Petrology of Upper Cretaceous island-arc ore-magmatic centers from Central Srednogorie, Bulgaria: Magma evolution and paths

Borislav K. Kamenov, Yotzo Yanev, Rossen Nedialkov, Robert Moritz, Irena Peytcheva, Albrecht von Quadt, Stanislav Stoykov, Aneta Zartova

Abstract. Magmatic rocks of Late Cretaceous age from the Central Srednogorie, Bulgaria show marked variations in its geochemistry. The present study is focused on the common features in the magma evolution paths of several ore-magmatic systems: Elatsite, Chelopech, Medet, Assarel, Elshitsa and Capitan Dimitrievo considered as links of a petrological across-arc transect. The whole range of SiO₂ is large (40-73%). The evolution from intermediate to more basic stages is a common characteristic for most of the centers, but it is complicated by fractional differentiation and mixing of magmas. High-K calc-alkaline to shoshonitic series predominate, calc-alkaline being only in the middle of the transect. The geochemical peculiarities are typical for an enriched mantle source and indicate a subduction-related volcanic-arc setting. Melting degrees are estimated as small for both ends of the transect and higher for the central parts.

The magmatic activity started at the northern end of the transect at 92.1 Ma, gradually became younger and finished at the border to the Rhodopes massif at 78 Ma. The ${}^{87}Sr/{}^{86}Sr$ ratios (0.704-0.706), suggest melts generated in a mantle source, modified by the addition of crustal materials. Pb-isotope analyses and ε -Hf values show an increase of the radiogenic component from North to South. The subduction slab retreat model is applied to explain the trenchward migration of the magmatic activity along the transect length.

Key words: island-arc system, magma evolution, mineralogy, geochemistry, geochronology

Addresses: B.K. Kamenov, R. Nedialkov, A. Zartova – Faculty of Geology and Geography, Sofia University, 1000 Sofia, Bulgaria; E-mail: kamenov@gea.uni-sofia.bg; Y. Yanev – Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia; R. Moritz – Earth Science Section, University of Geneva, 1211 Geneva, Switzerland; A. von Quadt - Isotope Geochemistry and Mineral Resources, Department of Earth Sciences, ETH-Zurich, CH-8092 Zurich, Switzerland; I. Peytcheva – Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113-Sofia, Bulgaria; S. Stoykov - University of Mining and Geology, 1700 Sofia, Bulgaria

Борислав К. Каменов, Йоцо Янев, Росен Недялков, Робер Мориц, Ирена Пейчева, Албрехт фон Куадт, Станислав Стойков, Анета Зартова. Петрология на горнокредните островнодъгови рудно-магматични центрове от Централното Средногорие, България: еволюционни пътища на магмите

Резюме. Магматичните скали с къснокредна възраст от Централното Средногорие в България показват забележими вариации в своята геохимия. Настоящото изследване е съсредоточено върху общите особености в пътищата на магматичната еволюция на няколко рудно-магматични центрове: Елаците, Челопеч, Медет, Асарел, Елшица и Капитан Димитриево, разглеждани като звена от един петроложки трансект, напречен на Средногорската вулканска дъга. Целият размах на съдържанията на SiO₂ в скалите е голям (40-73%). Еволюцията от промеждутъчни към по-базични етапи е обща характеристика за повечето от центровете, но тя е усложнена от фракционна кристализация и смесване на магми. Преобладават високо-К калциево-алкалната до шошонитовата серия, като типична калциево-алкална серия се среща само в средата на трансекта. Геохимичните особености са типични за обогатен мантиен източник и са показателни за островнодъгова обстановка, свързана със субдукция. Степента на топене е оценена като малка за двата края на трансекта и по-висока – за централната му част.

Магматичната дейност е започнала в северния край на трансекта преди 92,1 Ма и постепенно се е подмладявала, като е завършила на границите с Родопския масив преди 78 Ма. Началните отношения ⁸⁷Sr/⁸⁶Sr (0,704-0,706) предполагат, че топилките са се генерирали в мантиен източник, видоизменен от добавка на корови материали. Анализите на оловни изотопи и стойностите є-Hf са показателни за увеличаване на радиогенния компонент от север на юг. Предложен е "slab retreat" модел (изправяне на субдукционната зона) за да се обясни миграцията на магматичната дейност към жлеба (обратна на класическата миграция в островните дъги).

Introduction

The Apuseni-Banat-Timok-Srednogorie Upper Cretaceous metallogenic and magmatic province is particularly well suited for a study of the genetic relationship between calc-alkaline magmatism, porphyry-style and epithermal ore deposits. The reason is that the igneous and hydrothermal products are still linked to the present-day lithosphere structure, as depicted by seismic tomography (Spakman, 1986; Wortel, Spakman, 2000; Stampfli, Borel, 2004). The magmatism in the province reveals the interaction of processes from the lithospheric scale down to individual ore-magmatic centers, and also has created fertile ore-forming magma-hydrothermal systems of great practical significance (Mitchell, 1996; Jankovich, 1997). Europe's only world-class porphyry copper deposit (Medet) and Europe's largest gold producing mine (Chelopech) are related to this magmatism (Andrew, 1997) and they are localized in the Srednogorie segment of the province in Bulgaria.

In spite of the many publications regarding the geology, tectonics and ore mineralizations in this segment there is still a shortage of basic up-to-date petrological and geochemical data. Most of the past ideas were based on unreliable geochemical data. The relative and absolute timing of this magmatism within the geodynamic evolution of the region was supposed, but not always supported well. Geochronological constraints published before 2000 were based mainly on K-Ar methods (Chipchakova, Lilov, 1976; Boyadjiev, 1981; Boyadjiev, Lilov, 1981; Lilov, Chipchakova, 1999). The general regularities were not fully decoded. They have not been used in a comparative aspect for correlation and unification of the existing schemes.

Abundant new data for the central part of the Srednogorie were accumulated during the last several years, and although valuable, they were concentrated only on specific ore-magmatic centers (Amov, 1999; Kouzmanov et al., 2001a; Peytcheva et al., 2001, 2003; von Quadt et al., 2002; 2004; Stoykov et al., 2002, 2003; Handler et al., 2003; Kamenov et al., 2003b; Peytcheva, von Quadt, 2003; Georgiev, Lazarova, 2003; Nedialkov et al., 2007). Attempts for generalizations started to appear immediately after the initial gaining of the modern cumulative sets of data and various reviews on the geology, geochemistry, and geochronology were reported (Ivanov et al., 2001; Kamenov et al., 2003a, 2004; von Quadt et al., 2003a, 2003b, 2005; Peytcheva et al., 2004).

The present study is an attempt to correlate all available, up-to-now published, reported and new data, devoted to the magmatism in the central part of the Srednogorie with the hope that it will aid the inter-regional comparisons of the magmatic history of the area. The aim of the present study is to complete this information and to a certain degree to fill the gaps in our knowledge and understanding. We believe that a compila-tion of the new high-precision geochronolo-gical data would be a proper basis for critical analysis of the geodynamic models and for inferring the provenance of the Late Cretaceous magmatism. Tracing out the following oremagmatic centers: Elatsite, Chelopech, Medet, Assarel, Elshitsa and Capitan Dimitrievo (Fig. 1) we demonstrate a transect, situated in the western part of the Central Srednogorie. Comparing and reconsidering the petrographic diversity and nomenclature, the rock-forming mineralogy, geochemical variations and magma evolution paths of these volcanic and



Fig. 1. On the left - simplified geological sketch map of the ore-magmatic centers in the studied transect located in the Central Srednogorie (from Bogdanov, 1987, modified by the authors; Panagyurishte deep-fault zone after Tsvetkov, 1976). Ages – in Ma. Vertical hatch - Rhodopes type metamorphic complexes; slanting hatch - Balkan type metamorphic and magmatic complexes; white - pre-Upper Cretaceous basement (including Hercynian granites) and post-Upper Cretaceous cover formations. IYSZ - Iskar-Yavoritza Shear Zone. Numbers in circles indicate the ore-magmatic centers. On the right - a tectonic sketch of the Alpine thrust belt in the Eastern Mediterranean (from Georgiev et al., 2001) with the line of the transect in the Upper Cretaceous volcanic arc. VIA - Vardar-Izmir-Ankara suture

plutonic centers is the main object of the paper. It will be shown that the centers share several compositional characteristics, which suggest similar to identical mantle sources. The purpose of this study is also to find some geochemical criteria, which might contribute to the understanding of mantle melting process. We would like to demonstrate how comparative investigations of various ore-magmatic centers from the transect allow clarification of some problems involving magma genesis and evolution, composition of mantle sources and the geodynamic setting. All these problems have been long discussed and are difficult to solve if individual centers are considered in isolation.

Geological setting

The Mesozoic evolution of Bulgaria was associated closely with the geodynamic development of the Northern Tethys (Sengör et al., Ziegler. 1990; Dabovski, 1988; 1991; Dabovski et al., 1991; Dercourt et al., 1993; Ricou, 1994; Stampfli et al., 2001). During the Late Cretaceous the arc magmatism was manifested from the Apuseni Mountains of Romania in the northwest, through the Timok zone in Serbia to the Srednogorie zone in Bulgaria (Vassilev, 1982; Jankovich, 1997) (Fig. 1), forming an important magmatic belt. One of the first-order segments of this belt is the Srednogorie zone divided into 3 sectors: Western, Central and Eastern (Bonchev, 1976). The zone is interpreted to represent either a product of northward subduction of the Tethian oceanic crust (present day Vardar-Izmir-Ankara suture - Boccaletti et al., 1974, Aiello et al., 1977; Hsü et al., 1977; Vassileff, Stanisheva-Vassileva, 1981; Dabovski et al., 1991) or of intra-continental rifting (Bonchev, 1976; Boyadjiev, 1979; Popov, 1981, 1996) and a zone of post-collisional I-type magmatism due to break-off of the subducted lithosphere (Neubauer, 2002). The idea about subductionrelated origin assumes that Western Vardar Ocean (opened during the Early Cretaceous and closed at the end of the Cretaceous times -Stampfli, Borel, 2004) was subducted under the continental edge of the Euroasian plate.

The crustal thickness beneath the Central Srednogorie is in the order of 32-45 km (Shanov, Kostadinov, 1992). The Upper Cretaceous magmatic products are volcanic, subvolcanic and plutonic. The sedimentary-volcanic exposures form several WNW-trending strips, filling the Panagyurishte trough (Dimitrov, 1983; Dimitrova et al., 1984) and the Chelopech syncline (Moev, Antonov, 1978), bordered by WNW trending faults.

Most of the bigger plutons are concentrated in the Maritza Intrusive Belt (Dabovski, 1968). They are intruded into the highly uplifted and eroded southern bounding blocks of Panagyurishte trough. Recent studies in the area (Ivanov et al., 2001) dealing with the kinematics of the deformation of the granitoids, favour an extensional tectonic setting in the framework of arc development for the intrusion of the plutons in the central and southern parts of the transect. The emplacement of these plutons is probably influenced by a strike-slip tectonic regime, associated with the Iskar-Yavoritza shear fault zone (Ivanov et al., 2001). This regional dextral strike-slip shear zone crosses exactly the Elshitsa centre.

The post-Cretaceous cover is formed by various, mainly terrigenous sedimentary rocks in Upper Eocene, Pliocene and Quaternary deposits of the Plovdiv graben.

Stanisheva-Vassileva (1980) and Dabovski et al. (1991) summarized the major oxide petrochemical features of the magmatic rocks in Bulgaria. Some geochemical characteristics of the REE analyzed from Upper Cretaceous igneous rocks are discussed in Boyadjiev (1984), Boyadjiev et al. (1988), Daieva, Chipchakova (1997). A subductionrelated setting was suggested and the authors generally did not find any essential differences in the concentrations and distributions of these elements in the different rock varieties and between the individual igneous centers.

The magmatic and metallogenic transect described here stretches NNW-SSE from the town of Etropole in the north to the town of Peshtera in the south. A number of positive gravity and magnetic anomalies (Dobrev et al., 1967; Tsvetkov, 1976) separate this area, interpreted as Panagyurishte deep-fault zone, from the adjacent crustal blocks. Important ore deposits are located on the intersections of this zone with WNW-oriented faults. Most of them were mined before or are in production at present (Vassilev, 1982; Bogdanov, 1987; Popov, Popov, 2000 and references therein). The ore fields and the areas of magmatic activity represent genetically related ore-magmatic foci of magmatic and hydrothermal activity.

Geology of the ore-magmatic centers (Fig. 2)

Elatsite. The Elatsite porphyry copper deposit (Bogdanov, 1987; von Quadt et al., 2002; Tarkian et al., 2003) is associated with subvolcanic bodies and dykes intruded into metamorphic rocks of Cambrian age (Haidutov et al., 1979) and into the granodiorites of the Vejen pluton (314 Ma, Kamenov et al., 2002). The economically ore mineralized part of the Elatsite deposit is close to 1 km², but judging from the area of the dyke outcrops extending from the mine the magmatic area is over 20 km². The estimated size of the magmatic chamber at depth is 7 km long and 4 km wide (Popov, Kovachev, 1996). Quartz-monzodiorite porphyries (unit 1) are the first and voluminously most important part of the early ore-related group of dykes (includes the subvolcanic body called "the big dyke" in the deposit). Granodiorite porphyries (unit 2) and aplites (unit 3) completed the ore-related stage (von Quadt et al., 2002). The syn- and close-to syn-ore dykes and subvolcanic bodies from the first three units are incorporated into this orerelated stage. The dykes from the later post-ore mafic stage comprise unit 4 (microdiorite, micromonzodiorite, diorite porphyry and their quartz-bearing varieties) and unit 5 (mainly quartz-diorite porphyry). U-Pb geochronology (von Quadt et al., 2002) revealed 92.3 Ma (unit 1), 91.84 (unit 2) and 91.42 Ma (unit 5, postore stage). A monzodiorite porphyry dyke vielded ages of 90.78 (amphibole) and 91.72

(biotite; both Ar-Ar method, Handler et al., 2003). An Rb-Sr isochron plot of biotite and feldspar from rock unit 2 yields an age of 90.55 Ma (von Quadt et al., 2002). These ages coincide partly with previous K-Ar determinations of 90-91 Ma (Lilov, Chipchakova, 1999).

Chelopech. The present day unroofed part of the volcano occupies an area of 5.5 x 3.5 km and in its central part is up to 1200 m thick (Popov et al., 2002). The Au-Cu epithermal deposit is localized within the volcano. Drilling operations cut volcanic rocks with thickness over 2000 m probably representing the neck of the volcano. It consists of the products of 3 phases (Popov, Mutafchiev 1980; Stoykov et al., 2002): dome-like bodies (andesites and latites to trachydacites), lava to agglomerate flows (andesites and latites to dacites and trachydacites) and Vozdol lava breccia neck (andesites to shoshonites and latites). The lava flows contain fully crystallized fine-grained enclaves with more basic compositions indicating mingling between two magmas. U-Pb zircon age of the rocks from the first phase is 92.2 Ma, and of the second and third ones is 91.4-91.5 Ma (Stovkov et al., 2003). A thermal-tectonic event of 89.95 Ma (biotite from andesite of lava breccia neck) was recorded by Ar-Ar methods (Handler et al., 2003).

The basement beneath the volcano consists of Cenomanian-Turonian conglomerates and coarse-grained sandstones with coalbearing interbeds, deposited on the metamorphic formations. The volcano is covered by cross-bedded sandstones with small coal lenses of fluvial or coastal origin, also of Turonian age (Stoykov, Pavlishina, 2003).

Geophysical data show the presence of a positive magnetic anomaly 20 km in diameter, which is located between the Chelopech volcano and the Elatsite intrusive dykes in the north (Popov et al., 2002). The anomaly is interpreted as a large magnetic body corresponding to a shallow magmatic chamber. These authors proposed that the Chelopech volcano and the Elatsite dykes are parts of a common



Fig. 2. Total alkalis vs. SiO₂ (TAS) (left) and K₂O vs. SiO₂ (right) diagrams for studied centers with serial trends (the arrows). The classification fields are marked as in Le Maitre (1989). The separated fields correspond to the phases in a given ore-magmatic centre (see the text). Abbreviations of the rocks (in all figures): Gb - gabbro; Gb-p - gabbro porphyry; Mgb - monzogabbro; QMz - quartz-monzonite; QM-p - quartz-monzonite porphyry; Md - monzodiorite; QMd - quartz-monzodiorite; QMd-p - quartz-monzodiorite porphyry; D-p - diorite porphyry; Qd-p - quartz-diorite porphyry; Gd - granodiorite; Gd-p - granodiorite porphyry; Gr - granite; Apl - aplite; Hyb - hybrid rocks; Cum - cumulative rock; TB - trachybasalt; Sh - shoshonite; BA - basaltic andesite; A - andesite; L - latite

volcano-plutonic structure, representing one ore-magmatic system.

Medet. The Medet pluton (Ushev et al., 1962; Chipchakova, 2002) is a small stock-like body (~3 km²) containing the first porphyry copper deposit found in Europe (Ushev et al., 1962; Popov, Bairactarov, 1979). Magnetic anomalies suggest that the pluton is located in and above the roof of a larger and deeper intrusive body. The pluton is emplaced at the intersection of the NNW-oriented Panagyurishte deep-seated fault zone with faults developed along the contact between the Paleozoic granitoids (305 Ma, Peytcheva et al., 2004) and metamorphic basement rocks (Popov, Popov, 2000).

The pluton consists of the following main ore-productive phases: (i) quartz-monzodiorite (equigranular and rarely porphyritic with transitions to quartz-monzonite); (ii) granodiorite (transitions between quartz-diorite and granodiorite are also known); (iii) porphyry quartz-monzodiorites, granodiorites, and quartz-monzonites as dykes and small intrusive bodies. Post-ore aplitic granosyenites and aplite-pegmatites cut all of these rocks. K-Ar ages are 90-88 Ma for the quartz-monzodiorite (Lilov, Chipchakova, 1999) and 88-87 Ma - for the K-silicate alteration (Chipchakova, 2002). The Ar-Ar age of amphibole from granodiorite is 85.70 Ma (Handler et al., 2003) and 90.4 Ma is that of biotite (Lips et al., 2004). New U-Pb zircon ages range 89.63-90.36 Ma (Peytcheva et al., 2004; von Quadt et al., 2004).

Assarel. The ore-magmatic center comprise the Assarel stratovolcano, numerous subvolcanic to hypabyssal bodies and dykes, and the Assarel porphyry copper deposit (Angelkov, Parvanov, 1980; Strashimirov,

1993; Popov et al., 1996; Strashimirov et al., 2002), located in the central part of the stratovolcano. The basement consists of gneisses and Paleozoic plutonic rocks. The stratovolcano encompasses an area of 15-18 km². The following volcanic units are distinguished (Nedialkov et al., 2007): (i) andesites to latites; (ii) basaltic andesites with small mafic rounded enclaves; (iii) subvolcanic andesites to dacites. A small and strongly hydrothermally altered subvolcanic body is intruded into the central part of the deposit. Several dykes outcrop in the northern part and are less affected by the alteration: (i) quartz-diorite to quartz-monzonite porphyry; (ii) quartz-monzonite porphyry to granodiorite porphyry; (iii) granite porphyry (Nedialkov et al., 2007).

U-Pb zircon ages are 90 Ma for a sample from the subvolcanic andesite and 90.23 Ma for the porphyritic quartz-diorite (von Quadt et al., 2003a, b; Nedialkov et al., 2007).

Elshitsa-Boshulya (called Elshitsa in all diagrams and tables). This is the largest intrusive body (ca. 125 km²) outcropping in the transect, according to geophysical interpretations and drillings (Boyadjiev, Chipchakova, 1962; Dabovski, 1964; Ivanov et al., 2001). The pluton is part of the Elshitsa-Radka ore field, which includes the epithermal deposits Radka, Elshitsa, Chervena Mogila and the porphyry copper deposits Tsar Assen and Vlaikov Vrah (Bogdanov et al., 1970; Tsonev et al., 2000). Volcanic and subvolcanic exposures accompany the plutonic rocks and they are localized within the deformed Upper Cretaceous depressions. The pluton is situated on the junction of the Panagyurishte NNW deep-fault zone (Tsvetkov, 1976) with WNW faults. Country rocks of the pluton are

metamorphic rocks and Paleozoic granitoids (Dabovski, 1964). Earlier authors (Boyadjiev, Chipchakova, 1962) favoured the assimilationcontamination processes as responsible for the marginal part of the pluton, believed to consist of an early phase of gabbro, hybrid varieties, granodiorite, granite, granophyres. Vein type granitoids, aplites, and several group dykes follow the main intrusive rock types. According to new observations (Ivanov et al., 2001; Georgiev, Lazarova, 2003) the pluton is part of a big laccolith-like layered intrusion formed as a result of mingling and mixing of mafic and felsic magmas in a large granitic magma chamber. The dating of different parts of the system also supports this interpretation. U-Pb zircon ages of 86.62 Ma from the granites and of 86.11 Ma from the Elshitsa subvolcanic dacites are very close (Peytcheva et al., 2003). In the Boshulya part, the level of the system with different degrees of mingling and mixing of the granitic and gabbroic magma, an age of 84.6 Ma was determined for the granodiorites, and 82.16 Ma for the gabbros (Peytcheva, von Quadt, 2003). Andesite breccia in the volcanic rocks, accompanying the pluton records an event of 80.21 Ma (Ar-Ar method on hornblende, Handler et al., 2003). A Re-Os age of molybdenite from the porphyry coppr deposit Vlaikov Vrah is ca. 80 Ma (Kouzmanov et al., 2001b).

Capitan Dimitrievo pluton. The pluton contains pyrite-chalcopyrite small-scale mineralization of no economic significance and is situated in the southernmost end of the studied transect. Intruded into the basement of the Rhodopian lithotectonic units (gneisses and marbles), near to the border area with Srednogorie zone, the pluton represents a fragment (~18 km²) of a larger igneous body. prevoius (Dabovski, The ideas 1969: Boyadjiev, 1986) postulated that the pluton is a multy-stage body crystallized inward. New studies (Kamenov et al., 2003b) revealed that the petrographic diversity resulted from magma mixing process between granodioritic or monzonitic and gabbro magmas, combined with fractional crystallization. A strong hightemperature syntectonic foliation is found. The range of the rocks is gabbro, monzogabbro, monzodiorite, quartz-monzodiorite, granodiorite, and aplite. The geochemistry confirms the presence of two trends – a high-K calcalkaline and a shoshonitic one. U-Pb dating on single zircons from the quartz-monzodiorite, the main rock variety of the pluton, is 78.7 Ma. The 206 Pb/²³⁸U age of two most concordant points from the gabbro and monzogabbro is calculated as 78.6 Ma (Kamenov et al., 2003b).

Rock-forming mineralogy

The volcanic rocks are generally highly porphyritic with intergranular or pilotaxitic textures predominating in the groundmass. These rocks include microlitic plagioclase, amphibole, Fe-Ti oxides (titanomagnetite, magnetite, and ilmenite), rare clinopyroxene, and occasional alkali feldspar and biotite in the groundmass. Phenocrysts of plagioclase, amphibole, minor biotite, titanite and occasionally clinopyroxene are present in variable proportions. The accessories are apatite, zircon, and Ti-magnetite. The plutonic varieties are medium-grained, essentially equigranular and rarely porphyritic. The main rock-forming minerals in the gabbro, gabbrodiorite and diorite are plagioclase and clinopyroxene. The modal quantities of quartz, orthoclase and biotite increase in the intermediate and acid plutonic phases. The accessories are the same as in the volcanic rocks, but rarely may include allanite as well. Details of the mineralogy are presented in Table 1. The rock-forming composition is determined on the base of more than 800 new microprobe analyses.

Mafic fine-grained enclaves are observed in some of the lava flows (Chelopech, Assarel) and in Elshitsa-Boshulya and Capitan Dimitrievo plutons. They contain the same minerals, but their composition is of a different chemistry and usually in disequilibria with the host rock. Rounded and chilled rims of the enclaves are typical. *Plagioclase* spans much of the crystallization history throughout the magmatic series (Fig. 3), generally decreasing in anorthite composition from basic to acid rocks (from An_{80} to An_{15}). An interruption of this tendency is observed in the later dyke stages (Elatsite, Capiatan Dimitrievo) and Assarel basaltic andesites. Sharp increasing of the anorthite composition in some of the intermediate zones is observed and it is due to magma-mixing processes.

Amphiboles are nearly ubiquitous both as phenocrysts and groundmass phases in the volcanics or as rather big anhedral grains in the plutonic rocks. The presence of amphibole is unusual for arc volcanic rocks. In some of the samples amphibole is the dominant phase. Amphiboles in the ore-productive dykes in Elatsite, in Chelopech volcanics, in basaltic andesites of Assarel, and in some of the Capitan Dimitrievo monzogabbros and in the granodiorites are classified as magnesiohastingsite and edenite (according to the classification of Leake et al., 1997 - Fig. 4). Most of the amphibole compositions in the basic phases are tschermakitic, but the more evolved magmatic phases contain usually magnesiohornblende or magnesiohastingsite and edenite with higher Si p.f.u. Tschermakite and magnesiohornblende are also characteristic species for the post-ore dykes of Elatsite, in Chelopech lava flows and in the most of the rocks of Medet. Assarel and Capitan Dimitrievo centers. Vozdol lava breccia amphiboles in Chelopech fall near the boundaries of the pargasite, ferropargasite, ferroedenite, hastingiste and magnesiohastingsite fields. Zoning within amphiboles is not systematic. Reverse zoning (with rims that are lower in Fe, Ti, Al and higher in Si and Mg) is more common than normal zoning. Two groups of amphiboles with different alkalinities are distinguished: (i) more-alkaline $[(Na+K)_A>$ 0.5 p.f.u.] encompassing the ore-related early dykes of Elatsite, Chelopech volcanics, and Capitan Dimitrievo granodiorites, and (ii) lessalkaline $[(Na+K)_A < 0.5 \text{ p.f.u.}]$ including the post-ore dykes of Elatsite, all Medet plutonic rocks, most of Assarel and most of the Capitan Dimitrievo plutonic rocks (gabbro and quartzmonzodiorite).

Clinopvroxene is the dominant mafic phase in the gabbros of Elshitsa and Capitan Dimitrievo. Pyroxene compositions for individual centers plot as tight clusters on a Ca-Fe-Mg diagram. The clinopyroxene from the orerelated stage of the dykes in Elatsite and some clinopyroxenes (cpx^{II}) from Capitan Dimitrievo have similar composition and are classified as diopsides. The clinopyroxenes from the postore stage dykes in Elatsite and from the main and wider presented generation (cpx^I) in the gabbro from the Elshitsa and Capitan Dimitrievo centers are augites. None of the rocks show a consistent pattern of intracrystal pyroxene zonation, except some Capitan Dimitrievo augites, in which the rims are more calcic. The vast majority of our analyses record crystallization from a liquid comparable to the emplaced gabbroic magma (Cr₂O₃<0.10 wt.%, average Mg[#] 68-71, Al/Ti 41-45). However, there are some clinopy-roxene grains in Capitan Dimitrievo cored by low-Cr₂O₃ crystals and rimmed by moderate-Cr₂O₃ zones $(Cr_2O_3 0.10-0.15; Mg^{\#} 72-75; Al/Ti 25)$. The last ones are observed as small individual crystals and their presence suggests a much more complex open-system evolution and probably multiple replenishment events in the magma chambers.

Biotite shows little if any zonation within grains. Most of the biotite from the dykes and from the ore-productive magma centers is partly to entirely chloritized. The variations in the averaged Mg[#] values are small and usually they range between 0.43-0.55. The biotites from the Capitan Dimitrievo center have some differences between rock varieties in their ^{IV}Al in the biotite p.f.u., probably related to the depth of the crystallization.

Elatsite dykes with ore-related sta Batsite dykes with granodiorite po porphyry copper post-ore stage: deposit post-ore stage: Chelopech volcano shoshonite, ma with Au-Cu (Pb-Zn) trachydacite	ze: 1, quartz-monzodiorite porphyry; 2, rphyry; 3, aplite 4, microdiorite; 5, quartz-diorite porphyry inly latite and andesite, dacite to	pl, cpx (Wo _{44.5-48} , Mg [#] 73-74), Mg-hastingsite (Si 5.91-5.93, Mg [#] 55-59) pl, cpx (Wo ₄₀₋₄₂ , Mg [#] 73-74), Mg-hornblende and tschermakite (Si 6.5-7.58, Mg [#] 70-85)
		1, cpx (Wo ₄₀₋₄₂ , Mg [#] 73-74), Mg-hornblende and tschermakite (Si 6.5-7.58, $Ae^{\#}$ 70-85)
	1	pl, Mg-hastingsite, hastingsite, pargasite, Fe-pargasite to Fe-edenite (Si 6.4- $6.6, \text{Mg}^{ \#}$ 48-67)
	claves	pl, Mg-hastingsite (Si $5.9-6.1$, Mg ^{\pm} 70-84)
Medet pluton with <u>pre-ore st</u> porphyry copper	<i>pre-ore stage</i> : quartz-monzodiorite; granodiorite <i>post-ore stage</i> : quartz-monzodiorite porphyry,	pl, Mg-hornblende (Si 6.6-6.8, Mg [#] 54-74 core, 53-59 rim); pl, Mg-hornblende (Si 6.7-7.4, Mg [#] 65-67 core, 56-64 rim), K-feldspar
deposit granodiori	granodiorite porphyry, aplite	$(Or_{84}Ch_{0.5-1})$
Volcanic r Assarel stratovolcano basaltic an	<i>Volcanic rocks</i> : 1, amph-andesite to latite; 2, cpx-amph. basaltic andesite; 3, bi-amph. andesite to dacite	1) pl, amph (Si 6.6-7.0, Mg [#] 55-65); 2) pl, amph (Si5.9-6.2, Mg [#] 66-77), cpx (Wo ₃₅₋₄₃ , Mg [#] 76-78); 3) pl, amph (Si 6.3-6.6, Mg [#] 61-66), bi, qz
rphyry copper		
deposit Plutonic re monzonite	<i>Plutonic rocks</i> (porphyry): quartz-diorite, quartz- monzonite and granite	
Elshitsa pluton with Cu gabbro; hy	gabbro; hybrid rocks (quartz-monzogabbro, quartz-	pl, bi(^W Al 2.5-2.6, Mg [#] 53-56, Ti 0.375), amph , cpx (Wo ₄₀₄₄ , Mg [#] 65-73)
	monzonite, quartz-diorite); granodiorite, granite,	
phyry copper deposit granophyre, aplite		
	gabbro and monzogabbro;	pl, amph (Si 6.2-6.9, Mg [#] 59-64), bi (^{IV} A1 2.62-2.75, Mg [#] 49-52) cpx ¹ (Wo ₄₂₄₅ ,
copper mineralization granodiori	granodiorite; K-feldspar $(Or_{88-92}, Cn_{0-0.9})$;	pl, amph (Si 6.7-6.9, $Mg^{#}$ 48-54), bi (^{IV} Al 2.14-2.56, $Mg^{#}$ 43-55) $cpx^{II}(W_{0,5,49})$

	~
	5
1	e
	11
-	5
	3
- 1	Ξ.
	2
	2
i	Ξ.
- !	50
	2
- 1	2
-	5
į	5
1	2
3	5
4	5
1	С,
3	2
-	50
. 1	õ
2	Ξ.
- 3	2
	5
;	ž
- 1	-
	Ξ
ł	50
	20
•	3
	13
. 1	0
7	7
1	Ż.
1	2
1	0
	-
	σ
	2
	σ
;	2
-	Ζ,
1	d.
1	2
j	2
	δv
	2
	3
1	š
1	4
1	e
	2
1	S
1	2
5	Ò.
5	J
	-
	Ð
7	Ĕ
7	Ħ
F	

Plagioclase anorthite composition is demonstrated in Fig. 3; $Mg^{\#} = 100 Mg/(Mg + Fe) p.f.u.$; Si and ^{IV}Al are coefficients for formula unit (p.f.u.); Wo - wolastonite, Cn - celzian and Or - orthoclase components



Fig. 3. Plagioclase compositional ranges based on microprobe results, displayed for the rocks of the studied centers. Rock abbreviations are as in Fig. 2



Magnetite is Al-, Mn-, Ca-, and Cr-poor. Ti-rich magnetites are recorded in the volcanic rocks and Ti-poor ones in the plutonic rocks, where they generally associate with ilmenite with moderate quantity of pyrophanite and hematite exsolutions. The amount of oxidation exsolution is rather high within the deposits, in response to post-emplacement vapor-phase alteration. Magnetite commonly exhibits oxidation to titanite and maghemite around cracks and the rims of grains.

Potassium feldspar is orthoclase, Ba- and anorthite-poor. All post-magmatic K-feldspars in the porphyry copper deposits are microclines.

The existence of rough layering in the rocks, abundant mafic chilled enclaves and cumulative pockets of mafic minerals, as well as typical gabbro plume-like strips are characteristic features in most of the outcrops. Cores of hornblende and plagioclase in disequilibria with the evolved magma, complex normal, oscillatory and reverse zonings, patchy replacements of plagioclase and clinopyroxene, some saw-tooth resorptions, the unusual peaks of anorthite composition in some of the intermediate zones of the feldspars (Fig. 3) are mineralogical indications of magma-mingling and magma-mixing phenomena. All these together with the occurrence of many mapped variegated transitional petrographical varieties support this idea as likely and well grounded.

Fig. 4. $(Na+K)_A vs.$ Si (p.f.u.) microprobe data for amphiboles from individual ore-magmatic centers. Fields are from Leake et al. (1997). Amphibole abbreviations: Ed - edenite; MHa - magnesiohastingsite; MHb - magnesiohornblende; Tsc – tshermakite.

Rock abbreviations: Bi-Hb A - biotite-amphibole andesite; the other abbreviations are as in Fig. 2, (c - core; r - rim)

Center	Rock type	P, kbar	Rock type	P, kbar
Elatsite	post-ore dykes	4.0-4.5	ore-dykes	6.0-6.5
Chelopech	volcanic rocks	4.2-5.1	enclaves	6.0-6.5
Medet	plutonic rocks	4.0-4.5	-	-
Assarel	andesites	4.0-4.3	basaltic andesites	6.0-7.0
Elshitsa	acid plutonic rocks	3.5-4.2	gabbro	6.0-6.5
Capitan Dimitrievo	plutonic rocks	3.9-4.3	mafic dykes	6.5-7.0

 Table 2. Barometric estimates for initial hornblende crystallization

Geobarometric estimations

On selected amphibole samples with temperature estimations (Blundy, Holland, 1990) close to the isothermal solidus of the systems involved we applied the empirical geobarometer of Johnson and Rutherford (1989) and the generalized results are shown in Table 2. Pressure calculations cluster in two levels of crystallization, corresponding to depths of approximately 10-12 km and 15-20 km. The deepest crystallization conditions are recorded for the mafic enclaves in Chelopech, ore-related dykes in Elatsite, basaltic andesites in Assarel and for the mafic dykes in the Capitan Dimitrievo pluton. Relatively shallower crystallization depths are recorded for the acid component of the mixing process in Elshitsa (Ivanov et al., 2001). All these data are in concordance with the recalculations of the positive magnetic anomalies (Cvetkov et al., 1978; Dobrev et al., 1986) postulating that the lower boundaries of the magnetic bodies are localized at depths of 15-18 km.

Geochemistry

Although several papers discuss the geochemistry of the magmatic rocks in the transect (Boyadjiev, 1984, 1986; Boyadjiev et al., 1988; Daieva, Chipchakova, 1997), most are based on analyses of few samples, performed in times long ago and by not quite reliable methods. Often these papers include major oxides only (Stanisheva-Vassileva, 1980; Dimitrov, 1983). This summary incorporates the principal data of those published major oxides analyses, but is mainly based on

the large recently presented and unpublished data sets compiled by the authors, including *REE* and trace elements (Stoykov et al., 2002; von Quadt et al., 2002; Kamenov et al., 2003a; Nedyalkov et al., 2007). A total of 103 new whole-rock silicate analyses for major oxides, 98 new analyses for trace elements, including rare earth elements (REE) and over 780 electron microprobe analyses on rock-forming minerals were used in this compi-lation. The trace and *REE* determinations were carried out using the laser ablation ICP-MS method. Major oxides were performed mainly by wet silicate analysis. Some examples of the most important representative chemical analyses selected from all the ore-magmatic centers are given in the Appendix.

Major elements

A wide range of magmatic compositions extending from basic (cumulates, gabbro) through intermediate (quartz-diorite, quartzmonzodiorite, quartz-monzonite; basaltic andesite, andesite, shoshonite, and latite) to acid (granodiorite, granite, aplite; dacite, and trachydacite) rocks is established. On a TAS diagram, the igneous rocks of the individual magmatic centers plot on continuous trends (Fig. 2), usually in the silica saturated fields, in some of the centers also in silica oversatured fields. The high-K to medium-K trends predominate almost in the whole transect. The widest spread of the SiO₂ contents is observed in the plutonic rocks. The volcanic rocks, compared to plutonic ones, show more restricted range in their composition, the Chelopech rocks being the most monotonous

without basic representatives. Compositional resemblance is revealed among the trends of all magmatic centers and this is a conclusive argument in favour of their common origin. Most of the samples from Assarel fall within the Medet trend with the exception of the basaltic andesites, which are more basic and typically calc-alkaline. In spite of the notion of some geophysists (Grigorov, 1961) and some of the petrologists (Boyadjiev, Chipchakova, 1962) that Elshitsa and Capitan Dimitrievo plutonic centers could be parts of a common batholith under the cover of the younger sedimentary formations, we have found chemical differences in their magma evolution paths. Two trends are revealed in the Capitan Dimitrievo data, which are not observed in Elshitsa pluton. Two trends are revealed also for the ore-related and post-ore dykes in Elatsite.

A typical calc-alkaline trend is established only in the central part (Elshitsa pluton and partly in Assarel center). Going to the north (Chelopech-Elatsite) and to the south (Capitan Dimitrievo pluton) high-K calc-alkaline and even shoshonitic trends prevail. The bilateral decreasing of the general alkalinity of the magmas toward the central part of the transect is a remarkable compositional feature of the transect.

Some of the northern centers (Elatsite, Chelopech, Assarel) reveal a chemical evolution trend which is characterized by more silicic early stage and more mafic late activity. Probably the existence of chemically zoned magma chambers could explain this special feature.

REE-patterns

The chondrite-normalized *REE*-patterns of the magmatic rocks in the transect are generally very similar suggesting a common genetic relationship. The patterns (Fig. 5, Fig. 6) resemble closely those of typical island-arc subduction-related magmas (Thorpe et al., 1976) with enrichment of light *REE* (*LREE*) over heavy rare earth elements (*HREE*) and

relatively flat distribution of the latter is sometimes observed. Light *REE* concentrations and the slopes of the *REE* patterns increase steadily from medium to high-K suites. The *LREE*–fractionation is moderate ($La_N/Yb_N=3-8$ in the gabbro and 8-20 in the evolved acid rocks). The most enriched rocks are typical for the magmatic centers located in both ends of the transect (namely Elatsite and Capitan Dimitrievo). Very weak *HREE* fractionation is demonstrated only in the Chelopech volcanic rocks.

In contrast to the data published by Boyadjiev et al. (1988) and Daieva and Chipchakova (1997) most of the patterns do not show negative Eu-anomalies, suggesting that no essential plagioclase fractionation or plagioclase-bearing sources were involved in magma generation. The exceptions are the unit 3 (aplite) and unit 5 (quartz-diorite porphyry) of Elatsite, the granophyres of Elshitsa and some quartz-bearing varieties of the Capitan Dimitrievo patterns, where these anomalies are weakly expressed. Eu anomalies >5% are uncommon and this similarity in behaviour between Eu and the other REE indicates high Eu^{3+}/Eu^{2+} , as well as Fe^{3+}/Fe^{2+} ratios in our orogenic rocks (Gill, 1981). The lack of Eu anomaly in Chelopech volcanic rocks assumes also the presence of a chemically zoned magmatic chamber there (Stoykov et al., 2002). Probably, judging from the decreasing SiO₂ in the later rocks (Fig. 2) in some of the other centers, the same speculation is also valid.

Trace-element distributions

The general trace element characteristics of representative samples from the magmatic rocks in the transect are shown in Fig. 7 and Fig. 8 as a series of multi-element plots normalized to the average MORB value of Pearce (1983). All patterns are typically enriched in *LILE* and depleted in the *HFSE* and in the compatible (Sc and Cr) elements, characteristic of subduction-related magmas (Pearce, 1982). The clear negative (relative to the neighbouring Ce and Th normalized values) anomalies



Fig. 5. Chondrite-normalized *REE*-patterns for representative samples from the individual ore-magmatic centers. Bi A - biotite andesite; Bi-Hb A - biotite-amphibole andesite; the other abbreviations are as in Fig. 2

for Nb are indicative of the island-arc settings (e.g. Saunders et al., 1980; Thompson et al., 1984). The strongest Nb-depletion (in relation to MORB values) is noted for the gabbro of Elshitsa and Capitan Dimitrievo centers (0.2-0.3 x MORB).

The $(Ta/Nb)_N$ ratio may reflect also *HFSE* fractionation in the source and it is always > 1 in the transect rocks, being even quite higher in the Elshitsa center.

An interesting peculiarity of the MORBnormalized models is that they are enriched not only in LIL elements, but at the same time, though in smaller degrees, in all elements from Ce to Sm, similar to some transitional and anomalous volcanic-arc suites (Pearce, 1982). The exception is Elshitsa center, where the basic rocks show the typical calc-alkaline signature of depleted contents of Zr and Hf relative to MORB. The most plausible explanation of this peculiarity is that the magma source of the magmatic rocks in the transect had been enriched before the Late Cretaceous subduction or that mixing between two differing in their generation depths magmas occurred in the transect. The tapping of sublithospheric source areas probably provided the components in excess of normal MORB abundances.

There are some characteristic differences between the volcanic and plutonic rocks. Volcanic rocks from Chelopech and Assarel show positive peaks for Hf and the later, more evolved plutonic rocks show a typical Baminimum.

The ratio (Rb/Th)_N generally decreases from northern to the southern centers, reflecting the decreased significance of the crustal component in the younger magmatic centers. In Elatsite, Chelopech, and Assarel and in the quartz-monzodiorite from Medet this ratio is close to 1 indicating a stronger Rb-bearing fluid addition to the source of the porphyry system. Contrarily, in Elshitsa and in Capitan Dimitrievo it is clearly < 1.

The normalized abundances (relative to MORB) of phosphorus are between 0.8 and 3 in the northern centers (all samples in Elatsite,



Fig. 6. Chondrite-normalized *REE*-patterns for representative samples from Elshitsa and Capitan Dimitrievo centers. Rock abbreviations are as in Fig. 2

Chelopech and Assarel and the monzonite porphyry in Medet). In Elshitsa they are 0.6 up to 2, but in the southernmost center, Capitan Dimitrievo, the enrichment of P is the highest -(4-8 x MORB). Clear fractionation of P relative to Zr from the north to the south of the transect is revealed. The ratio $(P/Zr)_N$ is ≈ 1 in Elatsite, a bit > 1 in Chelopech, Medet and Assarel, clearly >1 in Elshitsa plutonic rocks and >>1 in the Capitan Dimitrievo gabbro. The corollary is that a progressive Zr-depletion and P-enrichment of the magmas is established from north to south.

Sc-depletion, relative to all *LILE* and a large part of the *HFSE* is rather strong in the whole transect. Relative to the neighbouring Yb and Cr elements clear Sc depletions appear in unit 3 of Elatsite, felsic rocks in Medet and

in Elshitsa, and in the quartz-monzonites of Capitan Dimitrievo. The only case of distinct Sc-enrichment relative to the neighbouring elements and relative to MORB is found in the Elshitsa gabbro, where the hybrid rocks show also a clear positive Sc-anomaly.

Distinct and marked negative Ti-anomalies are present almost in all MORB-normalized patterns. The post-ore dykes in Elatsite are characteristic for their slightly negative Tianomalies, in comparison with the strongly negative Ti anomalies in the ore-productive stage of dyke formation. Negative Zr-anomalies also are typical for most of the centers. The lack of Zr-anomalies in comparison to Hf and the weakest Ti-anomalies is a specific peculiarity of the Elshitsa rocks (the exception is the felsic component in the center).



The low Ti and Zr normalized abundances in the rocks require the availability of stable Tiand Zr-phases in the mantle source (Pearce, Parkinson, 1993).

Negative Cr-anomalies are observed in most of the magmatic centers, but in the Elshitsa center Cr is least depleted, relative to MORB in contrast to the other centers, where stronger Cr-depletions are found. This finding implies that a spinel-lherzolite source in Elshitsa is highly probable (Pearce, Parkinson, 1993) and we have to determine the reason for this weak Cr-depletion.

Two different trends are recognized regarding Sr and K within the transect. The first one is when the ratio $(Sr/K)_N \ll 1$ (Elatsite, Chelopech, Assarel, Medet, and Capitan Dimitrievo centers). One of the strongest Srdepletions for the rocks in the transect is noted in the Elshitsa granites. This pattern is typical for calc-alkaline arc-derived magmas with transitional alkalinity (Pearce, 1982). It expresses the lower incompatibility of Sr in comparison to K. The second pattern $[(Sr/K)_N > 1]$ is revealed in the basaltic andesites of Assarel, in the gabbro of Elshitsa and Capitan Dimitrievo plutons. This pattern is characteristic for the tholeiitic affinity in the basic members of the rock suites. We use this trend in one of the next paragraphs to select the most primitive rocks, suitable for more detailed geochemical study of the source characteristics.

REE and trace element evidence for magma-mixing

Magmas of diverse composition often coexist within reservoir systems and sometimes even erupt simultaneously. The field evidence

Fig. 7. MORB-normalized diagrams for representative samples from individual ore-magmatic centers. Normalization values after Pearce (1982). Rock abbreviations are as in Fig. 2



Fig. 8. MORB-normalized diagrams for representative samples from Elshitsa and Capitan Dimitrievo centers. Rocks abbreviations as in Fig. 2

described above in the centers Chelopech, Assarel, Elshitsa and Capitan Dimitrievo are in line with the model proposed by Wiebe, Collins (1998) and give strong arguments for magma mixing during rock genesis. Some of these arguments have already been published for the Elshitsa (Ivanov et al., 2001; Georgiev, Lazarova, 2003; Peytcheva, von Quadt, 2003a) and Capitan Dimitrievo centers (Kamenov et al., 2003). The most obvious and widespread feature of the rocks indicative of mixing, is disequilibria among their rock-forming minerals. Mineral compositions out of equilibrium with their bulk host, reverse and complex zonings, resorption textures and other mineralogical features, have already been discussed in the section "Rock-forming mineralogy". The mineralogical arguments for mixing (Vernon, 1990) are strongest in the Elshitsa and Capitan Dimitrievo centers, where disequilibria features are multiple and consistent throughout simultaneous emplacements.

An important chemical argument for mixing, in addition to the petrographical and

mineralogical features, is its ability to explain some trace element concentrations in excess to those predicted by crystal fractionation. Binary mixing behaviour is internally consistent with the *REE* characteristics of the basic and acid rock varieties within the transect. The withincenter differences among basic rocks, such as incompatible element abundances and LREE/HREE ratios are also reflected in the general *REE*-characteristics of the silicic rocks present in some of the centers. Therefore, these differences, as well as ⁸⁷Sr/⁸⁶Sr ratios, which are roughly identical in associated basic and silicic rocks, are preserved throughout diffeentiation processes and are not noticeably modified by crustal assimilation (Peytcheva et al., 2001, 2003, 2004; von Quadt et al., 2003a, 2005). Magma-mixing is especially well expressed chemically in the Elshitsa (Ivanov et al., 2001; Georgiev, Lazarova, 2003) and Capitan Dimitrievo (Kamenov et al., 2003) centers. Mingling-mixing is supported by their REE patterns (enlarged in Fig. 6) where the hybrid rock varieties (e.g. monzodiorite) have patterns placed between the possible endmember components for the LREE and in some cases MREE (Capitan Dimitrievo, f. i.). It is also clear from the plot that mixing alone is not viable in explaining the geochemical variations among the hybrid varieties. In Elshitsa the MREE- and HREE-distributions are enriched more than both of the granites and the gabbro samples. Monzonite rocks from Capitan Dimitrievo are also difficult to be explained by simple mixing of basic and acid melts, because their HREE-distributions are at the same level as the ones from the acid rocks. The HREE and some of the MREE are concentrated more in the mafic minerals and a fractionation of these minerals during the mixing process could produce these peculiarities. These elements owe their distributions to a different process and a mixing together with fractionation crystallization (MFC) does not contradict the available geochemical data. Thus, the more

57

complex MFC process is evidenced not only by the mineralogy and petrology but by geochemistry of the *REE* as well.

The presence of two (different) MORBnormalized patterns is in concordance with the idea of mixing of two parental magmas, probably derived from different crust-mantle levels. The increased influx of slab-derived hydrous fluids could stabilize feldspars and introduce fluids rich in potassium components into the mantle wedge (Hickey et al., 1986), thus bringing about Sr << K in the first pattern. The lower f_{O2} during the crystallization of the basic magmas is compatible with the second pattern of Sr and K distribution [(Sr/K)_N>1] (Osborn, 1979) and requires a deeper source level. The barometric estimations (Table 2) record also two levels of crystallization in agreement with the idea of different sources of the basic and acid components of mixing. The existence of both members of the mixing is evident in the geochemistry of the trace elements. The MORB-normalized patterns for typical samples from Elshitsa and Capitan Dimitrievo (Fig. 8) reveal that the hybrid rock varieties, defined by other petrographical and mineralogical criteria, show patterns in their LIL-elements (K, Rb, Ba, Th) between the endmember components. The elements Nb, Ce, Zr, Hf, Sc and Cr in Elshitsa and Nb, Ce, Zr, Hf, Sm, Y and Yb in the Capitan Dimitrievo hybrid rocks are also consistent with a process of mixing. Since the normalized abundances of the elements Ta, P, Sm, Ti, Y and Yb in Elshitsa case lie above the patterns of both possible mixing components, a simple twocomponent mixing as the only process of the magma evolution path does not explain the overall behaviour of these elements. The same is valid for the Capitan Dimitrievo example, where the behaviour of the elements Ta, P, Ti, and Cr is not in line with such a simple process of magma evolution. Fractionation of apatite, Ti-Fe oxides and some other accessories could be responsible for this feature. The small



Fig. 9. Discrimination diagrams after Müller et al. (1992) for representative samples from individual oremagmatic centers. IOP - initial oceanic arcs; LOP - late oceanic arcs; CAP - continental arcs; PAP - postcollision arcs; WIP - within-plate setting

difference between both cases, not compatible with simple mixing is due to different proportions of the mixing components and to a certain extent to different progress of the fractionation in the examples. Magma mixing is undoubtedly accompanied by crystallization and dissolution, so that simple binary mixing models are not likely and the effects of fractionation and mixing were superimposed. A combination between mingling-mixing and fractional crystallization is required (MFC) to explain better the geochemical variations. This more complex magma evolution process may be adopted to fit the trace-element distributions and in some centers, like Capitan Dimitrievo case, even three-component mixing (Kamenov et al., 2003b) is a possible viable mechanism.

A more refined determination of the mixing mechanism awaits more detailed isotope information, specially designed sampling and experimental work. However, using the estimates of timing, total pressure, mineralogical, petrographical and geochemical features of the rocks, we have at least an idea of these processes, leading to new thoughts on the origin of the magmatic rocks in the studied area.

Geodynamic discriminations

The applied tectonic discriminations (Fig. 9, 10) supplement the conclusions from the geochemistry for a continental-margin subduction-related setting. Most of the samples generally plot in the continental-arc potassic fields (Müller et al., 1992), although a small overlap with ocean-floor fields (late oceanicarc) occurs for some of the basic rocks from the Elshitsa and Capitan Dimitrievo centers (Fig. 9). The abundances of some HFSE (according to Fig. 10 from Thiéblemont and Tégyey, 1994) classify the samples mainly in subduction-related settings. Certain dispersion of the samples in the discrimination plots is consistent with the idea, suggested by the geochemical data, for different sources of the basic and acid mixing magmas or their differentiation.

Isotope and age characteristics

Sr-, Nd-, Pb- and Hf isotope tracing on whole rocks and on minerals suggest a mixed crustmantle origin of the parental magmas



Fig. 10. Nb_n/Zr_n vs. Zr discrimination diagram (according to Thiéblemont and Tégyey, 1994) for representative samples of rocks from individual oremagmatic centers. Normalization is to the primordial mantle values of Zr 9.714 ppm and Nb 0.615 ppm. Settings: A - within-plate; B - collision-related; C - subduction-related

(Peytcheva et al., 2001, 2004; Kamenov et al., 2003a, 2004; von Quadt et al., 2003a, b, 2005). Initial Sr ratios (corrected for the intrusion age) range between 0.70401 (Boshulya gabbro) and 0.70583 (granodiorite porphyry of Vlaykov Vrah from the Elshitsa magmatic center). The Sr-isotopic trend from north to south is quite different. ENd value increases also towards southern centers and it seems that the northern centers contain higher input of crustal contamination. Available ϵ -Hf_{T-90} data lie in the range between -0.03 and +10. Specific values range from +0.2 to -3.2 (T~90 Ma) in Assarel to about +5 in the north (Elatsite and Chelopech) and increase up to +9.9 (T~80 Ma) in the south. The inherited zircons (and these with inherited cores) record mainly Early Paleozoic crustal sources (most likely protoliths of the hosting metamorphic rocks), but in some cases the Hercvnian granites have also been assimilated (von Quadt et al., 2003a). The negligible influence of the assimilated rocks on the Sr isotope characteristics is due possibly to the specific characteristics of their protoliths (low Rb/Sr ratio of a young crust of mixed crust-mantle origin). These already published isotope data provide support also for the idea that the parental magmas originated from an enriched mantle source with crustal contamination indicated by moderately radiogenic Pb. The decrease of the radiogenic components in younger centers to the south is probably the result of lesser amounts of crustal material assimilated in the magmas (von Quadt et al., 2003a, 2005). Von Quadt et al. (2005) proved that the Upper Cretaceous rocks could not be interpreted by a single model involving assimilation of old Variscan basement.

The recently performed high-precision U-Pb single zircon and Ar-Ar datings in the Panagyurishrte district (Kamenov et al., 2003a, 2004; von Quadt et al., 2003b, 2005; Handler et al., 2003) indicates that the magmatic activity started on the north (Elatsite and Chelopech) at 92.1 Ma and progressively decreased to the south, where it finished at 78.7 Ma (Capitan Dimitrievo pluton), so the time span of the magmatism was around 14 Ma.

Discussion

The petrological and geochemical data of the individual ore-magmatic centers gave support for assumptions for the relative contribution of the various sources in magma generation processes and the character of the mantle. Below we try to find some lines of evidence to constrain the degree of melting, as well as the evolution of these parameters along the transect length, i.e. across the island-arc system.

Source characteristics

There is a general consensus that magma generation in island-arc settings reflects contributions of various components - mantlederived and subduction-related. The estimation of the relative contributions to the magmas depends on the physical model for magma generation in the volcanic arc. We accept as likely the model (Davies, Stevenson, 1992; Kay, 1980; Pearce, Peat, 1995) that the subduction component reaches the fusible part of the mantle by a three-stage process: (i) aqueous fluid recharge due to breakdown of hydrous minerals at depth (Tatsumi et al., 1983); (ii) metasomatism of the mantle lithosphere; (iii) aqueous fluid migration to the site of melting. We assume that slab-induced flow may be locally reversed beneath the arc itself, allowing mantle decompression to contribute to melt generation (Ida, 1983).

With the purpose of estimating the contributions of the mantle and the slab we examined only the most primitive rocks (MgO>5 wt.%) from the individual centers. Although magmas at 5 wt.% MgO are not primary, they lie not far away from the olivine – Cr-spinel cotectic and are fairly close to primary compositions for incompatible trace elements. Such samples were found only in Assarel (basaltic andesite), Elshitsa (gabbro) and Capitan Dimitrievo (gabbro, monzogabbro, monzodiorite).

MORB-normalized extended patterns for these samples have been constructed (Fig. 11) to distinguish among different classes of compatible and noncompatible elements, coming from the widespread opinion that compatible elements are mantle-derived and the noncompatible elements are contributed by melting of the subducting slab. Pearce and Parkinson (1993) classified the elements into several classes of compatibility with respect to spinellherzolite melting at 1200°C. The subduction and the mantle inputs are estimated in every individual case (Table 3) in accordance with element abundances relative to MORB, respectively found to lie above, near to or below a MORB-base line in the Fig. 11.

The main conclusion from the patterns is that contrary to the normal petrochemical across-arc zoning in island arcs, a decrease of the incompatibility of the slab-derived components directed to the center of the transect (from Assarel and Capitan Dimitrievo to Elshitsa) is revealed. In contrast, the compatibility of the moderate compatible (MC) and the very high compatible (VHC) Mg-

Cent	ter	Assarel	Elshitsa	Capitan Dimitrievo		
Slab- related	HI MI SI	Ba, U, Pb Rb, Th, Sr K, <i>LREE</i> , P	- Cs, Ba Rb, Th, U, Pb, (Ba)	Cs, Rb, Ba, Th, U, Pb K, La, Sr, P, (Th, U) Ta, Ce, Na, P, Pr, Nd, (Sr)		
Telaleu	SC	Nb, MREE, Na, Zr, Hf	K, LREE, Sr, P, Na, (U)	Nb, Zr, Hf, MREE		
Mantle-	SC MC	Mn, Co Ti, Y, <i>HREE</i> , Ca, Al, Sc, Fe, Mg	Sc, Co, Mg, (Cr) Ti, Ta, Nb, Y, Ca, <i>MREE</i> , <i>HREE</i> , Al, Hf,	Mn, Co Ti, Y, Al, Mg, <i>HREE</i> , Ca, Sc, Fe, Mg, (Nb,Zr, Hf)		
derived	VHC	Cr, Ni	Zr, Mn, Fe, Cr, Ni	Cr, Ni		

Table 3. Behaviour of elements during arc magma generation in the transect

HI - high incompatible; MI - moderate incompatible; SI - slight incompatible; SC - slight compatible; MC - moderate compatible and VHC - very high compatible with respect to spinel-lherzolite melting at 1200°C (Pearce, Parkinson, 1993)



Fig. 11. MORB-normalized extended patterns for the most primitive rock samples from Assarel (basaltic andesite), Elshitsa and Capitan Dimitrievo. Normalization after Pearce and Parkinson (1993). Abbreviations are as in Fig. 2

related elements (Sc, Mg, Cr, Ni) also decreases. We suppose that this difference is probably due to the higher melting degree of the source mantle in the case of Elshitsa. There, the MORB-normalized ratio is $(La_N/Ce_N) > 1$, indicating less oxidizing, or reducing conditions in the source (Ben Othman et al., 1989).

Pearce and Parkinson (1993) separate a variety of types of island-arc magmas derived from a spinel-lherzolite mantle by normalizing the abundances of the compatible elements to the elements of the fertile MORB-mantle (FMM). These types can be related to melting and depletion-enrichment events in the mantle. Comparing the spidergrams relative to FMM for the selected primitive samples of Assarel, Elshitsa and Capitan Dimitrievo (Fig. 12) we may say that they are a combination of patterns from Northern Fiji and Scotia Sea (type 1) and of "alkalic basalts" from Grenada (type 2 of Pearce and Parkinson, 1993). The distinguishable features are the ratios (Nb/Zr)_N and $(Zr/Yb)_N > 1$. The mantle enrichment in the studied magmatic centers is dominated by Nb, Zr, Ti and to lesser extent Y and Yb. The isotopic evidence that these elements are mainly mantle-derived and not introduced from the crustal contamination is the conclusion (von Quadt et al., 2005) for the insignificant crustal input into the southern magmas. The small, but distinct negative Ti anomaly relative to the neighbouring elements (Zr and Y) is suggestive of the presence of residual amphibole and biotite in the mantle source (Pearce, Parkinson, 1993). According to the same authors both magma types are derived from a metasomatized mantle, which had not been considerably depleted by previous melting events. This inference rejects the possibility for the Srednogorie arc to be interpreted as a continental rift, as Popov (1981, 1996) assumes.

Constraints on the degree of melting

It is interesting that the normalized abundances in Assarel and Capitan Dimitrievo (Fig. 12) are in the order VHI>HI>MI and Nb_N 10-40. In this respect the patterns match the theoretical pattern for the low melting of a FMM (Fig. 9-a of Pearce and Parkinson, 1993). In contrast to these patterns, the Elshitsa gabbro pattern with its shape and with Nb_N 6-9 matches the case for a bit higher degree of melting of an enriched source. These purely qualitative FMM estimations for the degree of melting are supplemented by the indications from other geochemical results. The observations of the slightest degree of compatibility in Elshitsa for the conservative elements signify that the central parts of the transect are quite different geochemically from Assarel and Capitan Dimitrievo centers. We have already mentioned that the Elshitsa center is the only one with a typical calc-alkaline compositional trend. The only case of distinct relative and absolute Sc-enrichment for the basic and even the hybrid rocks is also Elshitsa. The specific lack of Zr-anomalies with respect to Hf and the weakest Ti-anomalies relative to MORB in the basic rocks of Elshitsa along with the slightest Cr-anomalies there, are other clues for the higher melting degree of the enriched mantle source in comparison with the other magmatic centers.

A quantitative approach to the problem is to use the conservative elements in the way proposed by Pearce and Parkinson (1993). We constructed Nb vs. Yb plot, which effectively separates source depletion from degree of melting (Fig. 13). The results of this study indicate that 4 out of the 6 samples fall in the field of the continental arcs. Part of the dispersion off this field is probably due to the fact that these samples are weakly fractionated. It is noticeable that centers localized on the middle part of the transect, like Elshitsa (Fig. 1) require higher melting degrees. The deduced degrees of melting are: Capitan Dimitrievo ~5-15%; Elshitsa ~20-25%; Assarel ~15-20%. Not more than 10 % of this melting is probably due to fluid addition to the source (Pearce, Peate, 1995); the rest of this estimated value is caused by decompression. A possible rapid rise of the parental magma along the shear zones may facilitate the decompressional melting. The



Fig. 12. FMM (Fertile MORB Mantle)-normalized patterns (normalizing values in Pearce and Parkinson, 1993) for the most primitive rock samples from Assarel (basaltic andesite), Elshitsa and Capitan Dimitrievo centers. In the bottom – suprasubduction

regional dextral strike-slip fault of Iskar-Yavoritza shear zone (Ivanov et al., 2001) crosses just the Elshitsa center and clearly contributes to some of its peculiarities – a higher degree of melting, its unique calcalkaline character, extensive evidence for mingling and mixing, and other specific geochemical peculiarities.

Across-arc geochemical and temporal migration

The established temporal migration of the magmatism (Kamenov et al., 2003a, 2004; von Ouadt et al., 2003b, 2005; Peytcheva et al., 2004) is southward trench directed, i.e. exactly opposite of the typical across-arc zoning in supracrustal space. We assume that this is related to a slab retreat (Fig. 14). It is possible that this process was a result of variations between the subduction and convergence rates of the continental plates. The ratio between these rates is considered to control the dip of subduction (Royden, 1993). The same model was supposed also for the Panagyuriste magmatic area by von Quadt et al. (2003a) and for the Timok magmatic complex (also Upper Cretaceous) (Banješević et al., 2003; Cvetković et al., 2006).

The generation of high-K calc-alkaline magmas require participation of a metasomatised hornblende-bearing mantle source (stable between 50 and 100 km depth), and the shoshonitic magmas – the metasomatised phlogopite-bearing mantle (stable between 100 and 200 km – Pearce et al., 1990; Sato et al., 1997). This is our reason to suggest that the magma generation level of the mantle component of the magmatic products in the studied transect have been somewhere at around 100 km.

volcanic rocks of type 1 (shaded area) and of type 2 "alkali basalts" (bold line) after Pearce and Parkinson (1993) are given for comparison



Fig. 13. Nb vs. Yb plot for the same samples as in Fig. 12. Theoretical contours for degree of melting (from 5% to 40 %), degree of mantle depletion (below FMM line) and the continental arcs field are from Pearce and Parkinson (1993). Abbreviations: Ass - Assarel; Els - Elshitsa and CD - Capitan Dimitrievo

The simplified provisional model in Fig. 14 highlights some of our data. It does not contradict the presented petrological, geochemical and age-relationship facts concerning the fertility of the mantle wedge, the subduction nature of the source and the age regularities across this part of the arc. Volcanic arc magmas owe their compositions to many factors, varying systematically with tectonic setting. For example, enriched lithosphere may become incorporated in the source of volcanic arc magmas in many different ways. A more detailed model requires more precise geophysical data for the geometry of the subducting slab and specific isotope studies, but the general idea proposed probably can explain at least some of the peculiarities of this arc-magmatism.

The preservation of volcanic rocks in the northern and central parts of transect is consistent with the interpretation that progressively deeper crustal levels are preserved from north to the south in the arc system.

Summary and conclusions

1. The compilation of all available reliable and newly obtained petrological data reveals a large range of rock varieties. Geochemically the rocks are *LILE*-enriched with prevailing high-K calc-alkaline and shoshonitic trends. The only exception is the Elshitsa trend where a typical calc-alkaline trend is demonstrated. Two trends in the transitional in alkalinity field rocks are revealed only for Capitan Dimitrievo.

2. Later and more basic magmatic stages follow the moderately acid magmatic stages in the Elatsite, Chelopech and Assarel centers probably because of the existence of chemically zoned magma chambers.

3. The petrographic and geochemical data are consistent with some combinations of magmamixing and fractional crystallization (MFC) processes dominating in the magma evolution paths. Petrological and mineralogical criteria for a magma mixing process are observed in almost every center, but the role of mixing is



Fig. 14. Cartoon presentation of the slab retreat model for the studied transect of the Central Srednogorie based on the thermal and dehydration models of Iwamori (1998) and Manning (2004). New-obtained U-Pb ages on zircon are shown to the ore-magmatic centers

more strongly expressed chemically in the Elshitsa and Capitan Dimitrievo centers.

4. An important point is that all geochemical signatures are typical for island-arc magmas of subduction-related origin. A fertile MORB source (FMM) is deduced from the geochemical data for the whole transect. Our data support the idea that this source contained probably hornblende, phlogopite, apatite, rutile and spinel in addition to the usual lherzolitic minerals.

5. Specific geochemical bilateral zoning directed from the northern and southern ends of the transect to its center is revealed, and a higher degree of melting in the Elshitsa center in comparison to the southern and northern ends of the transect is supposed. We assume

that the strike-slip shear zones known in the middle part of transect (Elshitsa) stimulated probably the higher degree of decompressional melting of the source there. The levels of magma crystallization were nearly equal, which is why clear classical across-arc zoning is not observed.

6. The rejuvenation of magmatic ages to the southern end of the transect and the revealed regularities of the isotope ratios support the slab retreat model for the geodynamic evolution. Changing subduction geometry during the Srednogorie orogeny (slab retreat) could produce this temporal across-arc regularities, but because the slab in Cretaceous time was still hot, only stretching in the middle part of the transect is perceived. The

continental rift genesis of the magmas in the transect is not supported by the new geochemical data.

Acknowledgments: This research has been carried out in the framework of the GEODE program of the European Science Foundation and the program SCOPES of the Swiss Science Foundation.

References

- Aiello, E., C. Bartolini, M. Boccaletti, P. Gochev, J. Karagjuleva, V. Kostadinov, P. Manneti. 1977. Sedimentary features of Srednogorie zone (Bulgaria): An Upper Cretaceous intra arc basin. *Sediment. Geol.*, **19**, 39-68.
- Amov, B. 1999. Lead isotope data for ore deposits from Bulgaria and the possibility for their use in archaeometry. *Berliner Beiträge zur Archäometrie*, 16, 5-19.
- Andrew, C. 1997. The geology and genesis of the Chelopech Au-Cu deposit, Bulgaria: Europe's largest gold resource. In: S. Harney (Ed.), *Europe's Major Gold Deposits*. Abstracts volume. Newcastle, N. Ireland, Irish Association for Economic Geology, 68-72.
- Angelkov, K., B. Parvanov. 1980. The Assarel porphyry copper deposit, Bulgaria. In: *European Copper Deposits*. Belgrade, Spec. Publ., 1, 59-62.
- Banješević, M., V. Cvetković, D. Koželj, I. Peytcheva, A. von Quadt. 2003. The Timok magmatic complex and Ridanj-Krepoljin zone: geodynamic evolution. In: *Geology and Metallogeny of Cooper and Gold Deposits in the Bor Metallogenic Zone*. Conference "100 Years Cooper Institute of Bor". Bor, Serbia and Montenegro, 22-25 October, 199-202.
- Ben Othman, D., W.M. White, J. Patchett. 1989. The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling. *Earth Planet. Sci. Lett.*, 94, 1-21.
- Blundy, J.B., T.I. Holland. 1990. Calcic amphibole equilibria and a new amphibole-plagioclase geothermometer. *Contrib. Mineral. Petrol.*, **104**, 208-224.
- Boccaletti, M., P. Manetti, A. Peccerillo. 1974. Hypothesis on the plate tectonic evolution of the Carpatho-Balkan arcs. *Earth Planet. Sci. Lett.*, 23, 193-198.

- Bogdanov, B. 1987. *The Copper Deposits in Bulgaria*. Sofia, Technica Press, 388 p. (in Bulgarian, with an English abstract).
- Bogdanov, B., P. Popov, N. Obretenov. 1970. Structural characteristics of the Elshitsa ore field. *Rev. Bulg. Geol. Soc.*, **31**, 3, 303-313 (in Bulgarian with an English abstract).
- Bonchev, E. 1976. Lineament-geosynclinal zones zones of impermanent rift genesis. *Geol. Balcanica*, 6, 1, 86-100.
- Boyadjiev, S. 1979. The Middle Alpine magmatism in the Srednogorie Zone in conditions of telescoped riftogenesis. *Rev. Bulg. Geol. Soc.*, 40, 3, 224-235 (in Bulgarian with an English abstract).
- Boyadjiev, S. 1981. Potassium-argon studies of the Middle Alpine intrusions in the Central Srednogorie. *Geochem., Mineral., Petrol.*, 14, 28-46 (in Bulgarian with an English abstract).
- Boyadjiev, S. 1984. Geochemistry of rare-earth elements in Middle Alpine plutons from the Central Srednogorie, Bulgaria. *Geol. Zbornik Geolog. Carpath.*, **35**, 3, 377-388.
- Boyadjiev, S. 1986. Petrology and geochemistry of Kapitan-Dimitrievo pluton. *Geochem., Mineral., Petrol.*, 20/21, 97-127 (in Bulgarian with an English abstract).
- Boyadjiev, S., S. Chipchakova. 1962. Petrology of Elshitsa-Boshulia pluton. *Ann. Direct. générale de géol.*, **13**, 8, 5-71 (in Bulgarian with an English abstract).
- Boyadjiev, S., P. Lilov. 1981. K-Ar determinations of the Alpine intrusions from the Central Srednogorie. C. R. Acad. bulg. Sci. 34, 4, 549-551.
- Boyadjiev, S., D. Matanov, Z. Chubriev. 1988. Geochemistry of the rare-earth elements and some petrogenetic features of the neointrusives from the Central Srednogorie. *Year Book of the Committee of Geology*, *Bulgaria*, 28, 127-149 (in Bulgaria with an English abstract).
- Chipchakova, S. 2002. Wall-rock alterations in the Medet porphyry copper deposit, Central Srednogorie. *Geochem., Mineral., Petrol.*, **39**, 67-74 (in Bulgarian with an English abstract).
- Chipchakova, S., P. Lilov. 1976. On the isotope age of the Upper Cretaceous magmatic rocks from the western part of the Central Srednogorie and related ore mineralizations. C. R. Acad. bulg. Sci., 29, 1, 101-104.
- Cvetkov, K., D. Yosifov, N. Obretenov. 1978. Features of the main ore controlling structure in the Central Srednogorie. *Rev. Bulg. Geol. Soc.*,

39, 1, 41-50 (in Bulgarian with an English abstract).

- Cvetković, V., H. Downes, D. Prelević, M. Lazarov, K. Resimić-Šarić. 2006. Geodynamic significance of ultramafic xenoliths from Eastern Serbia: Relics of sub-arc oceanic mantle. J. Geodyn., doi: 10.1016/j.jog.2006.11.003, 1024.
- Dabovski, C. 1964. Structural features of the Elshitsa-Boshulia pluton. *Ann. Direct. générale de recherches géol.*, **14**, 19-46 (in Bulgarian with an English abstract).
- Dabovski, C. 1968. On the character and development of the Maritsa Neointrusive zone. Bull. Geol. Inst., Ser. Geotect., Startigr., Lithol., 17, 95-98 (in Bulgarian with an English abstract).
- Dabovski, C. 1969. Structure of the Capitan Dimitrievo pluton. *Rev. Bulg. Geol. Soc.*, **30**, 2, 142-154 (in Bulgarian with an English abstract).
- Dabovski, C. 1991. Modern concepts on the evolution of the Alpine orogen in the Eastern Mediterranean and the Carpathian-Balkan area: A review and some problems of Bulgarian geotectonics. *Geotect., Tectonophys., Geodynam.*, 22, 45-79 (in Bulgarian with an English abstract).
- Dabovski, C., A. Harkovska, B. Kamenov, B. Mavrudchiev, G. Stanisheva-Vassileva, Y. Yanev. 1991. A geodynamic model of the Alpine magmatism in Bulgaria. *Geol. Balcanica*, 21, 4, 3-15.
- Daieva, L., S. Chipchakova. 1997. Geochemical features of the Upper Cretaceous magmatites from Panagyurishte volcano-intrusive region, Central Srednogorie. *Geochem., Mineral., Petrol.*, **32**, 85-99 (in Bulgarian with an English abstract).
- Davies, J.H., D.J. Stevenson. 1992. Physical model of source region of subduction zone volcanics. J. Geophys. Res., 97, 2037-2070.
- Dercourt, J., L.-E. Ricou, B. Vrielynk. 1993. Atlas Tethys. Palaeoenvironmental Maps. Paris, Gauthier-Villars, 307 p., 14 maps.
- Dimitrov, C. 1983. Senonian initial volcanic rocks south of Panagyurishte and Strelcha, Bulgaria. *Rev. Bulg. Geol. Soc.*, 44, 2, 95-128 (in Bulgarian with an English abstract)
- Dimitrova, E., I. Nachev, I. Slavov. 1984. Stratigraphy of the Late Cretaceous in Panagyurishte region. *Paleontol., Stratigr., Lithol.*, **19**, 65-84 (in Bulgarian with an English abstract).
- Dobrev, T., L. Dimitrov, S. Pishtalov, V. Ivanova, R. Radkov. 1967. Studies on the deep structure of east Bulgaria based on geophysical data. *Rev.*

Bulg. Geol. Soc., **28**, 1, 35-54 (in Bulgarian with a German abstract).

- Dobrev, T., M. Uzunova, N. Tashev. 1986. Structure of Maritsa deep-fault zone and its expression in the geophysical fields. *Geol. Balcanica*, 16, 6, 33-59 (in Russian with an English abstract).
- Georgiev, G., C. Dabovski, G. Stanisheva-Vassileva. 2001. East Srednogorie-Balkan rift zone. In: P.A. Ziegler, W. Cavazza, A.H.F. Robertson, S. Crasquin-Soleau (Eds.), *Peri-Tethys Memoir 6: Peri-Tethyan Rift/Wrench Basins and Passive Margins*. Mém. Muséum nat. d'histoire nature, Paris, **186**, 259-293.
- Georgiev, N., A. Lazarova. 2003. Magma mixing in Upper Cretaceous plutonic bodies in the southwestern part of Sredna Gora zone, Bulgaria. C. R. Acad. bulg. Sci., 56, 4, 47-52.
- Gill, J. 1981. Orogenic Andesites and Plate Tectonics. Berlin, Springer-Verlag, 385 p.
- Grigorov, B. 1961. The magnetic field of R. P. Bulgaria. *Geophys. Inst. Bulg. Acad. Sci. Announcements*, 2, 109-115 (in Bulgarian with a Russian and a French abstracts).
- Handler, R., F. Neubauer, S. Velichkova, J. Ivanov. 2003. ⁴⁰Ar/³⁹Ar age constraints on the timing of the formation of Cu-Au deposits in the Panagyurishte region, Bulgaria. In: F. Neubauer, R. Handler (Eds.), *Geodynamics and Ore Deposit Evolution of the Alpine-Balkan-Carpathian-Dinaride Province*. Final GEODE-ABCD (2003) Workshop, Seggauberg, Austria, Programme and Abstracts, 22-24 March, p.28.
- Haydoutov, I., Y. Tenchov, S. Yanev. 1979. Lithostratigraphic subdivision of the Diabase-Phyllitoid Complex in the Berkovista Balkan Mountain. *Geol. Balcanica*, **9**, 3, 13-25.
- Hickey, R.L., F.A. Frey, D.C. Gerlach, L. Lopez-Escobar. 1986. Multiple sources for basaltic arc rocks from the southern volcanic zone of the Andes (34°-41° S): trace element and isotopic evidence for contributions from subducted oceanic crust, mantle and continental crust. *Earth Planet. Sci. Lett.*, **91**, 5963-5983.
- Hsü, K.J., I.K. Nachev, V.T. Vuchev. 1977. The evolution of Bulgaria in the light of plate tectonics. *Tectonophysics*, 40, 245-256.
- Ida, Y. 1983. Convection in the mantle wedge above the slab and tectonic processes in subduction zones. J. Geophys. Res., 88, 7449-7456.
- Ivanov, J., B. Henry, D. Dimov, N. Georgiev, D. Jordanova, N. Jordanova. 2001. New model for Upper Cretaceous magma emplacement in the southwestern parts of Central Srednogorie –

petrostructural and AMS data. *Romanian Journal of Mineral Deposits*, **79**, (supplement 2), 60-61.

- Iwamori, H. 1998. Transportation of H₂O and melting in subduction zones. *Earth Planet. Sci. Lett.*, 160, 65-80.
- Jankovic, S. 1997. The Carpatho-Balkanides and adjacent area: A sector of the Tethyan Eurasian metallogenic belt. *Mineral. Deposita*, **32**, 426-433.
- Johnson, M.C., M.J. Rutherford. 1989. Experimental calibration of aluminium-in amphibole geobarometer with application to Long Valley caldera (California) volcanic rocks. *Geology*, 17, 837-841.
- Kamenov, B.K., A. von Quadt, I. Peytcheva. 2002. New insight into petrology, geoche-mistry and dating of the Vejen pluton, Bul-garia. *Geochem.*, *Mineral.*, *Petrol.*, **39**, 3-25.
- Kamenov, B.K., R. Moritz, R. Nedyalkov, I. Peytcheva, A. von Quadt, S. Stoykov, Y. Yanev, A. Zartova. 2003a. Petrology of Late Cretaceous ore-magmatic centers from the Central Srednogorie, Bulgaria: Magma evolution and sources. In: F. Neubauer, R. Handler (Eds.), *Geodynamics and Ore Deposit Evolution of the Alpine-Balkan-Carpathian-Dinaride Province*. Final GEODE-ABCD (2003) Workshop, Seggauberg, Austria, Programme and Abstracts, 22-24 March, p. 30.
- Kamenov, B.K., A. von Quadt, I. Peytcheva. 2003b. Capitan Dimitrievo pluton in Central Srednogorie, Bulgaria: Mineral chemistry, geochemistry and isotope evidence for magma-mixing origin. *Geochem., Mineral., Petrol.*, 40, 21-53.
- Kamenov, B., Y. Yanev, R. Nedyalkov, R. Moritz, I. Peytcheva, A. von Quadt, S. Stoykov, A. Zartova. 2004. An across-arc petrological transect through the Central Srednogorie Late Cretaceous magmatic centers in Bulgaria. In: *Proceedings of the Conference of theBulg. Geol. Soc., "Geology 2004",* Sofia, December 16-17, 35-37.
- Kay, R.W. 1980. Volcanic arc magmas: implications of a melting-mixing model for element recycling in the crust-upper mantle system. J. Geol., 88, 497-522.
- Kouzmanov, K., R. Moritz, M. Chiaradia, C. Ramboz. 2001a. Mineralogy, fluid inclusion study, and Re-Os dating of Mo-bearing mineralization from Vlaikov Vrah porphyry copper deposit, Panagyurishte District, Bulgaria.

In: EUG XI, Journal of Conference Abstracts, 6, 1, p. 557.

- Kouzmanov, K., R. Moritz, M. Chiaradia, C. Ramboz. 2001b. Sr and Pb isotope study of Au-Cu epithermal and porphyry-Cu deposits from the southern part of the Panagyurishte district, Sredna Gora Zone, Bulgaria. In: L.A. Piestrzyski (Ed.), *Mineral Deposits at the Beginning of the* 21st Century. Balkema Lisse the Netherlands Swets & Zeitlinger Publ. (Proceedings of the joint 6th biennial SGA-SEG Meeting, Krakow), 539-542.
- Leake, B.E., A.R. Woolley, C.E.S. Arps, W.D. Birch, M.C. Gilbert, J.D. Grice, F.C. Hawthorn, A. Kato, H.I. Kish, V.G. Krivovichev, K. Linthout, J. Laird, J. Mandarino, W.V. Maresch, E.H. Nickel, N.M.S. Rock, J.C. Schumacher, D.C. Smith, N.C.N. Stephenson, L. Ungaretti, E.J.W. Whittaker, G. Youzhi. 1997. Nomenclature of amphiboles. Report of the Subcommittee on amphiboles in the IMA on new minerals and mineral names. *Eur. J. Mineral*, 9, 623-638.
- Le Maitre, R.W. (Ed.) 1989. A Classification of Igneous Rocks and Glossary of Terms. Oxford, Blackwell Sci. Publ., 193 p.
- Lilov, P., S. Chipchakova. 1999. K-Ar dating of the Upper Cretaceous magmatic rocks and hydrothermal metasomatic rocks from Central Srednogorie. *Geochem., Mineral., Petrol.*, 36, 77-91 (in Bulgarian with an English abstract).
- Lips, A.W., R.J. Herrington, G. Stein, D. Kozeli, K. Popov, J.R. Wijbrans. 2004. Refined timing of porphyry copper formation in the Serbian and Bulgarian portions of the Cretaceous Carpatho-Balkan Belt. *Econ. Geol.*, **99**, 601-609.
- Manning, C.E. 2004. The chemistry of subductionzone fluids. *Earth Planet. Sci. Lett.* 223, 1-16.
- Mitchell, A.H.G. 1996. Distribution and genesis of some epizonal Zn-Pb and Au provinces in the Carpathian and Balkan region. *Transactions Instit. Mining and Metallurgy*, **105**, B1, 127-138.
- Moev, M., M. Antonov. 1978. Stratigraphy of the Late Cretaceous in the eastern part of Stargel-Chelopech strip. *Ann. Ecole Sup. Mines et Géol.*, 23, Fas.II Géol., 7-30 (in Bulgarian with a Russian abstract).
- Müller, D., N.M.S. Rock, D.I. Groves. 1992. Geochemical discrimination between shoshonitic and potassic rocks from different tectonic settings: A pilot study. *Mineral.*, *Petrol.*, 46, 259-289.

- Nedyalkov, R., A. Zartova, R. Moritz. 2007. Magmatic rocks and evolution of the Late Cretaceous magmatism in the region of the Assarel porphyry copper deposit, Central Srednogorie. *Rev. Bulg. Geol. Soc.*, 68, 1-3 (in press).
- Neubauer, F. 2002. Contrasting Late Cretaceous with Neogene ore provinces in the Alpine-Balkan-Carpathian-Dinaride collision belt. In: D.J. Blundell, F. Neubauer, A. von Quadt (Eds.), *The Timing and Location of Major Ore Deposits in an Evolving Orogene.* Geol. Soc. London, Spec. Public., **204**, 81-102.
- Osborn, E.F. 1979. The reaction principle. In: H.S. Jr. Yoder (Ed.), *The Evolution of the Igneous Rocks – Fiftieth Anniversary Perspectives*. Univ. Press Princeton, 133-170.
- Pearce, J.A. 1982. Trace element characteristics of lavas from destructive plate boundaries. In: R.S. Thorpe (Ed.), Andesites. Orogenic Andesites and Related Rocks. Chichester, J. Wiley, 525-548.
- Pearce, J.A. 1983. Role of the sub-continetal lithosphere in magma-genesis at active continental margins. In: C.J. Hawkesworth, M.J. Norry (Eds.), *Continental Basalts and Mantle Xenoliths.* Natwich, Shiva, 230-249.
- Pearce, J.A., I.J. Parkinson. 1993. Trace element models for mantle melting: application to volcanic arc petrogenesis. In: H.M. Prichard, T. Alabaster, N.B.W. Harrison, C.R. Neary (Eds.) *Magmatic Processes and Plate Tectonics*. Geol. Soc. London, Spec. Public., **76**, 373-403.
- Pearce, J.A., D.W. Peate. 1995. Tectonic implications of the composition of volcanic arc magmas. Ann. Rev. Earth Planet. Sci., 23, 251-285.
- Pearce, J.A, J.F. Bender, S.E. De Long, W.S.F. Kidd, P.J. Low, Y. Güner, F. Saroglu, Y. Yilmaz, S. Moorbath, J.G. Mitchell. 1990. Genesis of collision volcanism in Eastern Anatolia, Turkey. J. Volcanol. Geotherm. Res., 44, 189-229.
- Peytcheva, I., A. von Quadt. 2003. U-Pb-zircon isotope system in mingled and mixed magmas: an example from Central Srednogorie, Bulgaria. In: Abstracts of the Contrib. EGS-AGU-EUG Joint Assembly, Nice, France, CD version.
- Peytcheva, I., A. von Quadt, B. Kamenov, Z. Ivanov, N. Georgiev. 2001. New isotope data for Upper Cretaceous magma emplacement in the southern and south-western parts of Central Srednogorie. *Romanian Journal of Mineral Deposits*, **79** (supplement 2), 82-83.
- Peytcheva, I., A. von Quadt, K. Kouzmanov, K. Bogdanov. 2003. Timing and mineralization in

Elshitsa and Vlaykov Vrah Cu (Au) deposits of Central Srednogorie, Bulgaria: constraints from U-Pb zircon and rutile geochronology and Hfzircon and Sr whole-rock tracing. In: F. Neubauer, R. Handler (Eds.), *Geodynamics and Ore Deposit Evolution of the Alpine-Balkan-Carpathian-Dinaride Province*. Final GEODE-ABCD (2003) Workshop, Seggauberg, Austria, Programme and Abstracts, 22-24 March, p. 46.

- Peytcheva, I., A. von Quadt, M. Frank, B. Kamenov, C.A. Heinrich. 2004. The subcontinental lithosphere beneath Central Srednogorie (Bulgaria): U-Pb and Hf zircon, Nd and Sr whole rock constraints. In: *Goldshmidt Conference, Conference Abstracts Supplement, Geochim. Cosmoshim. Acta.* Copenhagen, Denmark, v. A 624.
- Popov, P. 1981. Magmotectonic features of the Banat-Srednogorie Belt. *Geol. Balcanica*, **11**, 2, 43-72.
- Popov, P. 1996. On the tectono-magmatic evolution of the Balkan Peninsula Alpides. In: P. Popov (Ed.), *Plate Tectonic Aspects of the Alpine Metallogeny in the Carpathian-Balkan Region*. UNESCO-IGCP Project 356. Proceedings of the Annual Meeting, Sofia, 1, 5-17.
- Popov, P., Bairaktarov, I. 1979. Structure of the molybdenum-copper deposit Medet. Ann. Ecole sup. Mines et géol., 22, Fas. II–Géol., 197-215 (in Bulgarian with an English abstract).
- Popov, P., V. Kovachev. 1996. Geology, composition and genesis of the mineralization in the central and southern part of the Elatsite-Chelopech ore field. In: P. Popov (Ed.), *Plate Tectonic Aspects of the Alpine Metallogeny in the Carpathian-Balkan Region*. UNESCO-IGCP Project 356. Proceedings of the Annual Meeting, Sofia, 1, 159-170.
- Popov, P., I. Mutafchiev. 1980. The structure of the Chelopch Cu-ore field. Ann. École sup. Mines et géol., 25, Fas. II–Géol., 25-41 (in Bulgarian with an English abstract).
- Popov, P., K. Popov. 2000. General geologic and metallogenic features of the Panagyurishte ore region. In: S. Strashimirov, P. Popov (Eds.), *Geology and Metallogeny of the Panagyurishte Ore Region. Guide to Excursion A and C.* ABCD-GEODE (2000) Workshop, Borovets, Bulgaria, 1-7.
- Popov, P., S. Strashimirov, R. Arnaudova, M. Kanazirski, K. Popov. 1996. Geology and genetical model of the porphyry copper deposits from the Assarel – Medet ore field. In: P. Popov (Ed.), *Plate Tectonic Aspects of the Alpine*

Metallogeny in the Carpathian-Balkan Region. UNESCO-IGCP Project 356. Proceedings of the Annual Meeting, Sofia, 1, 175-196.

- Popov, P., R. Radichev, S. Dimovski. 2002. Geology and evolution of the Elatsite-Chelopech prohyrycopper-massive sulfide ore field. *Ann. Univ. Mining and Geol.*, 43/44, part 1–Geol., 31-44.
- Ricou, L.-E. 1994. Tethys reconstructed: plates, continental fragments and their boundaries since 260 Ma from Central America to south-eastern Asia. *Geodinam. Acta*, 7, 169-218.
- Royden, L.H. 1993. The tectonic expression of slab pull at continental convergent boundaries. *Tectonics*, **12**, 303-325.
- Sato, K., T. Katsura, E. Ito. 1997. Phase relations of natural phlogopite with and without enstatite up to 8 GPa: Implication for mantle. *Earth Planet. Sci. Lett.*, **146**, 511-526.
- Saunders, A.D., J. Tarney, S.D. Weaver. 1980. Transverse geochemical variations across the Antarctic Peninsula: Implications for the genesis of calc-alkaline magmas. *Earth Planet. Sci. Lett.*, 46, 344-360.
- Sengör, A.M.C., D. Altiner, A. Cin, T. Ustaomer, K.J. Hsü. 1988. Origin and assembly of the Tethyside orogenic collage at the expense of Gondwanaland. In: M.G. Audley-Charles, A. Hallam (Eds.), *Gondwana and Tethys*. Geol. Soc. London, Spec. Public., **17**, 77-112.
- Shanov, S., I. Kostadinov. 1992. Configuration of the deep geophysical discontinuities beneath the territory of Bulgaria. *Geol. Balcanica*, **22**, 2, 71-79.
- Spakman, W. 1986. Subduction beneath Eurasia in connection with the Mesozoic Tethys. *Geol. Mijnbow*, 65, 145-153.
- Stampfli, G., G. Borel. 2004. The TRANSMED transects in space and time: Constraints on the paleotectonic evolution of the Mediterranean domain. In: W. Cavazza, F. Roure, W. Spakman, G.M. Stampfli, P.A. Ziegler (Eds.), *The TRANSMED Atlas – The Mediterranean Region* from Crust to Mantle. Berlin-Heidelberg, Springer-Verlag, 53-80.
- Stampfli, G.M., J. Mosar, P. Favre, A. Pillevuit, J.C. Vannay. 2001. Permo-Mesozoic evolution of the western Tethys realm: the Neo-Tethys – East Mediterranean Basin connection. In: P.A. Ziegler, W. Cavazza, A.H.F. Robertson, S. Crasquin-Soleau (Eds.), *Peri-Tethys Memoir 6: Peri-Tethyan Rift/Wrench Basins and Passive Margins*. Mém. Muséum nat. d'histoire nature., Paris, **186**, 51-108.

- Stanisheva-Vassileva, G. 1980. The Upper Cretaceous magmatism in Srednogorie Zone, Bulgaria: a classification attempt and some implications. *Geol. Balcanica*, **10**, 2, 15-36.
- Stoykov, S., P. Pavlishina. 2003. New data on a Turonian age of the sedimentary and volcanic succession in the southeastern part of the Etropole Stara Planina Mountain, Bulgaria. C. R. Acad. bulg. Sci., 56, 6, 55-60.
- Stoykov, S., Y. Yanev, R. Moritz, I. Katona. 2002. Geological structure and petrology of the Late Cretaceous Chelopech volcano, Srednogorie magmatic zone. *Geochem., Mineral., Petrol.*, 39, 27-38.
- Stoykov, S., Y. Yanev, R. Moritz, D., Fontignié. 2003. Petrology, Sr- and Nd- isotope characteristic of the Late Cretaceous magmatic rocks from south-eastern Etropole Stara planina, Srednogorie magmatic zone. In: Jubillee collection "50 Years Mining and Geological University, Sofia", 161-166.
- Strashimirov, S. 1993. Features in distribution of ore minerals in the western periphery of the porphyry copper deposit Assarel. Ann. Univ. Mining and Geol., 39, part 1 - Geol., 79-93 (in Bulgarian with an English abstract).
- Strashimirov, S., R. Petrunov, M. Kanazirski. 2002. Porphyry copper mineralizations in the Central Srednogorie zone, Bulgaria. *Mineral. Deposita*, 37, 587-598.
- Tarkian, M., U. Hünken, M. Tokmakchieva, K. Bogdanov. 2003. Precious-metal distribution and fluid-inclusion petrography of the Elatsite porphyry copper deposit, Bulgaria. *Mineral. Deposita*, **38**, 261-281.
- Tatsumi, D.R., M. Sakuyama, H. Fukuyama, I. Kushiro. 1983. Generation of arc basalt magmas and thermal structure of the mantle wedge in subduction zones. J. Geophys. Res., 88, 5815-5825.
- Thiéblemont, D., M. Tégyey. 1994. Une discrimination géochimique des roches differenciées témoin de la diversité d'origine et de situation tectonique des magmas calco-alkalins. C. R. Acad. Sci., Paris, **319**, II, 87-94.
- Thompson, R.N., M.A. Morrison, G.L. Hendry, S.J. Parry. 1984. An assessment of the relative roles of crust and mantle in magma genesis: an elemental approach. *Phil. Trans. Royal Soc. London*, Ser. A, **310**, 549-590.
- Thorpe, R.S., P.J. Potts, P.W. Francis. 1976. Rare earth data and petrogenesis of andesite from the

North Chilean Andes. *Contrib. Mineral. Petrol.*, **54**, 65-78.

- Tsonev, D., K. Bogdanov, K. Popov. 2000. The volcanic-hosted sulphide (VHS) deposits from the southern part of the Panagyurishte ore region, Bulgaria. In: *Geodynamics and Ore Depo*sits Evolution of the Alpine-Balkan-Carpathian-Dinaride Province. ABCD-GEODE Workshop. Borovets, Bulgaria. Abstract vol., p. 85.
- Tsvetkov, K. 1976. Some data of the geologicalgeophysical prospects for the distribution of the porphyry copper mineralizations in the Panagyurishte region. In: *Problemi Rudoobrazovania* (*Problems of Ore Formations*). Sofia, Publ. House Bulg, Acad. Sci., 1, 191-198 (in Russian).
- Ushev, A., S. Marinova-Chipchakova, K. Angelkov. 1962. The Medet pluton and the associated copper deposit Medet – Panagyurishte district. In: *Contributions à la géologie de la Bulgarie*, 1, 69-147 (in Bulgarian with a French abstract).
- Vassilev, L. 1982. The Stednogorie zone as a metallogenetic conception. *Geochem., Mineral., Petrol.*, **16**, 77-92 (in Bulgarian with an English abstract).
- Vassileff, L., G. Stanisheva-Vassileva. 1981. Metallogeny of the Eurasian copper belt: Sector Bulgaria. *Geol. Balcanica*, **11**, 2, 73-88.
- Vernon, R. H. 1990. Crystallization and hybridism in microgranitoid enclave magmas: microstructural evidence. J. Geophys. Res., 95, 17849-17859.
- von Quadt, A., I. Peytcheva, B. Kamenov, L. Fanger, C.A. Heinrich, M. Frank. 2002. The Elatsite porphyry copper deposit in the Panagyurishte ore district, Srednogorie zone, Bulgaria: U-Pb zircon geochronology and isotope-geochemical investigations of magma-tism and ore genesis. In: D.J. Blundell, F. Neubauer, A. von Quadt (Eds.), *The Timing and Location of Major Ore Deposits in an Evolving Orogen.* Geol. Soc. London. Spec. Public., 204, 119-135.
- von Quadt, A., I. Peytcheva, V. Cvetković. 2003a. Geochronology, geochemistry and isotope tracing of the Cretaceous magmatism of East-Serbia and Panagyurishte district (Bulgaria) as part of the Apuseni-Timok-Srednogorie metal-

logenic belt in Eastern Europe. In: Eliopoulos et al. (Eds.), *Mineral Exploration and Sustainable Development*. Rotterdam, Millpress, 407-410.

- von Quadt, A., I. Peytcheva, C. Heinrich, M. Frank, V. Cvetković, M. Banješević. 2003b. Evolution of the Cretaceous magmatism in the Apuseni-Timok-Srednogorie metallogenic belt and implications for the geodynamic reconstructions: new insight from geochronology, geochemistry and isotope studies. In: F. Neubauer, R. Handler (Eds.), *Geodynamics and Ore Deposit Evolution* of the Alpine-Balkan-Carpathian-Dinaride Province. Final GEODE-ABCD (2003) Workshop, Seggauberg, Austria, Programme and Abstracts, p. 60.
- von Quadt, A., I. Peytcheva, M. Frank, R. Nedyalkov, B. Kamenov, C.A. Heinrich. 2004. Subduction-related rocks in Medet Cu porphyry deposit: sources and magma evolution. In: *Goldschmidt Conference, Conference Abstracts Supplement, Geochim. Cosmochim. Acta.* Copenhagen, Denmark, vol. A 626.
- von Quadt, A., R. Moritz, I. Peytcheva, C.A. Heinrich. 2005. Geochronology and geodynamics of Late Cretaceous magmatism and Cu-Au mineralization in the Panagyurishte region of the Apuseni-Banat-Timok-Srednogore belt, Bulgaria. Ore Geology Reviews, 27, 95-126.
- Wiebe, R.A., W.J. Collins. 1998. Depositional features and stratigraphic sections in granitic plutons: implications for the emplacement and crystallization of granitic magma. J. Struct. Geol., 20, 1273-1289.
- Wortel, M.J.R., W. Spakman. 2000. Subduction and slab detachment in the Mediterranean-Carpathian region. *Science*, **290**, 1910-1917.
- Ziegler, P.A. 1990. *Geological Atlas of Western and Central Europe*. 2nd ed. Shell International Petroleum Mij. BV, The Hague, 232 p.

Accepted February 12, 2007 Приета на 12. 02. 2007 г.

Magmatic center		Elatsite										
Magmatic unite	1	l	2		3		2	1	4	5		
Sample	E/8-	E/15-a	E/43	E/41-g	E/16-v	E/8-g	E/42-g	E/16-b	E/46-b	E/19-b		
Rock	Md-p	Md-p	QMd-p	QMd-p	QSy-p	Sy-p	Gb-p	D-p	Qd-p	Gd-p		
SiO ₂	59.80	61.50	65.71	69.03	75.14	75.84	51.94	54.39	60.64	61.20		
TiO ₂	0.42	0.87	0.51	0.40	0.12	0.17	1.13	1.11	0.63	0.68		
Al_2O_3	16.91	15.32	14.46	13.44	12.30	12.07	16.54	16.41	14.87	14.93		
Fe_2O_3	2.58	2.00	1.32	0.60	0.45	0.44	3.20	2.93	1.51	1.34		
FeO	2.31	4.51	4.49	4.05	1.02	0.70	6.64	5.74	6.28	4.48		
MnO	0.18	0.35	0.39	0.44	0.12	0.06	0.51	0.24	0.48	0.21		
MgO	2.25	3.00	2.12	1.27	0.36	1.10	4.73	3.98	3.28	2.95		
CaO	5.60	4.54	2.68	2.35	1.22	0.42	5.86	6.06	4.78	5.73		
Na ₂ O	4.30	3.44	4.30	3.61	3.15	3.06	2.78	3.96	3.36	3.64		
K ₂ O	3.76	2.60	3.58	4.40	4.60	5.32	3.53	2.52	2.63	2.16		
P_2O_5	0.31	0.25 0.21	0.25	0.17	0.10 0.07	0.09	0.31 0.21	0.33	0.24 0.12	0.31		
H ₂ O ⁻ LOI	0.24 0.99	1.26	0.17 0.82	0.07 0.60	0.07	0.07 0.29	2.27	0.11 1.96	1.32	0.16 1.78		
Total	0.99 99.68	100.57	100.08	100.43	0.89 99.54	99.63	100.02	99.74	1.52	99.57		
Cr	23	56	77	72	47	39.03	65	41	100.13	68		
Ni	23	21	45	41	16	4	19	19	58	44		
Co	8.2	17.0	12.4	8.3	1.9	1.5	26.3	23.1	17.9	13.8		
Sc	9.4	19.6	12.4	7.4	2.9	2.8	36.3	23.3	19.0	17.5		
Ŷ	18.1	28.5	19.5	16.6	14.3	10.2	33.6	30.2	240	21.6		
Nb	5.1	13.7	10.9	11.4	12.1	7.4	10.2	14.0	9.4	8.5		
Zr	97	206	142	115	80	74	173	209	159	162		
Hf	2.6	5.4	3.7	3.3	2.9	2.9	4.4	0.50	4.1	4.1		
Cu	207.3	50.5	42.1	34.6	51.5	140.8	44.8	53.2	62.3	44.7		
Zn	33.1	80.2	53.5	39.3	12.3	11.8	90.5	80.7	75.0	69.8		
Mo	2.7	3.1	8.7	9.7	2.3	2.8	4.3	2.8	13.3	4.0		
Sr	919	374	329	231	95	94	396	361	411	397		
Ba	763	784	664	634	573	226	1135	732	760	713		
Rb	85	117	102	175	203	164	156	100	90	88		
Та	0.31	0.95	1.03	1.12	1.46	0.80	0.62	0.76	0.76	0.57		
Pb	11.05	21.52	23.02	18.63	8.61	8.55	9.58	13.63	20.01	16.30		
Th	9.91	15.25	12.78	18.69	25.18	18.71	7.24	9.43	10.38	10.06		
U	3.14	4.45 39.22	4.12	7.84	5.58	4.72	1.94	2.39	4.16	4.14		
La Ce	30.73 58.74	39.22 72.06	35.95 62.26	32.70 54.35	25.11 44.82	23.45 39.29	34.37 65.96	39.15 77.52	32.50 61.26	30.27 57.86		
Pr	6.55	72.00	6.61	5.69	44.82	39.29	7.89	9.05	6.96	6.47		
Nd	26.44	28.16	25.08	20.15	16.33	11.90	32.76	35.74	27.93	26.61		
Sm	4.70	4.75	4.57	3.74	2.97	1.90	6.64	7.06	5.55	4.96		
Eu	1.46	0.96	1.15	0.92	0.61	0.24	1.73	1.92	1.39	1.14		
Gd	3.52	4.07	3.61	2.92	2.34	1.61	6.41	5.17	4.51	4.47		
Tb	0.56	0.66	0.64	0.46	0.40	0.27	1.04	0.98	0.67	0.67		
Dy	3.10	4.39	3.54	2.64	2.21	1.46	5.98	5.29	4.20	3.82		
Но	0.71	0.88	0.72	0.62	0.52	0.31	1.23	1.14	0.84	0.81		
Er	1.97	2.16	1.96	1.58	1.50	0.97	3.33	3.01	2.52	2.36		
Tm	0.29	0.41	0.26	0.27	0.29	0.20	0.50	0.48	0.34	0.30		
Yb	2.36	3.97	2.11	1.91	2.11	1.41	3.67	3.11	2.47	2.18		
Lu	0.34	0.39	0.28	0.34	0.28	0.24	0.55	0.50	0.36	0.32		

Appendix. Selected chemical analyses (major oxides in wt.% and trace elements in ppm) of rocks from the transect of the Central Srednogorie

Magmatic center			Chelopech		Medet					
Magmatic unit	dome-li	ke body	lava	flows	Vozdol neck			pluton		
Sample	Ch 113	Ch 121	Ch 37	Ch 56	Ch 10	Med 1	Med-b	58b	10B1	58
Rocks	Lat	And	And	Da	Lat	D-p	Mz	Gd-p	Ар	Gr-ap
SiO ₂	61.22	60.57	61.07	63.01	57.11	56.28	66.54	64.48	75.10	75.58
TiO ₂	0.54	0.53	0.49	0.51	0.65	0.84	0.47	0.52	0.17	0.33
Al_2O_3	17.98	17.87	17.68	16.36	18.35	14.77	14.90	14.50	12.20	12.21
Fe_2O_3	5.01*	5.18*	4.56*	4.94*	7.03*	1.95	1.52	2.10	0.86	0.36
FeO	-	-	-	-	-	4.56	2.26	2.20	0.64	0.74
MnO	0.14	0.16	0.13	0.12	0.12	0.14	0.13	0.14	0.01	0.07
MgO	1.44	1.94	1.49	1.63	1.75	7.22	2.25	1.92	0.56	0.56
CaO	3.38	4.45	4.90	4.91	4.87	7.10	1.70	5.51	1.35	2.04
Na ₂ O	5.32	4.28	4.21	3.39	4.19	2.74	4.13	3.96	2.28	2.99
K_2O	2.70	2.50	2.95	2.74	3.27	1.19	3.37	3.08	5.87	4.44
P_2O_5	0.25	0.25	0.22	0.23	0.26	0.20	0.32	0.39	0.14	0.34
H_2O^-	-	-	-	-	-	0.16	0.26	0.12	0.14	0.10
LOI	1.73	2.47	1.54	1.16	1.55	2.48	2.09	0.65	0.45	0.35
Total	99.71	100.20	99.24	99.00	99.15	99.63	99.94	99.57	99.76	100.11
Cr	10	10	12	14	15	118	89	20	290	20
Ni	3	2	2	2	4	56	47	4	20	3
Co	50	21	7	10	13	84	19	9	5	1
Sc	6	8	10	10	9	232	-	15	-	1
Y	23	24	24	20	18	7	-	19	-	4
Nb Zr	7 121	8 134	8 126	7 98	6 127	-	-	5 87	-	6 69
Zr Hf	121	134 6	126	98	6	20	-	87 6	-	69
Cu	25	15	10	26	35	20 7	39	51	143	48
Zn	46	57	90	20 72	137	12	143	44	24	15
Mo	-	-	-	-	-	-	145	-	-	-
Sr	1430	904	1013	781	871	97	170	852	_	340
Ba	870	778	732	1441	768	39	-	542	-	459
Rb	72	74	67	63	46	2	63	115	110	154
Та	-	-	-	-	-	-	-	-		-
Pb	17	18	12	16	15	62	5	8	8	11
Th	4	6	3	3	3	7	-	7	-	28
U	-	-	-	-	-	22	-	1	-	5
La	-	-	28.3	22.9	21.0	17	-	44	-	19
Ce	-	-	60.2	49.3	44.7	464	-	52	-	36
Pr	-	-	6.7	5.3	5.2	-	-		-	-
Nd	-	-	27.7	24	22.8	203	-	27	-	13
Sm	-	-	5.4	4.9	4.6	-	-	-	-	-
Eu	-	-	1.3	1.26	1.27	-	-	-	-	-
Gd	-	-	3.5	3.3	3	-	-	-	-	-
Tb	-	-	-	-	-	-	-	-	-	-
Dy	-	-	3.5	3.1	3	-	-	-	-	-
Но	-	-	0.73	0.66	0.64	-	-	-	-	-
Er	-	-	2	1.8	1.7	-	-	-	-	-
Tm	- 1	-	0.28	0.26	0.24	-	-	-	-	-
Yb	-	-	1.7	1.5	1.4	-	-	-	-	-
Lu	-	-	0.24	0.22	0.18	-	-	-	-	-

Magmatic center						Assarel						
Units		vo	lcanic roc	ks		plutonic rocks						
Phases	I			Ι	III	I II III						
Sample	30	177	25	BKX1	51	AC313a	38	310B	180(2)	314	310A	
Rock	Lat	And	BA	BA	And	Qd-p	QM-p	QM-p	Gd-p	Gr-p	Gr-p	
SiO ₂	56.71	58.02	53.00	55.55	59.76	59.13	57.61	61.29	63.15	69.48	71.49	
TiO ₂	0.69	0.78	0.90	1.07	0.66	0.70	0.73	0.55	0.56	0.40	0.12	
Al_2O_3	17.01	17.47	17.00	16.29	16.33	17.24	15.63	16.76	15.90	14.74	14.56	
Fe_2O_3	3.30	4.20	4.33	4.96	2.55	3.30	2.49	2.43	2.62	0.27	0.63	
FeO	3.29	2.61	3.27	3.36	2.90	3.20	4.22	2.22	1.81	1.26	1.10	
MnO	0.17	0.10	0.23	0.21	0.12	0.13	0.21	0.25	0.17	0.03	0.07	
MgO	3.43	2.44	4.77	3.85	3.81	3.05	2.69	2.56	1.91	2.66	1.24	
CaO	4.08	6.50	9.39	8.68	3.95	5.22	5.77	4.84	5.03	2.30	2.10	
Na ₂ O	5.26	3.28	2.48	3.26	4.31	4.14	3.88	2.86	3.09	4.50	2.63	
K_2O	3.32	2.60	0.60	0.61	2.77	2.56	2.70	4.63	3.34	1.43	4.43	
P_2O_5	0.40	0.26	0.35	0.29	0.18	0.27	0.39	0.20	0.25	0.14	0.11	
H_2O^2	0.18	0.22	0.61	0.18	029	0.24	0.10	0.16	0.17	0.38	0.14	
LOI	1.84	1.31	2.62	1.39	2.17	1.35	3.32	1.46	1.70	1.88	1.07	
Total	99.68	99.79	99.55	99.70	99.80	100.53	99.74	100.20	99.70	99.47	99.69	
Cr	25	40	23	51	18	157	37	110	47	314	191	
Ni	5	9	6	12	3	10	8	6	5	15	6	
Co	4	19	13	21	16	14	13	11	7	7	5	
Sc	5	13	18	28	20	16	10	6	-	12	2	
Y	26	24	2	29	20	24	21	20	-	15	11	
Nb	7	7	7	8	6	7	8	5	-	9	8	
Zr	142	140	20	162	115	121	140	98	-	77	99	
Hf	9	8	6	11	7	7	5	7	-	18	8	
Cu	34	25	54	40	51	63	27	129	23	1641	62	
Zn	76	72	84	96	72	79	69	196	180	30	93	
Mo	-	-	-	-	-	-	-	-	-	-	-	
Sr	1042	715	424	814	517	526	399	539	-	264	318	
Ba	36	616	665	578	70	683	720	1394	-	411	880	
Rb	29	60	87	11	77	75	88	132	56	56	170	
Та	-7	-	- 34	-	- 59	-	-	-	-	-	-	
Pb Th	1	16 4		10	59 8	17	11 7	43 10	15	24 22	21 17	
U	1	4	7 1	2 2	8 1	6 1	1	10	-	5		
La	32	21	29	21	36	26	24.9	28	-	27	5 26	
Ce	42	42	62	38	56	20 46	51.8	28 46	-	55	43	
Pr	42	42	- 02	- 30	- 50	40	5.9	40	-		43	
Nd	23	23	-	25	21	22	24.1	-	-	17	11	
Sm	- 25	-	-	- 25	- 21	-	4.3	-	_	1/	-	
Eu	-	-	-	-	-	-	1.21	-	-	-	-	
Gd	-	-	-	-	-	-	3.2	-	_	-	-	
Tb	-	-	-	-	-	-	5.2	-	-	-	-	
Dy	_	_	-	_	-	_	3.1	-	_	_	-	
Но	-	-	-	_	-	_	0.67	_	_	_	-	
Er	-	-	-	-	-	-	1.8	_	-	-	-	
Tm	-	-	-	-	-	-	0.26	-	-	-	-	
Yb	-	-	-	-	-	-	1.6	-	-	-	-	
Lu	-	-	-	-	-	-	0.24	-	-	-	-	
Lu	-	-	-	-	-	-	0.24	-	-	-	-	

center Sample Rock SiO ₂ TiO ₂	3/BK28b Gb	5/BK							
SiO ₂	Gb		6/BK	1/BK-27b	2/BK-38	8/BK-40	10/BK	9/BK	4/BK
		Gb	Gb	Gr	Gr	Gr	Md	Gd	Gr
	50.68	51.20	50.91	72.92	70.18	70.96	55.45	68.50	69.12
ΠO_2	0.87	0.56	0.52	0.17	0.34	0.31	0.64	0.22	0.36
Al_2O_3	18.07	11.47	15.45	13.10	13.97	13.69	19.43	16.61	15.37
Fe ₂ O ₃	3.70	8.05*	6.52*	0.68	2.09	1.09	-	-	-
FeO	5.73	-	-	1.66	1.33	1.71	6.12*	2.01*	3.26*
MnO	0.25	0.15	0.13	0.18	0.14	0.15	0.14	0.08	0.07
MgO	5.38	11.97	9.44	0.60	1.19	1.45	4.21	0.77	1.36
CaO	11.60	14.46	15.87	2.53	2.68	3.20	8.00	2.94	4.42
Na ₂ O	2.24	1.20	1.34	3.52	3.68	3.85	3.15	3.13	3.26
K_2O	0.26	0.44	0.27	3.37	2.72	2.55	2.18	3.56	2.06
P_2O_5	0.22	0.08	0.07	0.13	0.17	0.18	0.18	0.09	0.10
H_2O^-	0.10	-	-	0.13	0.09	0.09	-	-	-
LOI	0.47	1.32	0.98	0.58	1.09	1.09	0.50	2.09	0.51
Total	99.53	99.72	100.54	99.63	99.63	99.78	100.00	100.00	99.98
Cr	47	743	132	37	31	39	62	14	27
Ni	30	112	78	17	9	10	16	4	6
Co	29.7	38.0	29.0	3.7	5.7	5.6	21	6	9
Sc	36.4	68.3	63.9	5.3	5.7	5.8	24.9	5.8	10.4
Y	19.1	14.4	12.6	11.5	10.0	11.9	16.9	11.9	10.1
Nb	1.72	1.72	1.24	5.50	4.23	4.49	4.39	5.55	3.15
Zr	58	42	31	69	92	102	99	100	95
Hf	1.5	1.1	0.8	2.2	2.65	2.54	2.74	3.01	2.25
Cu	47	41	70	48	18	28	87	14	10
Zn	52.2	47.5	34.8	20.4	10.7	19.9	69	57	25
Mo	4.98	0.44	0.56	4.56	1.51	4.40	-	-	-
Sr	713.6	240	337	208	316	286	662	298	405
Ba	73.8	97	66	551	814	550	403	430	521
Rb	9.46	6.8	4.7	121	78.8	105.7	47	115	66
Та	0.91	0.07	0.08	0.45	0.35	0.35	0.29	0.55	0.21
Pb	4.36	1.50	2.11	7.27	6.78	8.55	25.6	13.6	8.4
Th	1.98	0.72	0.82	17.04	12.01	12.13	5.16	11.16	5.41
U	0.55	0.19	0.28	4.25	1.80	2.36	1.55	1.99	0.95
La	11.9	5.85	5.25	22.40	27.73	26.54	22.67	23.29	22.48
Ce	25.86	13.95	11.77	35.99	45.73	44.95	43.91	39.75	35.68
Pr	3.58	1.98	1.64	3.45	4.47	4.35	5.29	3.89	3.67
Nd	16.13	9.84	7.96	12.30	13.6	15.73	22.44	14.14	13.23
Sm	3.52	2.57 0.79	2.72	2.12	2.61	2.71	4.50	2.58	2.74 1.08
Eu	1.115		0.80	0.46	0.77	0.65	1.15	0.67	
Gd Tb	3.48 0.545	2.67 0.49	2.22 0.41	1.76 0.32	1.8 0.27	2.12 0.29	3.58 0.55	2.18 0.33	1.64 0.30
Dy	0.545	0.49 2.86	2.44	0.32 1.55	1.62	0.29 1.75	0.55 3.25	0.33	0.30 1.71
Dy Но	3.14 0.68	2.86 0.60	2.44 0.59	0.38	0.34	0.38	3.25 0.64	0.41	0.38
H0 Er	1.925	1.63	1.39	0.38	0.34	0.38	0.64 1.75	1.18	0.38
Er Tm	0.265	0.20	0.20	0.17	0.96	0.23	0.27	0.21	0.16
Yb	0.265	0.20	1.33	0.17	0.14	0.23	0.27	1.64	1.17
Y D Lu	0.265	0.21	0.18	0.24	0.19	0.24	0.32	0.27	0.17

Magmatic		Capitan Dimitrievo									
Sample	BK/70v	BK/71a	BK/114	BK/135	BK/73	BK/30	BK/29	BK/128	BK/122	BK/121	BK/118
Rock	QGb	Gb	MGb	Md	Md	QMd	QMd	QMz	Gd	Gd	Gr
SiO ₂	45.91	47.82	50.82	52.39	52.41	55.25	56.91	58.48	65.93	67.83	69.29
TiO ₂	1.30	1.14	1.09	1.10	0.76	0.92	0.84	0.64	0.67	0.39	0.50
Al_2O_3	17.52	18.43	15.63	14.83	17.28	15.98	14.63	20.37	15.80	15.99	15.36
Fe_2O_3	5.97	4.50	5.40	6.45	5.69	4.48	5.05	3.38	1.03	1.29	0.59
FeO	6.60	6.04	5.70	4.92	4.29	3.96	4.08	0.60	2.45	1.01	1.76
MnO	0.42	0.37	0.41	0.35	0.27	0.27	0.25	0.05	0.07	0.05	0.09
MgO	5.79	5.00	3.98	4.68	3.65	3.78	3.53	1.34	1.12	0.82	2.62
CaO	10.29	10.50	9.31	8.24	8.50	7.96	6.91	6.98	3.87	3.87	0.45
Na ₂ O	3.21	3.50	3.19	2.87	3.77	3.07	3.14	3.91	4.29	4.21	4.64
K ₂ O	1.36	1.16	3.07	2.77	2.45	2.45	2.67	3.73	3.02	3.04	3.13
P_2O_5	0.73	0.83	0.68	0.68	0.49	0.58	0.58	0.50	0.59	0.72	0.76
H ₂ O ⁻	0.11	0.17	0.31	0.30	0.11	0.10	0.23	0.17	0.22	0.04	0.13
LOI	1.09	1.00	0.79	0.54	0.68	0.74	0.81	0.28	0.74	0.52	0.42
Total	100.30	100.46	100.39	100.12	100.35	99.54	99.63	100.43	99.80	99.79	99.74
Cr	25.5	30.0	27.1	26.0	26.4	29.0	23.6	1478	1242	377	186.2
Ni	7.4	6.3	9.3	5.3	5.4	3.1	4.0	58.4	60.7	22.3	30.1
Co	35.3	31.3	27.8	30.2	24.1	22.1	22.7	8.5	6.1	3.9	22.4
Sc	29.8	23.8	22.4	23.1	18.8	19.0	19.7	10.2	7.4	7.8	24.0
Y	38.4	22.8	31.9	37.4	24.0	30.5	23.6	81.4	22.7	20.7	20.5
Nb	4.30	1.48	5.50	7.93	3.53	6.32	5.04	42.36	33.76	20.93	2.71
Zr	54.3	21.8	140.5	210.9	150.9	204.7	159.9	843.6	559.2	444.3	92.8
Hf	1.91	0.93	3.56	5.66	4.07	5.44	4.55	24.69	15.29	11.27	2.63
Cu	107	80	53	79	95	81	58	31	18	12	76
Zn	108	92	101	76	78	68	86	64	46	38	68
Мо	2.92	1.58	3.72	3.33	2.13	1.31	3.6	58.6	50.0	14.6	8.0
Sr	970	1328	745	756	1041	749	685	912	480	555	751
Ba	215	341	542	452	537	464	414	2245	639	672	493
Rb	30	19	73	79	58	93	119	558	147	108	38
Та	0.35	0.19	0.98	0.51	0.46	0.35	0.27	3.71	2.23	1.59	0.14
Pb	9.3	8.9	24.1	19.9	22.5	21.9	26.9	138.8	48.3	44.0	19.0
Th	2.88	1.42	11.59	21.83	11.28	20.03	18.28	289.6	53.53	37.00	4.46
U	3.81	0.53	5.08	7.75	3.87	6.47	5.96	17.6	21.43	6.07	1.58
La	29.88	20.74	38.21	46.19	32.25	37.69	32.21	42.01	70.47	59.26	2.01
Ce	68.95	45.05	81.11	95.07	64.10	77.04	61.46	77.40	119.95	104.2	3.39
Pr	9.32	6.16	10.11	11.37	7.55	9.28	6.83	8.81	12.63	10.03	0.38
Nd	46.26	28.71	50.29	48.14	34.53	38.49	28.99	38.27	45.81	40.08	1.47
Sm	10.94	6.76	9.02	10.43	6.74	8.17	6.07	6.94	7.88	6.39	0.30
Eu	2.91	2.24	2.41	2.61	2.06	1.97	1.80	2.14	1.63	1.61	0.14
Gd	8.41	5.73	7.20	8.18	5.14	5.89	5.02	6.28	6.21	5.29	0.33
Tb	1.24	0.77	1.03	1.22	0.81	1.06	0.74	0.83	0.77	0.68	0.04
Dy	6.71	4.19	5.38	6.73	4.44	5.56	3.93	5.35	3.44	4.14	0.19
Ho	1.46	0.89	1.12	1.49	0.87	1.16	0.82	1.09	0.80	0.76	0.05
Er	4.02	1.81	3.23	3.86	2.47	2.94	2.49	2.82	1.96	2.31	0.24
Tm	0.54	0.25	0.49	0.52	0.31	0.45	0.44	0.38	0.35	0.37	0.02
Yb	3.67	2.16	3.33	3.88	2.59	3.28	2.37	3.09	2.79	4.33	0.21
Lu	0.58	0.33	0.48	0.60	0.39	0.47	0.40	0.43	0.46	0.57	0.04

Notes: 1. Rock nomenclature abbreviations: Gb - gabbro; Gb-p - gabbro porphyry; QGb - quartz-gabbro; MGb - monzogabbro; Mz - monzonite; QMz - quartz-monzonite; QM-p - quartz-monzonite porphyry; Md - monzodiorite; Md-p- monzodiorite porphyry; QMd - quartz-monzodiorite; QMd-p - quartz-monzodiorite porphyry; D-p - diorite porphyry; Qd-p - quartz-diorite porphyry; Sy-p - syenite porphyry; QSy-p - quartz-syenite porphyry; Gd - granodiorite; Gd-p - granodiorite porphyry; Gr - granite; Gr-p - granite porphyry; Gr - granite; Da - dacite.

2. The major oxides are obtained by classical wet silicate analysis performed in the Chemical Laboratory of the Faculty of Geology and Geography, Sofia University "St. Kliment Ohridski". The exception is Chelopech – XRF analysis in the Universities of Lausanne and Geneva, Switzerland.

3. The trace and *REE* determinations are carried out using laser ablation ICP-MS method by Dr. A. von Quadt in ETH Institute, Zurich, Switzerland and only for Chelopech – XRF analysis in the Universities of Lausanne and Geneva.

4. Blank - not detected.

5. * recalculated to total iron oxide