00	0.36	18.82	3.47	0.08	1.55	3.55	5.54	3.12	0.15	0.90	98.54	371	131	233	156	<20	53	6	4	4	10	28	18
311a	68.80	0.29	15.04	3.24	0.08	1.40	3.20	3.76	2.97	0.11	0.86	99.75	565	149	254	117	<20	48	5	5	4	15	41	18
315a	71.12	0.35	14.38	2.52	0.06	1.11	2.34	3.32	3.54	0.09	1.00	99.83	844	126	220	145	<20	46	6	8	7	10	20	20
316a	72.20	0.32	14.26	2.27	0.05	0.93	2.23	3.25	3.66	0.07	0.78	100.02	818	127	226	145	<20	28	5	7	8	15	20	18
317a	70.88	0.40	14.40	2.80	0.06	1.01	2.82	3.32	3.33	0.09	1.00	100.11	1063	116	253	160	<20	63	8	8	13	14	23	15
318a	73.49	0.34	13.56	2.10	0.03	1.03	0.97	4.94	2.84	0.09	0.64	100.03	162	83	78	260	<20	23	2	5	11	25	24	18
322c	68.24	0.35	15.35	2.96	0.07	1.55	2.79	3.33	3.23	0.09	1.04	99.00	983	129	340	115	20	56	4	4	5	27	18	15
322d	71.66	0.30	14.64	2.20	0.06	0.93	2.31	3.51	3.67	0.08	0.75	100.11	630	139	238	121	<20	24	3	3	3	36	22	15
323	71.64	0.28	14.71	2.07	0.06	0.98	2.25	3.51	3.60	0.07	0.87	100.04	718	159	194	131	<20	41	3	2	3	24	25	14
324	71.01	0.27	14.33	1.99	0.06	1.73	1.79	3.28	4.27	0.07	0.87	99.67	564	160	180	117	<20	20	3	2	3	28	11	14
327a	70.08	0.27	14.43	2.15	0.07	1.44	2.35	3.54	3.79	0.08	0.42	98.62	595	160	270	89	<20	40	2	2	3	36	20	20
328b	72.03	0.29	14.34	2.08	0.08	0.87	1.76	3.21	4.55	0.07	0.96	100.24	667	200	106	144	<20	28	1	1	14	34	26	11
329b	72.17	0.31	14.21	1.73	0.05	1.23	0.72	3.34	4.47	0.08	1.34	99.65	639	231	99	197	<20	<20	1	1	19	22	9	12
334a	69.63	0.22	14.99	1.91	0.09	1.05	1.52	5.03	4.33	0.36	0.52	99.85	202	296	62	83	<20	<20	4	3	3	26	37	14
336a	72.97	0.30	14.23	2.88	0.03	0.20	1.20	3.48	3.62	0.06	0.75	99.72	353	120	97	339	<20	25	3	5	15	48	35	11
337a	68.10	0.52	15.18	3.66	0.09	1.71	2.49	3.28	3.18	0.11	1.04	99.36	545	126	326	147	27	79	11	8	16	23	50	27
337c	71.16	0.38	14.53	2.44	0.06	1.30	2.30	3.13	3.83	0.09	0.75	99.97	843	126	220	125	<20	45	14	6	14	32	37	20
338a	70.51	0.36	14.58	2.56	0.07	1.20	2.43	3.43	3.82	0.09	0.87	99.92	914	129	217	153	<20	38	6	4	9	29	33	12
338d	70.72	0.37	14.67	2.57	0.05	1.38	2.45	3.41	3.48	0.09	0.87	100.06	1044	125	234	139	<20	49	6	5	7	29	30	15
339a	70.78	0.38	14.71	2.60	0.05	1.29	2.57	3.48	3.21	0.08	0.97	100.12	982	116	239	159	24	40	6	5	10	25	28	20

Table 1. *Continued*

Sample	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^t$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Ba	Rb	Sr	Zr	Cr	V	Ni	Co	Cu	Pb	Zn	Li
339b	75.01	0.28	12.62	1.96	0.02	1.04	1.23	3.85	3.60	0.04	0.58	100.23	577	107	208	232	<20	<20	2	2	6	25	35	12
340a	70.34	0.37	14.58	2.56	0.06	1.56	2.52	3.82	2.81	0.08	0.84	99.54	838	136	278	154	<20	43	5	3	7	37	33	36
340b	69.98	0.32	14.44	2.21	0.05	1.38	2.30	3.44	3.79	0.06	0.70	98.67	776	132	151	140	<20	26	6	5	6	40	30	30
341a	62.88	0.64	17.29	5.25	0.12	1.45	4.36	3.41	2.81	0.19	1.11	99.51	863	135	375	164	22	93	14	14	20	38	54	29
592a	70.89	0.32	14.67	1.74	0.06	0.90	1.60	3.11	5.81	0.08	0.80	99.98	875	212	291	130	<20	34	1	4	2	20	25	15
600b	73.67	0.20	13.77	1.61	0.07	0.60	1.56	3.35	4.51	0.07	0.65	100.06	626	282	358	100	<20	<20	1	2	3	11	18	3
611a	72.82	0.20	14.61	1.68	0.07	0.40	1.39	3.78	3.63	0.06	1.35	99.99	458	190	251	87	26	<20	1	1	4	65	28	11
612	73.28	0.17	13.62	1.25	0.06	0.40	0.69	4.84	4.61	0.04	0.85	99.81	553	204	81	153	<20	<20	1	1	1	6	9	11
622	73.65	0.27	13.50	1.49	0.09	0.83	1.06	3.73	3.85	0.07	1.45	99.99	722	189	120	105	<20	<20	1	1	2	22	29	11
624	73.92	0.03	13.29	2.24	0.03	0.40	0.77	3.79	4.04	0.05	1.20	99.76	249	251	89	93	<20	<20	1	1	8	24	17	12
626	68.97	0.52	14.63	3.34	0.10	1.11	3.06	3.34	3.43	0.12	1.50	100.12	513	132	238	183	<20	49	1	4	9	24	40	20
627	61.81	0.80	15.33	5.97	0.10	2.66	4.99	3.32	2.96	0.19	2.05	100.18	426	171	313	196	47	129	10	10	13	21	54	23
977	75.78	0.14	13.32	1.18	0.04	0.20	0.67	2.97	4.38	0.03	0.95	99.66	231	382	84	84	<20	<20	2	2	23	47	48	8
981a	73.42	0.16	13.58	1.39	0.06	0.20	1.27	3.25	4.85	0.03	1.50	99.71	503	245	93	125	<20	107	2	2	4	34	15	11
1067	74.53	0.15	13.27	1.34	0.06	0.20	0.97	3.64	4.58	0.04	0.98	99.76	351	249	143	108	<20	<20	1	1	2	59	20	18
1068	73.76	0.18	13.82	1.52	0.08	0.12	1.15	3.09	4.76	0.07	0.97	99.52	394	244	212	89	20	<20	2	2	2	61	32	21
1070	74.28	0.15	13.85	1.18	0.07	0.20	1.01	4.04	4.31	0.03	0.71	99.83	212	261	134	58	20	<20	2	2	2	79	29	20
1333	66.87	0.62	15.42	4.69	0.13	1.50	4.36	3.66	0.85	0.21	1.45	99.76	124	28	222	140	6	37	3	7	2	4	44	9
1337	63.76	0.72	15.49	5.41	0.12	2.06	4.51	5.11	0.99	0.24	1.44	99.85	136	24	211	128	12	54	2	12	3	7	33	8
1338	68.46	0.45	15.53	3.73	0.07	1.13	2.62	3.33	2.72	0.14	1.52	99.70	639	96	281	100	9	32	9	9	11	30	38	11
1340	71.37	0.39	13.62	1.64	0.08	2.07	1.29	3.84	3.82	0.07	1.53	99.72	298	214	144	111	8	14	4	3	8	38	18	8
1348	71.97	0.48	13.51	3.25	0.10	0.64	2.97	4.00	1.28	0.13	1.21	99.54	100	21	167	146	6	26	1	5	6	3	24	8
Avrg	70.83	0.34	14.50	2.49	0.07	1.00	2.15	3.63	3.66	0.09	1.02	99.77	600	170	207	137	12.6	34.4	3.9	4.1	7.1	30.9	28.7	14.8
Stdev	3.08	0.14	1.00	1.04	0.02	0.55	1.00	0.53	0.91	0.06	0.34	0.37	261	73	78	46	7.2	25.5	3.2	3.1	5.1	16.8	10.3	7.2
Leptitoid gneisses																								
252b	76.29	0.09	13.00	0.76	0.03	0.20	0.96	4.15	3.52	0.02	0.75	99.77	35	196	108	59	<20	<20	1	1	5	28	12	3
254a	76.00	0.07	12.96	0.73	0.03	0.13	0.89	3.65	4.81	0.02	0.56	99.85	71	283	97	54	<20	<20	1	1	3	66	40	5
255a	74.20	0.18	14.10	1.31	0.04	0.20	0.77	3.58	4.38	0.05	0.90	99.71	450	289	148	92	<20	<20	1	1	4	74	26	6
270a	76.00	0.19	12.10	1.10	0.08	0.31	1.17	3.21	4.86	0.05	0.80	99.87	337	296	142	60	<20	<20	1	1	15	69	17	5
272a	75.58	0.15	13.08	1.20	0.08	0.20	0.83	2.82	4.74	0.03	1.10	99.81	397	220	120	87	<20	<20	2	1	9	45	33	5
273a	76.49	0.10	12.69	0.78	0.07	0.20	0.69	2.86	5.35	0.01	0.60	99.84	76	305	57	63	<20	<20	1	1	5	78	11	2
277	77.10	0.14	12.20	0.25	0.01	0.20	0.75	3.26	5.30	0.02	0.68	99.91	168	415	114	48	<20	<20	1	1	7	126	3	1
278	76.32	0.16	12.20	0.55	0.02	0.20	0.96	2.36	6.74	0.01	0.48	100.00	109	481	44	58	<20	<20	1	1	10	81	7	1
395a	74.57	0.14	13.29	1.14	0.07	0.20	0.89	3.87	4.68	0.03	0.75	99.63	244	380	126	53	<20	<20	1	1	3	55	15	12
395b	75.79	0.10	13.12	0.98	0.09	0.20	0.69	3.96	4.19	0.01	0.65	99.78	130	477	66	74	<20	<20	1	1	2	47	15	14

Table 1. *Continued*

Sample	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^t$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Ba	Rb	Sr	Zr	Cr	V	Ni	Co	Cu	Pb	Zn	Li
595	76.10	0.13	12.31	1.40	0.07	0.14	0.78	3.58	4.54	0.03	0.60	99.68	261	349	116	77	<20	<20	1	1	5	40	7	2
597	75.97	0.10	12.69	1.13	0.03	0.44	0.77	2.53	5.23	0.02	0.85	99.76	344	340	143	62	<20	<20	1	1	2	39	5	3
599a	74.37	0.08	13.98	0.70	0.08	0.20	0.80	3.42	5.58	0.01	0.65	99.87	130	381	86	66	<20	<20	1	1	5	59	5	3
601a	74.41	0.14	13.48	0.95	0.10	0.20	1.00	3.73	4.77	0.02	0.90	99.70	293	340	114	81	<20	27	1	1	7	63	15	5
601c	74.55	0.20	12.97	1.37	0.07	0.20	0.17	3.17	5.40	0.03	1.65	99.78	451	297	220	109	<20	<20	1	1	13	37	3	2
604b	75.84	0.11	13.96	0.90	0.09	0.20	0.61	3.00	4.43	0.02	0.80	99.96	187	388	75	78	<20	<20	1	2	1	14	8	8
610	75.45	0.13	13.33	1.22	0.06	0.20	0.51	4.00	3.72	0.03	1.10	99.75	77	320	57	72	<20	<20	1	1	2	25	11	11
613	75.03	0.09	13.11	0.94	0.06	0.20	1.25	3.77	4.63	0.01	1.00	100.09	165	361	124	59	<20	<20	1	1	1	70	31	9
614	75.94	0.09	12.94	0.84	0.08	0.20	0.69	3.72	4.68	0.01	0.60	99.79	35	402	47	58	<20	<20	1	1	1	37	8	9
615	75.60	0.17	12.28	1.24	0.07	0.73	1.30	3.12	4.54	0.05	0.96	100.06	526	311	179	87	<20	<20	1	1	1	24	21	21
616	75.55	0.10	13.40	0.90	0.12	0.20	0.45	4.32	4.40	0.01	0.65	100.10	99	543	24	82	21	<20	1	1	1	69	19	11
617	71.52	0.05	16.74	0.40	0.06	0.20	0.26	5.43	4.58	0.01	0.50	99.75	101	278	111	109	<20	<20	1	1	1	33	1	5
618	76.73	0.09	13.42	0.80	0.09	0.20	0.35	4.42	3.64	0.01	0.45	100.20	35	355	32	74	<20	<20	1	1	1	36	12	8
621c	75.69	0.11	13.60	0.93	0.09	0.20	0.35	3.76	4.38	0.01	0.75	99.87	227	441	40	73	<20	<20	1	1	1	29	11	8
976	75.60	0.10	13.14	1.08	0.05	0.20	0.46	2.75	5.08	0.02	1.25	99.73	121	387	55	72	<20	<20	1	1	14	60	16	6
978	74.18	0.18	14.05	1.29	0.08	0.20	1.08	3.79	3.99	0.03	0.85	99.72	335	311	129	105	<20	<20	2	2	12	88	24	6
1063a	75.35	0.09	12.91	0.81	0.07	0.57	0.56	4.06	4.30	0.02	0.88	99.62	275	395	62	64	<20	<20	<1	<1	4	111	26	15
1065	76.28	0.11	12.86	0.71	0.09	0.20	0.71	3.74	4.34	0.01	0.77	99.82	164	364	57	70	20	<20	2	1	2	27	18	14
1066b	76.61	0.13	12.36	0.78	0.09	0.20	0.57	3.79	4.49	0.02	0.79	99.83	161	304	52	65	<20	<20	1	2	3	55	24	15
1071a	74.35	0.16	12.60	0.73	0.09	1.12	0.63	3.81	4.31	0.02	1.83	99.65	76	322	40	55	<20	<20	<1	<1	2	75	12	9
1071b	76.79	0.10	13.01	0.93	0.04	0.20	0.62	3.15	4.21	0.03	0.72	99.80	143	221	48	72	<20	<20	1	<1	3	31	18	9
1072a	76.33	0.12	12.40	0.79	0.08	0.20	0.37	3.52	4.89	0.01	1.11	99.82	154	306	47	61	<20	<20	4	1	3	38	18	8
Avrg	75.52	0.12	13.13	0.93	0.07	0.26	0.72	3.57	4.65	0.02	0.84	99.83	199	346	90	72	10.7	10.5	1.2	1.0	4.6	54.0	15.4	7.3
Stdev	1.09	0.04	0.86	0.27	0.03	0.20	0.28	0.61	0.62	0.01	0.31	0.14	133	76	47	16	2.6	3.0	0.6	0.3	4.1	25.9	9.3	4.9
Aplitoid gneisses																								
273b	72.97	0.25	14.35	1.75	0.08	0.20	1.47	3.80	4.28	0.05	0.65	99.85	401	202	228	96	<20	23	1	1	7	35	41	3
307b	75.95	0.12	12.97	0.95	0.08	0.20	1.56	3.30	3.53	0.04	1.05	99.75	31	177	109	112	<20	<20	1	1	2	3	4	5
311b	75.91	0.01	12.98	1.06	0.02	0.35	1.07	3.50	4.30	0.02	0.54	99.76	624	136	226	98	<20	<20	1	1	5	18	9	6
327b	76.32	0.07	13.18	0.95	0.02	0.20	0.75	2.04	5.58	0.03	0.55	99.69	817	202	231	70	<20	<20	1	1	4	56	1	8
329a	76.62	0.09	13.90	0.53	0.03	0.20	0.46	2.66	4.41	0.01	0.89	99.80	74	215	48	82	<20	<20	1	1	6	13	3	8
334b	74.45	0.04	14.08	0.76	0.05	0.20	0.55	3.40	6.02	0.17	0.16	99.88	121	330	37	56	<20	<20	4	1	3	18	3	3
337b	74.69	0.25	14.50	1.54	0.04	0.49	0.45	2.80	4.52	0.05	0.73	100.06	652	141	151	107	<20	<20	2	2	20	52	12	5
338b	76.14	0.08	13.36	0.88	0.04	0.20	1.16	3.91	3.51	0.01	0.35	99.64	630	104	158	73	<20	<20	2	1	7	72	7	3
341b	77.17	0.09	12.55	0.66	0.07	0.20	1.01	2.85	4.42	0.02	0.78	99.82	248	171	124	71	<20	<20	2	1	9	125	9	8
598b	78.00	0.12	10.94	0.65	0.03	0.20	0.26	3.41	4.51	0.06	1.66	99.84	229	401	134	58	<20	<20	1	1	26	86	13	8

Table 1. *Continued*

Sample	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^t$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Ba	Rb	Sr	Zr	Cr	V	Ni	Co	Cu	Pb	Zn	Li
601b	75.91	0.12	13.40	0.98	0.10	0.20	0.61	3.17	4.73	0.01	0.70	99.93	169	365	60	54	<20	<20	1	1	8	87	5	1
623	75.69	0.09	14.22	0.78	0.06	0.20	0.56	4.51	3.04	0.09	0.95	100.19	145	217	35	71	<20	21	1	1	2	32	4	3
628	77.75	0.10	11.43	0.58	0.06	0.20	0.42	3.79	4.55	0.02	0.92	99.82	35	372	22	73	<20	<20	1	1	2	61	9	3
1064	77.21	0.10	12.13	0.53	0.06	0.20	0.43	3.97	4.77	0.01	0.44	99.85	151	332	47	40	<20	<20	1	1	4	115	8	6
1072b	74.44	0.16	13.42	1.11	0.05	0.52	0.65	4.19	4.61	0.03	0.78	99.96	389	169	77	120	20	<20	4	1	3	11	17	14
1089	76.67	0.06	12.79	0.71	0.02	0.20	0.46	3.48	4.56	0.01	0.81	99.77	44	324	86	48	7	4	1	2	6	65	8	5
1332	75.45	0.10	13.15	0.91	0.03	0.20	0.24	4.32	4.59	0.04	0.81	99.84	104	280	57	76	3	6	2	2	5	20	14	5
1344	75.52	0.11	12.78	1.10	0.02	0.20	0.29	4.13	5.19	0.03	0.42	99.79	228	292	61	70	6	11	1	3	16	70	35	3
1346	74.06	0.12	13.78	1.04	0.03	0.54	0.47	3.60	4.81	0.04	1.12	99.61	267	259	87	74	7	11	1	2	6	60	40	3
1347	73.41	0.16	13.31	1.31	0.06	0.52	0.66	5.00	4.27	0.07	0.90	99.67	140	311	88	87	6	11	2	3	3	59	18	9
Avrg	75.72	0.11	13.16	0.94	0.05	0.27	0.68	3.59	4.51	0.04	0.76	99.83	275	250	103	77	9.5	10.9	1.6	1.4	7.2	52.9	13.0	5.3
Stdev	1.38	0.06	0.92	0.32	0.02	0.13	0.38	0.69	0.67	0.04	0.32	0.14	234	88	66	21	3.2	4.2	0.9	0.7	6.4	34.3	12.0	2.9
Aplitoid plagiogneisses																								
253b	77.55	0.10	12.96	0.92	0.08	0.20	0.42	5.75	1.22	0.01	0.75	99.96	35	140	149	43	<20	<20	1	1	4	21	10	5
300b	72.12	0.24	15.53	1.33	0.07	0.20	2.80	3.93	2.53	0.04	1.05	99.84	1027	88	598	97	<20	<20	4	1	3	7	19	21
342a	73.09	0.35	14.04	1.62	0.01	1.45	1.80	6.24	0.37	0.07	0.96	100.00	35	20	123	159	<20	30	7	4	7	9	13	9
593	77.11	0.11	12.75	1.31	0.01	0.20	1.27	5.76	0.80	0.02	0.60	99.94	35	104	164	78	<20	<20	1	1	2	32	8	1
598a	75.28	0.12	12.68	1.96	0.05	0.20	3.47	3.50	1.49	0.02	1.65	100.42	361	100	549	108	<20	<20	1	4	21	98	32	5
605a	76.86	0.10	14.48	0.52	0.08	0.20	0.28	6.33	0.51	0.02	0.70	100.08	35	60	32	76	<20	<20	2	2	50	13	2	3
621b	75.29	0.17	14.13	0.82	0.06	1.04	1.08	4.90	0.94	0.01	1.40	99.84	35	54	52	71	<20	<20	1	1	1	20	23	12
1335	76.64	0.08	13.32	0.64	0.01	1.01	1.16	5.46	0.51	0.03	0.74	99.60	20	10	93	64	13	4	2	1	6	6	3	3
1339	76.27	0.10	13.27	0.78	0.05	0.38	0.28	4.91	2.51	0.02	1.07	99.64	20	138	46	59	6	8	2	1	2	78	48	15
1342	76.66	0.07	13.59	0.67	0.01	0.64	1.20	5.23	0.78	0.01	0.74	99.60	264	47	184	66	5	3	4	4	9	18	6	3
1343	77.22	0.08	13.55	0.63	0.10	0.39	0.51	5.91	0.66	0.02	0.53	99.60	20	63	77	52	7	5	2	2	3	52	12	5
1345	79.45	0.12	11.25	1.03	0.01	0.20	0.49	4.99	1.49	0.02	0.62	99.67	20	98	67	53	7	12	1	3	17	26	14	3

Routine XRF was used to determine the major oxides on fused glass discs, and trace elements (Rb, Sr, Ba, Zr, Y, V, Cr) on pressed powder pellets. Cu, Zn, Pb, Ni, Co and Li have been analyzed by AAS technique. All analyses were performed in the Geological Institute of the Bulgarian Academy of Sciences using USGS-G-2 geochemical standard as reference. Average contents (Avrg) and and stahdard deviation (Stdev) values are added for rock groups represented by ≥ 20 samples. Contents below detection limits (Cr, V < 20 ppm and Co, Cu < 1 ppm) are included in calculation accepting 10 ppm and 0.5 ppm respectively.

Table 2
Whole-rock INA analysis of REE and other trace elements (ppm) in orthogneisses from the Asenitsa unit, Central Rhodope

Sample	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Cs	Ta	Nb	Hf	Sc	Th	U
Biotite and two-mica gneisses																
9	40.0	21.3		5.9	1.40	0.35		3.3	0.39					29	1.3	1.1
11	44.5	60.7		4.8	1.20	0.43		3.5	0.37					10	7.7	3.6
14	15.6	52.3		2.3	1.10	0.50		1.7	0.23					5	11.4	3.1
270b	32.1	71.8	19.0	1.5	0.70	1.10		2.0	0.10		1.3		3.60	3	16.0	1.2
272c	25.3	54.3	17.0	4.4	0.59	1.80		3.8	0.44	2.2	1.3		3.54	4	25.2	6.4
308a	25.1	52.8	15.0	3.5	0.74	1.80	4.41	5.0	0.67		1.7		4.60	8	18.8	2.8
311a	50.8	103.1	34.0	5.2	0.80	2.70	3.30	3.3	0.43		0.9		3.50	6	28.9	4.8
315a	53.4	111.7	25.0	6.6	1.18	2.00	4.20	4.2	0.51		1.1		4.80	7	35.9	5.3
316a	41.2	86.8	52.0	5.0	0.92	1.40	3.64	3.4	0.41		0.9		4.20	5	29.6	3.2
592a	18.4	37.6	9.2	1.1	0.30	0.21		6.2	0.70		2.6		3.00	3	21.8	1.4
600b	36.1	66.3	11.0	4.0	0.74	1.20		3.7	0.46	2.0	3.4	13.5	3.31	2	53.8	10.5
612	39.7	71.7	14.0	3.6	0.58	1.00		3.2	0.46	0.4	2.4	11.2	5.00	2	49.4	12.6
Leptitoid gneisses																
252b	22.6	57.1	9.0	3.0	0.42	2.00		4.6	0.57	1.0	3.1	6.4	3.35	2	61.6	5.9
270a	30.6	35.7	14.2	1.2	0.35	4.30		3.9	0.40		2.8		4.20	4	37.2	2.2
272a	14.9	27.5	17.0	2.7	0.28	1.00		3.2	0.48	1.4	2.4		2.88	3	28.3	3.0
273a										1.5	4.1		2.59	3	26.4	8.1
277	9.1	23.1	5.0	1.2	0.21	0.30		2.4	0.41	1.2	5.5	9.3	3.66	1	20.0	4.5
278	22.5	57.8	9.0	2.4	0.18	1.50		3.6	0.69	2.8	5.6	17.4	3.43	2	32.4	9.4
395a	24.1	58.8	7.0	3.1	0.40	1.30		4.9	0.84	4.5	5.3	13.0	3.45	3	45.4	11.3
395b	17.6	46.8	9.0	2.6	0.24	1.30		5.3	0.95	5.6	5.8	14.0	3.93	3	40.6	11.7
595	28.7	58.2	7.0	3.2	0.38	1.00		4.3	0.64	3.8	4.2	7.3	3.48	2	48.6	9.8
599a	8.9	18.1	8.0	1.3	0.09	0.60		3.7	0.62	1.6	5.6	26.0	4.41	2	36.4	10.2
600a	37.0	67.8	12.0	4.4	0.73	1.00		4.1	0.66	0.7	4.3	9.1	2.85	2	51.7	23.2
601a	37.8	75.2	15.0	4.7	0.51	1.00		5.0	0.76	1.9	5.5	12.6	3.15	2	57.5	20.9
604b	23.3	44.8	11.0	2.1	0.18	0.90		4.9	0.90	2.9	5.8	18.2	3.76	2	39.2	12.6
613	23.7	46.5	14.0	3.6	0.29	0.80		4.6	1.07	1.8	5.5	11.7	2.57	2	27.8	29.8
614	20.7	39.1	10.0	2.8	0.24	0.70		4.5	0.88	3.2	4.2	14.0	2.53	2	32.9	20.0
616	29.2	54.7	9.0	2.1	0.01	0.50		4.4	0.94	5.0	6.5	9.0	5.34	2	38.1	27.7
617	34.7	70.4	16.0	2.4	0.17	0.70		4.1	0.55	1.9	3.4	14.2	8.59	1	50.4	9.8
618	44.1	87.8	15.0	3.3	0.20	0.60		6.0	1.09	3.2	7.1	20.0	6.41	2	35.1	18.3
621c	13.9	33.6	5.0	1.7	0.12	0.40		5.0	0.94	3.2	5.6	13.3	3.22	3	31.7	12.4
Aplitoid gneisses																
273b	26.7	56.6	7.0	3.3	0.39	0.80		3.1	0.47	1.2	2.7		4.12	4	45.7	4.6
311b	18.3	33.8	5.0		0.68	1.41		2.9	0.34		0.6		2.80	1	40.6	5.3
337b										10.5						
601b	24.0	28.8	10.0	3.1	0.21	0.40		4.0	0.67	2.0	2.0	10.0	1.21	1	19.7	19.2
623	11.7	21.8	4.0	1.7	0.15	0.30		3.2	0.55	0.0	3.1	9.3	2.89	2	28.2	13.0
Aplitoid plagiogneisses																
253b	6.7	27.2		1.2	0.08	0.50		2.4	0.36	1.0	6.7	15.2	4.46	5	31.8	5.4
605a	10.6	17.5	6.0	1.3	0.16	0.90		3.6	0.66	0.5	4.5	14.0	3.89	2	36.5	17.2
621b	16.7	35.0	8.0	2.7	0.24	0.80		5.3	0.93	2.5	5.3	7.0	2.94	2	33.8	15.4

INA analysis of REE, Th, U, Hf, Ta, Cs, and Sc was carried out at 18 h irradiation by neutron flux of $1.6*10^{12}$ n/cm^2 s^{-1} with iron monitor and relative error 3 to 10% except for Tb (20%). Chromatographic Nb analysis were made by R. Boyadjeva. All analyses were performed in the Geological Institute of the Bulgarian Academy of Sciences using USGS-G-2 as reference.