2: Hydrothermal ore deposits related to post-orogenic extensional magmatism and core complex formation: The Rhodope Massif of Bulgaria and Greece

Peter Marchev a,*, Majka Kaiser-Rohrmeier b, Christoph Heinrich b, Maria Ovtcharova b, Albrecht von Quadt b, Raya Raicheva a

a Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev St., 1113 Sofia, Bulgaria
b Isotope Geology and Mineral Resources, Department of Earth Sciences, ETH Zürich, Sonneggstrasse 5, CH-8092 Zürich, Switzerland

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Abstract

The Rhodope Massif in southern Bulgaria and northern Greece hosts a range of Pb–Zn–Ag, Cu–Mo and Au–Ag deposits in high-grade metamorphic, continental sedimentary and igneous rocks. Following a protracted thrusting history as part of the Alpine–Himalayan collision, major late orogenic extension led to the formation of metamorphic core complexes, block faulting, sedimentary basin formation, acid to basic magmatism and hydrothermal activity within a relatively short period of time during the Early Tertiary. Large vein and carbonate replacement Pb–Zn deposits hosted by high-grade metamorphic rocks in the Central Rhodopean Dome (e.g., the Madan ore field) are spatially associated with low-angle detachment faults as well as local silicic dyke swarms and/or ignimbrites. Ore formation is essentially synchronous with post-extensional dome uplift and magmatism, which has a dominant crustal magma component according to Pb and Sr isotope data. Intermediate- and high-sulphidation Pb–Zn–Ag–Au deposits and minor porphyry Cu–Mo mineralization in the Eastern Rhodopes are predominantly hosted by veins in shoshonitic to high-K calc-alkaline volcanic rocks of closely similar age. Base-metal-poor, high-grade gold deposits of low sulphidation character occurring in continental sedimentary rocks of synextensional basins (e.g., Ada Tepe) show a close spatial and temporal relation to detachment faulting prior and during metamorphic core complex formation. Their formation predates local magmatism but may involve fluids from deep mantle magmas.

The change in geochemical signatures of Palaeogene magmatic rocks, from predominantly silicic types in the Central Rhodopes to strongly fractionated shoshonitic (Bulgaria) to calc-alkaline and high-K calc-alkaline (Greece) magmas in the Eastern Rhodopes, coincides with the enrichment in Cu and Au relative to Pb and Zn of the associated ore deposits. This trend also correlates with a decrease in the radiogenic Pb and Sr isotope components of the magmatic rocks from west to east, reflecting a reduced crustal contamination of mantle magmas, which in turn correlates with a decreasing crustal thickness that can be observed today. Hydrogen and oxygen isotopic compositions of the related hydrothermal systems show a concomitant

* Corresponding author. Tel.: +359 2 979 2240; fax: +359 2 72 46 38.
E-mail addresses: pmarchev@geology.bas.bg, pmarchev@yahoo.com (P. Marchev).
1. Introduction

For half a century, hydrothermal Pb–Zn vein and metasomatic replacement deposits in the Rhodope Massif have been the most important source of base metals in Bulgaria. They include the well-known Madan ore field, as well as the Madjarovo, Spahievo, and Zvezdel ore fields. Because of changes in the Bulgarian economy, mining operations for base metals in most of these deposits have been reduced or abandoned in recent years. A growing interest in precious metals, however, brought international exploration companies to the region and caused a change in exploration strategy, targeting the Au potential that is evident from old workings dating back to Thracian and Roman times. The most important exploration targets today are the upper parts of volcanic-hosted polymetallic epithermal systems of intermediate-sulphidation type (e.g., Chala and Madjarovo) and a new type of low-sulphidation Au systems hosted by clastic continental sediments (e.g., Ada Tepe, Stremsi and Rosino). Successful exploration in the Greek part of the Eastern Rhodopes led to the discovery of high-sulphidation gold deposits at Perama Hill and Sappes (Michael et al., 1995; McAlister et al., 1999).

The Rhodope Massif in southern Bulgaria and northern Greece shares virtually all of the major elements of the global-scale collision zone of the Alpine–Himalayan orogenic belt. A Middle Cretaceous to Early Tertiary history of compressional deformation and crustal shortening led to high-grade and locally high-pressure regional metamorphism as well as calc-alkaline plutonism in a major accretionary complex (Ivanov, 1989; Burg et al., 1990, 1995, 1996; Ricou et al., 1998). Crustal thickening was accompanied and followed by protracted extension, mainly of Oligocene age in the Rhodope Massif (Ivanov et al., 2000). There, extension was initiated by low-angle detachment faults, followed by block faulting, sedimentary basin formation, exhumation of high-grade metamorphic cores, extensive magmatism and erosion. Hydrothermal base- and precious-metal deposits were formed during these later stages of the orogenic collapse (Singer and Marchev, 2000; Marchev and Singer, 2002; Kaiser-Rohrmeier et al., 2004), similar to other parts of the Alpine–Balkan–Carpathian–Dinaride metallogenic belt (Mitchell, 1992, 1996; Mitchell and Carlie, 1994) and to some polymetallic ore districts in Canada and the western USA (Spencer and Welty, 1986; Berger and Henley, 1990; Beaudoin et al., 1991, 1992; John, 2001).

Because of its good exposure and comparatively well-studied tectonic and magmatic evolution, the Rhodope region was chosen for an international collaborative study within the Alpine–Balkan–Carpathian–Dinaride project of the Geodynamics and Ore Deposit Evolution programme of the European Science Foundation (ABCD–GEODE; Blundell et al., 2002; Heinrich and Neubauer, 2002; Lips, 2002). One aspect of this project was aimed at determining the critical mechanisms responsible for mineralization in environments of late orogenic collapse, high-grade metamorphism, extension and uplift. The Rhodope Massif is suitable for a regional study of ore formation in such a tectonic setting, allowing us to document the interplay between extensional-tectonic, magmatic and hydrothermal events in the late stages of an evolving orogen. This paper integrates new results of several subprojects and Ph.D. studies completed during the GEODE programme with previous data on Tertiary magmatism, tectonics and mineralization of the Rhodope region. Emphasis is placed on comparing the tectonic and volcanic setting of hydrothermal deposits, the space and time relationships between deformation, magmatism and ore deposition, and the likely sources of magmas and ore fluids based on isotopic data.
2. Geological overview

2.1. Geotectonic setting

The Rhodope and the Serbo-Macedonian Massifs are situated in southern Bulgaria, northern Greece and eastern Macedonia (Fig. 1). There, gneisses and granites prevail, which traditionally have been thought to represent a stable continental block of Variscan (Early Palaeozoic) or even of Precambrian age, which was preserved between the Srednogorie Zone and the Dinaride–Hellenide Belt of the Alpine–Himalayan orogenic system (Kober, 1928; Bonchev, 1971, 1988; Fig. 1). However, modern structural geology and geochronology has shown that the Rhodope and the Serbo-Macedonian Massif (Jones et al., 1992; Dinter and Royden, 1993) are a product of Alpine convergence between Africa and Europe and of consequent Cretaceous to Tertiary metamorphism and magmatism (Burchfiel, 1980; Ivanov, 1989; Burg et al., 1990, 1995, 1996; Jones et al., 1992; Ricou et al., 1998; Lips et al., 2000). Today, the Rhodope Massif is interpreted as one element within a larger-scale geodynamic history of dominantly south-vergent thrusting and north-dipping subduction accompanied by back-arc extension, which generally migrated southward from the Late Cretaceous to the present time (see also von Quadt et al., 2005, this volume). In the Rhodope Massif, the history of Alpine convergence was initiated by an inferred north-dipping subduction zone, which gave rise to Late Cretaceous calc-alkaline arc magmatism and porphyry Cu–Au and high-sulphidation epithermal Au–Cu mineralization in the Srednogorie Zone of central Bulgaria and eastern Serbia (Moritz et al., 2003; Peytcheva et al., 2003; von Quadt et al., 2003). From the Tertiary to the present time, plate convergence moved southward and evolved into extensional opening of the Aegean Sea as a back-arc basin; during Miocene to recent times, subduction of the eastern Mediterranean Sea plate has formed the presently active Hellenic Arc.

![Fig. 1. The position of the Rhodope Massif with respect to the main tectonic units of south-eastern Europe. SMM = Serbo-Macedonian Massif. Shaded area in the inset shows distribution of Eocene to Oligocene magmatic rocks.](image-url)
2.2. Tectonostratigraphic units of high-grade metamorphic rocks of the Rhodope Massif

The Rhodope Massif represents a large accretionary orogen that formed between the Srednogorie zone (underlain by European continental basement) and the present Aegean Sea. Complex nappe tectonics and crustal thickening resulted from accretion of dominantly continental crustal material followed by polyphase regional metamorphism and final structuring by major low-angle extensional faults. Metamorphism is dominantly of amphibolite-facies, with incipient migmatization in some areas, and local relics of high to ultra-high pressure eclogite facies metamorphism. A full structural and kinematic reconstruction has not yet been published. In the simplified map shown in Fig. 2, two major tectonostratigraphic complexes, the Gneiss–Migmatite Complex and the

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Fig. 2. Schematic geological map of the Rhodope Massif showing the metamorphic dome structures and major intrusive and volcanic areas and dyke swarms. BD=Bratsigovo–Dospat; Br= Borovitsa; Db= Dambaluk; HBTB= High-Ba trachybasalts; IT= Iran Tepe; KE= Kirki–Esimi; KV= Kotili–Vitinia; KZ= Kaloticho–Zlatograd; Le= Levochevo; LFD= Loutros–Fere–Dadia; Lz= Lozen; Me= Mesta; Md= Madjarovo; Pe= Perelic; Pt= Petrota; Sl= Sveti Ilija; Zd= Zvezdel; Yb= Yabalkovo. Plutons: CP= Central Pirin; RG= Rila granite; Sm= Smilian; Te= Tešhevo; Vr= Vrondou; Xt= Xanthi; Yg= Yugovo. Compiled from Ricou et al. (1998), Arikas and Voudouris (1998), Harkovska et al. (1998a), Marchev et al. (1998a, b, and unpubl. data), Nedialkov and Pe-Piper (1998); Yanev et al. (1998a) and 1:100000 map of Bulgaria. Inset shows distribution of Palaeogene intrusive and volcanic rocks and contours of crustal thickness taken from Shanov and Kostadinov (1992).
Variegated Complex, have been mapped mainly on the basis of dominant metamorphic rock composition. These units are separated, at least locally, by their degree of metamorphism and/or by mappable low-angle detachment faults, and thus they approximate the lower and upper plates of interpreted extensional core complexes (Wermicke, 1981).

The Gneiss–Migmatite Complex (Kozhoukharov et al., 1988; Haydoutov et al., 2001) corresponds to the Continental Unit of Ricou et al. (1998). It represents the tectonostratigraphically lower unit in extensional domes, and is sometimes bound on its top by mappable detachment faults. The main examples include the cores of the Central Rhodopean Dome in the Madan region, of the Kessebir and Biala Reka metamorphic domes in the Eastern Rhodopes (Burg et al., 1996; Ricou et al., 1998; Bonev, 2002) and the Kardamos and Kechros complexes in Greece (Mposkos and Krohe, 2000; Krohe and Mposkos, 2002; Fig. 2). The Sidironero complex has been correlated by Mposkos and Krohe (2000) with the lower unit of Papanikolaou and Panagopoulos (1981) and by Liati and Gebauer (1999) with the upper unit. The Gneiss–Migmatite Complex is dominated by orthogneisses and is characterized by widespread evidence of incipient melting, with subordinate paragneisses, marbles and amphibolites located mainly in its upper parts. Partially amphibolitized eclogites have been described within the Kechros and Sidironero complexes in Greece (Liati and Seidel, 1996; Mposkos and Krohe, 2000). Eclogite relicts also define an earlier tectonic thrust zone within the core of Central Rhodopean Dome (Kolčeva et al., 1986). The U–Pb age of zircons from a gabbro in the Variegated Complex overlying the Biala Reka dome shows Neoproterozoic cores (570 Ma) overgrown by Variscan rims (~300 to 350 Ma; Carrigan et al., 2003), implying that these rocks, and perhaps even their amphibolite-facies metamorphism, are of Pre-Alpine age. In the Eastern Rhodopes, the Variegated Complex is tectonically overlain by phyllites, albite gneisses, marbles and greenschist-facies metamorphosed mafic and ultramafic igneous rocks of Jurassic to Early Cretaceous age. These rocks traditionally have been described as part of the Circum-Rhodope Belt (Jaranov, 1960; Kockel et al., 1976; Fig. 2), but Ricou et al. (1998) recommend that this term be discarded.

Crustal thickness beneath the Rhodope Massif (Fig. 2, inset) has been examined by geophysical studies (Dachev and Volvovsky, 1985; Shanov and Kostadinov, 1992; Boykova, 1999; Papazachos and Skordilis, 1998). Seismic data by the latter authors indicate a crustal thickness of >50 km in the Northwestern Rhodopes (i.e., below the Rila Granite), decreasing to ca. 25 km under the dome structures of the Central and Southeastern Rhodopes, and thickening again to 32 to 35 km in the Northeastern Rhodopes, where the Variegated Complex disappears beneath Neogene sediments of the Thracian Basin (Ivanov and Kopp, 1969).

2.3. Alpine tectonic history of the Rhodope Massif

Ivanov (1989) and Burg et al. (1990) were the first to recognize two major phases or deformation styles
within the Rhodope Massif (see also Ivanov et al., 2000). The first compressional stage, with large-scale south-vergent thrusting and amphibolite-facies metamorphism, was suggested to have culminated during the Middle Cretaceous (110 to 90 Ma; Zagortchev and Moorbath, 1986). The subsequent extensional phase involved exhumation of the thrust complex and formation of brittle-ductile detachment and synthetic faults. It was proposed to have been initiated in the Late Cretaceous by the emplacement of weakly deformed granitoid bodies dated at ca. 80 Ma (Peytcheva et al., 1998a), and then continued with the formation of Early Tertiary graben structures filled with continental sediments and volcanic rocks.

Recent geochronological results indicate a more complicated and even longer tectono-metamorphic evolution, with overlapping periods of accretion and dilation (Ricou et al., 1998). They suggest a different geological evolution of the Central and Eastern Rhodopes with subduction and metamorphism in the Central Rhodopes in Jurassic times (185 to 140 Ma; Reischmann and Kostopoulos, 2002) and similar events in the Eastern Rhodopes in Early Cretaceous to Early Palaeocene times (120 to 62 Ma; Wawrzenitz and Mposkos, 1997; Mposkos and Krohe, 2000; Liati et al., 2002).

The onset of an extensional stage, as originally suggested by Ivanov (1989) for the Central Rhodopes, seems to have occurred in the Late Cretaceous to Early Palaeocene. It is marked by the metamorphism in the Kimi complex (73 to 62 Ma; Liati et al., 2002) and emplacement of a series of granitoids at the Biala Reka Dome and in the Rila area (~70 Ma; Marchev et al., 2004a; I. Peytcheva, pers. comm., 2003) and undeformed metamorphic pegmatites (65 Ma; Mposkos and Wawrzenitz, 1995). This magmatism was interpreted by Marchev et al. (2004a) as the southernmost continuation of calc-alkaline magmatism in the Srednogorie Zone, which was followed by series of granitoids of Early Eocene age (52 to 42 Ma; Ovtcharova et al., 2003). The ages of these granites, intruding what is interpreted as the upper plate of the Central Rhodopean Dome, coincide with SHRIMP ages of inferred metamorphic zircon growth in eclogites and orthogneisses obtained by Liati and Gebauer (1999) of the Sidironero complex near Thermes. This suggests that mid-crustal granite intrusion and mantle to lower-crustal metamorphism both occurred at the same time, prior to the extensional development of the core complex.

Extension along continuously mappable low-angle detachment faults formed the Central Rhodopean, Biala Reka and Kessebir metamorphic core complexes (Burg et al., 1996; Mposkos and Krohe, 2000; Ivanov et al., 2000; Krohe and Mposkos, 2002; Bonev, 2002), and led to the formation of sedimentary basins. Several unconformities developed during syntectonic continental and marine sedimentation (Boyanov and Goranov, 2001) and exhumation of UHP metamorphic lithologies. In the area north of the Kessebir dome structure, continental clastic sedimentation started in Maastrichtian–Palaeocene time (Goranov and Atanasov, 1992; Boyanov and Goranov, 1994, 2001), which is coeval with, or slightly later than, Late Cretaceous metamorphism and granitoid magmatism. Rb–Sr mineral isochrons (Peytcheva et al., 1992; Peytcheva, 1997; Wawrzenitz and Mposkos, 1997) and 40Ar/39Ar dating of muscovite, amphibole and biotite (Lips et al., 2000; Mukasa et al., 2003; Bonev et al., in press) from the Variegated and Gneiss–Migmatite complexes fall in the range 42 to 35 Ma, suggesting that they represent the latest episodes of uplift and cooling below the closure of these isotopic systems (~350°C). Similar ages, from Rb–Sr mineral isochrons of gneisses, constrain the extension and uplift of the Central Rhodopean Dome near Madan (Kaiser-Rohrmeier et al., 2004).

3. Distribution and compositional variation of Tertiary magmatism

Throughout the Rhodope Massif, the latest stages of extension are manifest by the development of Late Eocene to Oligocene sedimentary basins, followed by widespread Late Eocene to Early Miocene magmatism. Extensive volcanic and plutonic rocks, typically truncating the detachment faults in the Rhodope Massif, form part of an arcuate belt, 500 km long and 130 to 180 km wide (Fig. 2), that is known as the Macedonian–Rhodope–North-Aegean Magmatic Belt (Harkovska et al., 1989; Marchev et al., 1989; Marchev and Shanov, 1991). This zone extends to the NW into the Dinarides of Macedonia and Serbia (Bonchev,
1980; Cvetkovic et al., 1995), and also continues to the SE through the Thracian Basin into Western Turkey (Anatolia; Yilmaz and Polat, 1998; Aldanmaz et al., 2000). K–Ar dating of the volcanic rocks in the northern Dinarides (Pamić et al., 2000) suggests that this volcanism extends even further to the NW and may be connected with the Periadiatric tonalite suite (von Blanckenburg et al., 1998) and dyke swarms in the NW Alps (Venturelli et al., 1984; von Blanckenburg and Davies, 1995). This large magmatic belt, with associated hydrothermal ore deposits, extends across the boundaries of major Alpine tectonic units in southeastern Europe, such as the Vardar ophiolite zone, representing one of the major sutures of the former Tethys Ocean (Fig. 1). The magmatic belt is probably related to a lithosphere-scale low-velocity anomaly that has been identified by mantle tomography and may have been caused by late orogenic slab break-off (de Boorder et al., 1998).

Syn- to post-extensional Eocene to Oligocene igneous rocks of the Rhodope Massif (Figs. 2 and 3) can be subdivided into two zones separated approximately along the 25°E meridian: (1) the Central Rhodope Magmatic Zone and (2) the Eastern Rhodope Magmatic Zone (Harkovska et al., 1989; Marchev et al., 1989). A change in the present-day crustal thickness from west to east correlates with the varying composition of the igneous rocks (Marchev et al., 1989, 1994; Marchev and Shanov, 1991).

3.1. Igneous rocks of the Central Rhodope Magmatic Zone

Tertiary magmatic activity on the Bulgarian side of the western and the central Rhodopes, referred to as to the Central Rhodope Magmatic Zone, is located on tectonically thickened crust (42 to 50 km). It is represented by five volcanic centres (Mesta, Bratsigovo–Dospat, Perelic, Levocevo and Kotili–Vitinya) and two large plutons (Central Pirin and Teshevo) of predominantly acid composition (Fig. 2; Katskov, 1981; Eleftheriadis and Lippolt, 1984; Zagortchev et al., 1987; Harkovska et al., 1998a and references therein; Machev and Shanov, 2000, Machev et al., 2000). On Greek territory, the Vrondou pluton has been described by Kolocotroni and Dixon (1991) and Soldatos et al. (1998). Available K–Ar and Rb–Sr ages (Table 1) indicate that magmatism was active between 34 and 25 Ma. More precise U–Pb zircon data, where available, are similar to those obtained by K–Ar method. The Mesta volcanic rocks are associated with the contemporaneous Teshevo and Central Pirin granites to granodiorites (Arnaudov and Arnaudova, 1982; Zagortchev et al., 1987; Harkovska et al., 1998a). Age determinations of the Vrondou pluton suggest that it consists of Oligocene and Miocene intrusions (see references in Magganas et al., 2004).

The Mesta lavas and associated pyroclastic rocks are of rhyodacitic to dacitic composition, whereas rocks comprising the Bratsigovo–Dospat, Perelic and Kotili–Vitinya volcanic areas are petrophysically similar rhyodacite to rhyolite air-fall tuffs and strongly welded pumice-rich pyroclastic flows (Katskov, 1981; Eleftheriadis, 1995; Harkovska et al., 1998a). The Levochevo caldera, to the east of Perelic area, is filled with rhyolitic air-fall tuffs and non-welded to slightly welded pyroclastic flows. This explosive activity was followed by intrusion of dykes and subvolcanic bodies of latitic to high-K andesitic composition and late rhyolites (Harkovska et al., 1998a).

3.2. Igneous rocks of the Eastern Rhodope Magmatic Zone

The Eastern Rhodopes are underlain by progressively thinner (25 to 35 km) crust and expose a greater proportion of extrusive volcanic centres, which have a more variable magmatic composition (Figs. 2 and 3). Small intrusive bodies of gabbro, monzonite and syenite intrude the volcanic centres and metamorphic basement rocks, the largest of them being the Xanthi pluton (Kyriakopoulos, 1987; Del Moro et al., 1988; Mavroudchev et al., 1993; Christofides et al., 1998). The igneous rocks represent calc-alkaline, high-K calc-alkaline and shoshonitic magmas, including basalts, andesites, dacites, and rhyolites and their intrusive equivalents (Ivanov, 1963, 1964, 1968; Innocenti et al., 1984; Harkovska et al., 1989; Yaniev et al., 1989, 1998a; Marchev and Shanov, 1991; Eleftheriadis, 1995; Marchev et al., 1998a, 2004a; Arikas and Voudouris, 1998), and they show a general south to north enrichment in K2O (Fig. 4). Shoshonitic rocks in the Borovitsa volcanic area are accompanied by
Fig. 3. Schematic geological map of the Central and Eastern Rhodopes showing locations of hydrothermal ore districts, deposits and occurrences included in this study. Abbreviations as in Fig. 2.
rare ultrapotassic varieties (Yanev and Pecskay, 1997; Marchev et al., 1998a). Volcanic activity of the Petrola graben in Greece falls off this general potassium trend, consisting of early shoshonitic andesites and dacites, followed by late high-K calc-alkaline andesites (Arikas and Voudouris, 1998; Marchev et al. unpubl. data, 2002; Fig. 4). Extensive pyroclastic flows serve as stratigraphic markers in the Eastern Rhodopes. One pyroclastic eruption led to the formation of the large Borovitsa caldera (30 × 15 km; Iva-

<table>
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<th>Table 1</th>
<th>Summary of K–Ar, 40Ar/39Ar, Rb–Sr and U–Pb data for Palaeogene igneous rocks of the Rhodope Massif</th>
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<tr>
<td>Rb–Sr</td>
<td>K–Ar</td>
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<tr>
<td><strong>Eastern Rhodope</strong></td>
<td></td>
</tr>
<tr>
<td>Yabalkovo</td>
<td>39.10 ± 1.52</td>
</tr>
<tr>
<td>High-Ba trachybasalts</td>
<td>33.1 ± 1.3</td>
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<tr>
<td>Iran Tepe</td>
<td>36.5 to 35.0</td>
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<tr>
<td>Lozen</td>
<td>36.5 to 35.0</td>
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<tr>
<td>Madjarovo</td>
<td>32.3 ± 0.6</td>
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<td></td>
<td>31.6 ± 1.2</td>
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<tr>
<td>Borovitsa</td>
<td>35.36 ± 1.33</td>
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<td></td>
<td>30.63 ± 1.71</td>
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<tr>
<td>Zvezdol</td>
<td>31.93 ± 0.50</td>
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<td></td>
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<tr>
<td>Sveti Iliya</td>
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<tr>
<td>Dambalak</td>
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<tr>
<td>Kaloticho-Zlatograd</td>
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<td></td>
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<tr>
<td>Krumovgrad</td>
<td>27.9 ± 0.8</td>
</tr>
<tr>
<td>intra-plate basalts</td>
<td>26.1 ± 1.7</td>
</tr>
</tbody>
</table>

**Central Rhodopes**

| Mesta | 33.4 ± 1.6 | | Pecskay et al., 2000 |
| | 28.2 ± 1.0 |
| Bratsigovo-Dospat | 34 ± 3 | Palshin et al., 1974 |
| Perelic | 32.9 ± 1.2 | 31.25 ± 0.25 | Pecskay et al., 1991; Ovtcharova et al., unpubl. |
| | 29.0 ± 1.2 |
| Levochevo | 33.4 ± 1.4 | 32.58 ± 0.33 | Harkovska et al., 1998a; Ovtcharova et al., unpublished |
| | 30.2 ± 1.3 |
| Kotili-Vitinia | 30.6 to 24.6 | 30.78 ± 0.14 | Innocenti et al., 1984; Eleftheriadis and Lippolt, 1984; Ovtcharova et al., unpubl. |

**Central Pirin**

| Teshovo | 32 to 34 ± 2 |
| | 32.6 ± 0.61 |
| Vrondou (NE part) | 34 ± 2 |
| | 29 ± 1 |
| Vrondou (SW part) | 23.6 to 23.7 ± 0.5 | Magganas et al., 2004 |

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nov, 1972; (Figs. 2, 3, and 5)). Dykes of intraplate alkaline basalts and lamprophyres are described in the Biala Reka and Kessebir metamorphic domes (Mavroudchiev, 1964; Marchev et al., 1998b). Their primitive character along with abundant lherzolite xenolith fragments and high-pressure pheno- and megacrysts require derivation from mantle depths.

K–Ar age determination of the igneous rocks in the Eastern Rhodopes (Table 1) indicate that magmatism was active between 39 and 25 Ma, with the younger activity generally prevailing in the south (Eleftheriadis and Lippolt, 1984; Lilov et al., 1987; Marchev et al., 1998a; Yanev et al., 1998b). Precise ⁴⁰Ar/³⁹Ar ages demonstrate a shorter life span in several volcanic centres (e.g., ≤1 Ma at Madjarovo; Marchev and Singer, 2002; Marchev et al., 2004a). In the Greek part of the Eastern Rhodopes, an Oligocene igneous complex with volcanic rocks and coeval granitoid intrusions (35 to 28 Ma; Del Moro et al., 1988) is overlain by Lower Miocene volcanism (22 to 19.5 Ma; Pécskay et al., 2003).

3.3. Petrography and elemental and isotope geochemistry

The shoshonitic rocks are characterized by plagioclase rimmed with sanidine (e.g., Mackenzie and Chappel, 1972), accompanied by water-bearing phenocrysts (biotite ± hornblende), clinopyroxene and orthopyroxene. Mafic varieties have olivine or high-F phlogopite and pheno- or microphenocrystalapatite. Acid rocks consist of plagioclase, sanidine, clinopyroxene, biotite ± amphibole, accompanied by quartz in rhyolites. Titanomagnetite is a ubiquitous phenocryst phase, whereas ilmenite is absent in the mafic and intermediate rocks and very rare in the acid varieties. In all shoshonites, the ratio

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**Fig. 4.** K₂O versus SiO₂ plot for Tertiary igneous rocks from the Eastern Rhodope Magmatic Zone. Data from Arikas and Voudouris (1998), Eleftheriadis (1995), Innocenti et al. (1984), Nédialkov and Pe-Piper (1998); Marchev et al. (1998a, b and unpubl. data). Note the general decrease of K₂O contents from north to south, which corresponds to the spatial association of the shoshonites with intermediate-sulphidation mineralization and calc-alkaline and high-K calc-alkaline rocks with high-sulphidation deposits. Shoshonites from Petrota graben are the only exception, but they are older than the calc-alkaline rocks that are believed to be associated with mineralization. Field for the rocks associated with high-sulphidation gold deposits from Arribas (1995) is shaded.
Fe$_2$O$_3$/FeO is very high, ranging from 0.76 to 0.85 in the freshest intermediate and mafic samples (Table 2). These characteristics show that shoshonitic magmas had high water content (>3 to 5 wt.% H$_2$O) and crystallized at high oxygen fugacities (Carmichael, 1967; Burnham, 1979; Luhr, 1992; Candela, 1997).

Most calc-alkaline and high-K calc-alkaline rocks are strongly porphyritic. Plagioclase is the dominant phase in all rock types. In addition, basaltic andesites contain clinopyroxene or olivine in basalts. Andesites have either ortho- or clinopyroxene or clinopyroxene + amphibole ± biotite, which prevail in dacites and rhyodacites. Rhyolites contain plagioclase, sanidine, biotite ± amphibole and quartz phenocrysts. Titanomagnetite is present in all rocks. Compared to shoshonites, fresh calc-alkaline rocks have a lower Fe$_2$O$_3$/FeO ratio (0.41 to 0.48; Table 2), reflecting more reduced compositions.

Magmatic rocks from the Central and Eastern Rhodopes differ significantly in Sr isotope composition (Table 3) and show a strong dependence on crustal thickness (Marchev et al., 1989, 1994; Marchev and Shanov, 1991). Sr isotope ratios of Teshevo and Central Pirin granitoids and nearby coeval Mesta graben volcanic rocks are most radiogenic, and $^{87}$Sr/$^{86}$Sr gradually decreases to the south (Vrondou granitoids) and to the east-south-east (Bratsigovo–Dospat, Perelic and Kotili–Vitinia volcanic areas). Lavas from the Priabonian Iran Tepe volcano and the Eastern Rhodopes of Greece are the least radiogenic rocks with regard to their Sr isotope compositions, except for intraplate basalts at Krumovgrad.

Published Pb isotope data for the Rhodopean igneous rocks (Table 4) show a small range in $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb values. Mafic rocks from the Eastern Rhodopes and Vrondu pluton (Juteau et al., 1986; Marchev et al., 2004a) have higher $^{206}$Pb/$^{204}$Pb ratios. High-Ba trachybasalts have slightly lower $^{206}$Pb/$^{204}$Pb but have much more radiogenic $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb ratios. Krumovgrad intraplate basalts differ from all other rocks.
by higher $^{206}\text{Pb}/^{204}\text{Pb}$ at lower $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

Overall variations of the Sr and Pb isotopes in the calc-alkaline and shoshonitic rocks can be viewed as mixing between two broad end members — a low $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{206}\text{Pb}/^{204}\text{Pb}$, and low $^{207}\text{Pb}/^{204}\text{Pb}$ source, similar to local asthenosphere, represented by the intraplate basalts; and a high $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ component, represented by the Palaeozoic or older basement rocks.

### Table 2

<table>
<thead>
<tr>
<th>Locality</th>
<th>Sr</th>
<th>Pb</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>Madjarovo</td>
<td>51.21</td>
<td>58.26</td>
<td></td>
</tr>
<tr>
<td>Borovitsa</td>
<td>1.09</td>
<td>0.76</td>
<td>Marchev et al., 1998a</td>
</tr>
<tr>
<td>Zvezdel</td>
<td>18.37</td>
<td>17.06</td>
<td>Marchev et al., 2002, unpub. data</td>
</tr>
<tr>
<td>Kirki–Esimi–Petrola</td>
<td>3.11</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>Loutros–Fere–Dadia</td>
<td>5.06</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>Intraplate</td>
<td>9.00</td>
<td>5.18</td>
<td></td>
</tr>
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Analyses (1 and 2, 4 to 8) by classic wet analyses; analysis 1 from Marchev et al. (1998a); analyses 9 to 12 from Arikas and Voudouris (1998). High LOI in sample 3 is due to the hydrated (perlitic) groundmass.

### Table 3

<table>
<thead>
<tr>
<th>Locality</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern Rhodopes</td>
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</tr>
<tr>
<td>High-Ba trachybasalts</td>
<td>0.70688 to 0.70756</td>
<td>Marchev et al., 2004a</td>
</tr>
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<td>Borovitsa</td>
<td>0.70790 to 0.71199</td>
<td>Marchev et al., unpub. data</td>
</tr>
<tr>
<td>Madjarovo</td>
<td>0.70775 to 0.70861</td>
<td>Marchev et al., 2002, unpub. data</td>
</tr>
<tr>
<td>Zvezdel</td>
<td>0.70713 to 0.70737</td>
<td>Marchev et al., unpub. data</td>
</tr>
<tr>
<td>Perelic</td>
<td>0.70677 to 0.70745</td>
<td>Marchev et al., unpub. data</td>
</tr>
<tr>
<td>Kotelich–Zlatograd</td>
<td>0.70643 to 0.70713</td>
<td>Eleftheriadis, 1995</td>
</tr>
<tr>
<td>Kirki–Esimi, Petrola, Loutros–Fere–Dadia</td>
<td>0.7057 to 0.7080</td>
<td>Pecskay et al., 2003</td>
</tr>
<tr>
<td>Krumovgrad intra-plate basalts</td>
<td>0.70323 to 0.70338</td>
<td>Marchev et al., 1998b</td>
</tr>
</tbody>
</table>

| Central Rhodopes          |                                 |                  |
| Mesta                     | 0.71292 to 0.71296              | Harkovska et al., 1998a |
| Bratsigovo–Dospat         | 0.70931                        | Harkovska et al., 1998a |
| Perelic                   | 0.70929                        | Eleftheriadis, 1995 |
| Levochevo                 | 0.70900 to 0.70977              | Harkovska et al., 1998a |
| Kostili–Vitinia           | 0.70777 to 0.70852              | Innocenti et al., 1984; Eleftheriadis, 1995 |
| Central Pirin             | 0.71303 to 0.71521              | Harkovska et al., 1998a |
| Teshtovo                  | 0.71246 to 0.71263              | Harkovska et al., 1998a |
| Vrondou                   | 0.70520 to 0.70717              | Christofides et al., 1998 |
| Xanti                     | 0.70452 to 0.70783              | Christofides et al., 1998 |
3.4. Dyke swarms, volcano structures and extension

Numerous dyke swarms, trending E–W to ESE–WNW, are typical throughout the Rhodope Massif (Ivanov, 1960, 1983). The precise age of these dyke swarms and their relationship to the volcanic structures are controversial. Most authors (Boyanov and Mavroudchiev, 1961; Mavroudchiev, 1965; Yanev et al., 1998a) believe that they formed after the end of the major extrusive volcanic activity, during Late Oligocene and even Miocene time. Other authors (Kostov, 1954; Ivanov, 1960, 1972, 1983) have suggested that dyke swarms trace the position of large faults that served as the feeders to more extensive extrusive and intrusive magma emplacement.

Dyke swarms are from 15 to 65 km long. In the Northern Rhodopes they strike dominantly E–W, whereas those in the south strike mostly WNW–ESE (90° to 115°). Most dykes formed from relatively uniform acid magmas, but some swarms have composite (basic–intermediate–acid) or bimodal (basalt–rhyolite) compositions. Dyke swarms are obvious in the eroded metamorphic dome structures at Madan, Biala Reka and Kessebir. Many of these dyke swarms can be traced to depressions or calderas containing extensive volcanic material or to elongated subvolcanic intrusions (e.g., Borovitsa caldera).

Their role as feeder dykes of lavas is supported at Borovitsa and Zvездel also by the similarity of chemical compositions, K–Ar and 40Ar/39Ar ages (Harkovska et al., 1998b; Singer and Marchev, 2000), and generally by the regional age trend of dyke swarms and volcanism, both younging from north to south.

3.5. Origin of the Rhodope magmas

The Rhodope magmatism has been interpreted as typically collisional and resulting from the convergence between Africa and Europe throughout the Tertiary (Yanev and Bakhneva, 1980; Innocenti et al., 1984; Marchev and Shanov, 1991; Yanev et al., 1998a). In an attempt to explain the high 207Pb/204Pb ratios of the Oligocene–Miocene igneous rocks from the Greek part of the Rhodope Massif, Pe-Piper et al. (1998) suggested that they derived from melting of ancient enriched subcontinental lithospheric mantle. Francalanci et al. (1990), Nedialkov and Pe-Piper (1998) and Yanev et al. (1998a), following the model proposed by Foley et al. (1987), argue that the parental magmas have been generated from mantle sources, heterogeneously enriched by fluids and melts derived from previous subduction. However, this interpretation is at odds with the absence of

---

Table 4

<table>
<thead>
<tr>
<th>Locality</th>
<th>Number of analyses</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
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<tr>
<td>Eastern Rhodopes</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Borovitsa</td>
<td>9</td>
<td>18.63 to 18.76</td>
<td>15.64 to 15.73</td>
<td>38.74 to 39.07</td>
<td>Marchev et al., unpubl.;</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yanev, pers. comm.</td>
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<td>Lozen</td>
<td>1</td>
<td>18.70</td>
<td>15.69</td>
<td>38.90</td>
<td>Amov et al., 1993</td>
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<td>Madjarovo</td>
<td>6</td>
<td>18.68 to 18.80</td>
<td>15.65 to 15.68</td>
<td>38.72 to 38.83</td>
<td>Marchev et al., 1993;</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Marchev et al., unpubl.</td>
</tr>
<tr>
<td>Zvездel</td>
<td>2</td>
<td>18.72 to 18.73</td>
<td>15.65 to 15.68</td>
<td>38.75 to 38.90</td>
<td>Marchev et al., unpubl.</td>
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<tr>
<td>HBTB</td>
<td>2</td>
<td>18.72 to 18.73</td>
<td>15.74 to 15.76</td>
<td>39.07 to 39.14</td>
<td>Marchev et al., 2004a</td>
</tr>
<tr>
<td>Loutros–Fere–Dadia</td>
<td>2</td>
<td>18.86 to 18.92</td>
<td>15.69 to 15.74</td>
<td>39.01 to 39.12</td>
<td>Pe-Piper et al., 1998</td>
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<td>Central Rhodopes</td>
<td></td>
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<td>Mesta</td>
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<td>15.68</td>
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<td>Bratsigovo–Dospat</td>
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<td>38.88</td>
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<tr>
<td>Perelic</td>
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<td>18.67</td>
<td>15.68</td>
<td>38.92</td>
<td>Amov et al., 1993</td>
</tr>
<tr>
<td>Central Pirin</td>
<td>3</td>
<td>18.62 to 18.74</td>
<td>15.68 to 15.68</td>
<td>38.86 to 39.22</td>
<td>Amov et al., 1993</td>
</tr>
<tr>
<td>Teshevo</td>
<td>2</td>
<td>18.71 to 18.79</td>
<td>15.68 to 15.70</td>
<td>38.87 to 39.94</td>
<td>Amov et al., 1993</td>
</tr>
<tr>
<td>Vrondou</td>
<td>4</td>
<td>18.74 to 18.83</td>
<td>15.64 to 15.70</td>
<td>38.80 to 39.15</td>
<td>Juteau et al., 1986</td>
</tr>
<tr>
<td>Xanti</td>
<td>2</td>
<td>18.70 to 18.81</td>
<td>15.67 to 15.68</td>
<td>38.95 to 39.03</td>
<td>Pe-Piper et al., 1998</td>
</tr>
</tbody>
</table>

All samples are K feldspar except HBTB, Vrondou and Loutros-Fere-Dadia, which are from bulk rocks.
enriched or veined mantle xenoliths from the lithospheric mantle entrained in the late intraplate basalts (Marchev et al., 2004a). In the light of the geological setting and tectonic history summarized above, this late orogenic magmatism was more probably triggered by post-collisional extension (Christofides et al., 1998; Harkovska et al., 1998a; Marchev et al., 1998a, 2004a). The geochemical complexity of the late orogenic Rhodopean magmas can be ascribed to a combination of partial melting of an OIB-like enriched mantle, chemically and isotopically modified in the Rhodope metamorphic basement through the processes of crustal contamination, fractional crystallization, and magma-mixing (Marchev et al., 1989, 1994, 1998a, 2004a; Harkovska et al., 1998a). The order of emplacement of the mafic rocks in the Eastern Rhodopes, from high-Ba trachybasalts, through shoshonites, calc-alkaline and high-K calc-alkaline basalts, to purely asthenosphere-derived alkaline basalts, with a progressive decrease in the crustal component, has been interpreted to reflect upwelling asthenospheric mantle as the result of convective removal of the lithosphere by a mantle diapir. This explains the surprising similarity with processes of extension and magma evolution in the Western U.S. Cordillera and in the Menderes Massif in SW Turkey (Marchev et al., 2004a).

4. Hydrothermal base and precious metal deposits

The Rhodope Massif, like the entire Macedonian–Rhodope–North-Aegean Magmatic Belt, is characterized by numerous small to moderate-sized polymetallic ore deposits of variable composition and ore type, some of which are grouped into ore districts of global significance (Stoyanov, 1979; Mitchell and Carlie, 1994; Mitchell, 1996). Major ore deposits are localized at the eastern part of the Central Rhodopes and are absent in the western part of the Central Rhodopes, which are characterized by few small Pb–Zn and Sb deposits (Dimitrov, 1988; Dokov et al., 1989). The distribution and key characteristics of four major ore types are summarized below, more detailed descriptions of two examples being presented in Box 2–1 (Vassileva et al., 2005, this volume) and Box 2–2 (Marchev et al., 2005, this volume).

4.1. Metamorphic-hosted vein and replacement Pb–Zn–Ag deposits

Historically the most significant ore deposits in Bulgaria are Pb–Zn-dominated veins and marble-replacement bodies hosted by basement metamorphic rocks in the roof of large extensional domes. They are also associated with silicic dyke swarms, and their precise temporal and genetic relation to core complex formation and acid magmatism are a subject of recent study (Kaiser-Rohrmeier et al., 2004).

Ore fields associated with the Central Rhodopean Dome include Madan, Laki, Davidkovo, Eniovche and Ardino in Bulgaria, and Thermes as a continuation of the Madan ore field in Greece (Fig. 3, Box 2–1; Vassileva et al., 2005, this volume). Together, these comprise about 70 individual deposits. In total, ca. 114 Mt of Pb–Zn ore was processed from all ore fields between 1941 and 1995 (Table 5, Milev et al., 1996). Silver content in the ores varies between 12 and 53 g/t, except for higher values, up to 160 g/t, in the Ardino region. Presently, underground operations are active in the Laki and Madan ore fields.

The deposits comprise hydrothermal Pb–Zn veins, disseminated vein stockworks, and metasomatic replacements as the economically most important orebodies. All ore fields are spatially associated with the inferred detachment fault (Kaiser-Rohrmeier et al., 2004). The Madan ore field is located on the western slope of the dome, the Laki ore field on the northern slope and the Eniovche and Ardino deposits are located in the eastern periphery. Davidkovo is situated on the culmination of the dome less than a kilometre from the inferred but eroded hanging-wall detachment. There, the ore veins are hosted by homogenous gneisses and several marble horizons, as well as silicic dykes and volcanoclastic rocks. Mineralization is developed in stockworks and veins up to 3 m thick at the intersections of three NW-, E- and NE-trending fault structures in the footwall of the dome (Dragiev and Danchev, 1990; Ivanov et al., 2000). Veins invariably cut the detachment fault, and mineralization locally extends into overlying conglomerates of extensional basins. In the Madan ore field (Box 2–1; Vassileva et al., 2005, this volume), the deposits are closely related to six major subparallel NNW-trend-
ing faults (Kolkovski et al., 1996; Ivanov et al., 2000). Mineralization at the Laki ore field is controlled by four linear NNE-striking fault zones, the easternmost veins being located in or close to the western ring-fault of the Borovitsa caldera. Ore mineralization at Eniovche is localized along NWN-trending fault structures. The Davidkovo ore field (Figs. 2 and 3) consists of 10 prospects and several occurrences, veins and stockworks occurring at the intersections of three NW-, E- and NE-trending fault structures in the lower plate of the dome (Naphtali and Malinov, 1988; Kolkovski and Dobrev, 2000). Metasomatic orebodies in all ore fields developed at the intersections of steep veins with several marble horizons that occur both in the upper and in the lower plate. Metasomatic replacement extends up to 20 to 30 m away from the veins (Kolkovski and Dobrev, 2000).

The main minerals in the ore fields of the Central Rhodopean Dome are quartz, galena, sphalerite, pyrite, arsenopyrite, chalcopyrite and carbonates, including calcite and rhodochrosite (Bonev, 1982, 1991; Kolkovski et al., 1996). Distal Mn-skarns developed at the contacts to marbles, consisting of manganese clinopyroxenes and rhodonite, were subsequently replaced by manganese hydrous silicates, carbonates and finally by sulphides closest to the feeder veins (Vassileva and Bonev, 2003; Box 2–1, Vassileva et al., 2005, this volume). Arsenic (mainly as arsenopyrite) is widespread at Madan but subordinate at Laki (Kolkovski and Dobrev, 2000). Maneva et al. (1996) described vertical zonation within the Madan veins, with an increase of galena, chalcopyrite and pyrite at depth, and a regional increase of galena/sphalerite ratio away from the Borovitsa caldera. A general zonation of trace elements has been suggested by Maneva et al. (1996) with an upper zone enriched in Ag±Te in the least eroded Davidkovo ore district (Marinova and Kolkovski, 1995), and an intermediate level with Ag±Sb and a lower level with Ag+Bi>Sb for the rest of ore districts. Alteration of gneiss and amphibolite wallrocks produced narrow haloes of quartz–sericite–carbonate–pyrite and chlorite–carbonate–epidote, respectively, as well as local silicification (Bonev, 1968; Tzvetanov, 1976; McCoyd, 1995).

Early fluid inclusion studies at Madan indicated an increase of temperature during ore deposition from 250 to 260 °C in the upper levels to 280 to 350 °C in the lower levels and 280 to 320 °C in the metasomatic bodies (Kolkovski and Petrov, 1972; Kolkovski et al., 1978; Petrov, 1981; Strashimirov et al., 1985; Kras-teva and Stoyanova, 1988; McCoyd, 1995; Christova, 1996). In a recent study of the Petrovitsa vein of the Madan ore field, Kostova et al. (2004) showed that precipitation within the vein structure was mainly the result of cooling from about 310 to 285 °C over the investigated 400 m vertical interval. McCoyd (1995) established a similar temperature interval from fluid inclusion studies in quartz from Laki ore field but Christova (1996) noted much lower minimal temperatures. The largest temperature interval for the productive paragenesis (200 to 345 °C) was measured for the Davidkovo ore field (Naphtali and Malinov, 1988).

The polymetallic vein deposits from Madan and Luki precipitated from a slightly acid fluid with range of salinities from 0.5 to 5 eq. wt.% NaCl. The Na:K:Ca ratio determined from primary fluid inclusions in galena from Madan is 11:2:1 (Piperov et al., 1977). A Pb content of about 7 to 8 ppm and a Zn content of ca. 33 ppm were established at the present-day +668 m level, which represents a palaeodepth of about 1200 m (Kostova et al., 2004).

The age of the mineralization in the Madan and Laki ore districts has been determined by Ar–Ar dating (Fig. 5) of white mica from ore veins and altered wall rocks (Kaiser-Rohrmeier et al., 2004). Ages obtained from hydrothermal vein muscovite at Laki (~29.3 Ma) and Madan (~30.4 Ma) indicate a small but significant age difference for mineralization in the two ore fields. Sericite from alteration haloes of quartz–sphalerite–galena veins of the Madan ore field displays ages around 31 Ma, consistent with the vein muscovite. Mineralization at Eniovche is coeval with that at Madan.

Pb–Zn–Ag–Au veins in the Biala Reka Dome define the Popsko ore field, which was extensively explored but never mined. The mineralization is in 3 vein swarms (Table 5) covering ca. 100 km² at the northern periphery of the dome. Veins are hosted partly by large rhyolitic dykes or stocks and partly by metamorphic rocks of the Variegated Complex. The ore mineralogy and metal components of the Popsko ore field are similar to those from the Central Rhodopes, except for the elevated contents of Cu and Au in the former. Unlike the predominantly sericitic alteration at the Central Rhodope ore fields, the alteration mineralogy at Popsko (Pljushtev et al., 1995) is
## Table 5
Characteristics of hydrothermal ore deposits in the Eastern and Central Rhodopes

<table>
<thead>
<tr>
<th>Group of hydrothermal ore deposits (mines)</th>
<th>Ore bodies; production, (reserves)</th>
<th>Host geology</th>
<th>Ore-related minerals</th>
<th>Wall-rock alteration</th>
<th>Age of alteration (Ma)</th>
<th>Ore fluid T (°C); salinity (eq. wt.% NaCl)</th>
<th>Composition and type of associated igneous rocks</th>
<th>Age of igneous rocks (Ma)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymetallic (Pb-Zn-Ag) deposits</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Madan ore field</strong></td>
<td>Veins, stockwork, marble replacement in 6 NNE-trending faults; 95 Mt ore at 2.54% Pb and 2.10% Zn</td>
<td>Palaeozoic gneisses, amphibolite, mica schists, marbles, volcanic rocks</td>
<td>Quartz, galena, sphalerite, pyrite, arsenopyrite, chalcopyrite, pyrrhotite, tennantite-tetrahedrite, marcasite, cobalite, scarce Ag-Bi sulphosalts calcite, rhodochrosite, barite</td>
<td>Chlorite-carbonate–epidote; quartz-sericite–carbonate–pyrite; local silicification</td>
<td>29.95 to 30.76</td>
<td>230 to 350; 0.5 to 5</td>
<td>Rhyolite dykes and igmimbrites</td>
<td>30.78 to 32.58</td>
<td>Bonev, 1968, 1982; Kolkovski et al., 1978, 1996; McCoyd, 1995; Milev et al., 1996; Maneva et al., 1996; Kolkovski and Dobrev, 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004; McCoyd, 1995; Christova, 1996; Milev et al., 1996; Kolkovski and Dobrev, 2000; Singer and Marchev, 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004</td>
</tr>
<tr>
<td><strong>Laki ore field</strong></td>
<td>Veins and marble replacement in 4 NNE to N–S-trending faults; 14 Mt ore at 2.90% Pb and 2.16% Zn</td>
<td>Palaeozoic gneisses, amphibolite, mica schists, volcanic rocks adjacent to caldera margin</td>
<td>Quartz, galena, sphalerite, pyrite, arsenopyrite, chalcopyrite, calcite and rhodochrosite</td>
<td>Quartz-sericite–pyrite–adularia</td>
<td>29.19 to 29.37</td>
<td>200 to 330; 0.5 to 4.7</td>
<td>Shoshonitic intermediate to acid dykes, lavas and pyroclastic flows</td>
<td>34.57 to 31.76</td>
<td>Bonet, 1968; Bonev, 1982; Kolkovski et al., 1978, 1996; McCoyd, 1995; Milev et al., 1996; Maneva et al., 1996; Kolkovski and Dobrev, 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004; McCoyd, 1995; Christova, 1996; Milev et al., 1996; Kolkovski and Dobrev, 2000; Singer and Marchev, 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004</td>
</tr>
<tr>
<td><strong>Davidiyovo ore field</strong></td>
<td>Veins and stockworks at the intersection of NW, E–W, NE-trending faults</td>
<td>Palaeozoic gneisses, amphibolite, mica schists, volcanic rocks</td>
<td>Quartz, galena, sphalerite, rhodochrosite, Mn-calcite, calcite, pyrite, chalcopyrite, arsenopyrite, rare tennantite, enargite, bornite, tellurides</td>
<td></td>
<td>200 to 345</td>
<td></td>
<td>Rhyolite dykes and stocks</td>
<td>32.5</td>
<td>Nafpakti and Malinov, 1988; Marinova and Kolkovski, 1995; Ivanov et al., 2000; Kolkovski and Dobrev, 2000; Ovtcharova et al., 2003</td>
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<tr>
<td><strong>Eniovo ore field</strong></td>
<td>W–NW veins and small marble replacement; 4.6 Mt ore at 2.37% Pb and 2.17% Zn</td>
<td>Palaeozoic gneisses, amphibolite, mica schists, volcanic rocks</td>
<td>Quartz, galena, sphalerite, pyrite, chalcopyrite, arsenopyrite, scarce molybdenite, tennantite, enargite, bornite, Ag tellurides</td>
<td>Quartz-sericite</td>
<td>25.00</td>
<td></td>
<td>Rhyolite dykes and stocks</td>
<td>30.5</td>
<td>Milev et al., 1996; Kolkovski and Dobrev, 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004</td>
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<tr>
<td><strong>Artono ore field</strong></td>
<td>Marble replacement controlled by E–W faults; 0.4 Mt ore at 0.86% Pb and 4.19% Zn</td>
<td>Palaeozoic gneisses, amphibolite, mica schists, volcanic rocks</td>
<td>Sphalerite, chalcopyrite, galena, pyrite, pyrrhotite, marcasite, Ag-Fe, Mn-silicates and Mn-carbonates</td>
<td></td>
<td>320 to 360</td>
<td></td>
<td>Rhyolite and rhodocite dykes and stocks</td>
<td>32.5</td>
<td>Bonev, 1991; Milev et al., 1996</td>
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<tr>
<td><strong>Popko ore field</strong></td>
<td>Major N–NE and subordinate E–W and NE–NW vein swarms</td>
<td>Palaeozoic gneisses, mica schists, marbles, volcanic rocks</td>
<td>Quartz, hematite, pyrite, chalcopyrite, sphalerite-galena, gold–silver–sulphosalts, carbonates</td>
<td>Propylitic, argillie, quartz–adularia, carbonates</td>
<td>~32.87</td>
<td>230 to 260</td>
<td>Bimodal rhyolite–absarokite dykes and stocks</td>
<td>32.82</td>
<td>Breskovska and Gergelchev, 1988a; Plijushev et al., 1995; Marchev et al., 2003</td>
</tr>
<tr>
<td><strong>Epithermal Pb-Zn-Cu ± Ag–Au intermediate-sulphidation</strong></td>
<td>E–W to E–NE-trending veins and breccia zones; 1 Mt ore at 1.96% Pb and 1.72% Zn (1.5 Mt at 10 g/t Au)</td>
<td>Palaeogene volcanic and intrusive rocks</td>
<td>Quartz, galena, pyrite, sphalerite, chalcopyrite (hematite, euctrum, tennantite-tetrahedrite, Ag sulphosalts)</td>
<td>Propylitic, quartz-sericite–adularia, carbonate</td>
<td>(32.12)</td>
<td>190 to 280</td>
<td>Shoshonitic intermediate to acid dykes and monzonites</td>
<td>34.57 to 31.76</td>
<td>Radonova, 1973a; Dimitrov and Dimitrov, 1974; Maneva, 1988; McCoyd, 1995; Christova, 1995, 1996, 1998; Singer and Marchev, 2000</td>
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<tr>
<td>Location/Type</td>
<td>Description</td>
<td>Ore Minerals</td>
<td>Concentration</td>
<td>Ref.</td>
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<td>Zvezdel-Pcheloyad</td>
<td>E-W-trending veins and linear stockwork-like bodies; 4.9 Mt ore at 1.27% Pb and 1.60% Zn</td>
<td>Quartz, sphalerite, galena, pyrite, chalcopyrite, tennantite-tetrahedrite, Ag-Sb sulphosalts, electrum</td>
<td>152 to 300</td>
<td>High-K calc-alkaline to shoshonitic mafic-intermediate-acid lavas and dykes</td>
<td>31.9 to 31.13</td>
<td>Atanasov, 1965, Radanova, 1973b, Breskovska and Gergelchev, 1988; Marchev et al., 2004a</td>
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<td>Madjarovo</td>
<td>Radial veins; 10.8 Mt ore at 1.27% Pb and 0.66% Zn, 0.3 Mt Au at 2 to 3 g/t</td>
<td>Quartz, galena, pyrite, sphalerite, chalcopyrite, marcasite, tetrahedrite, bornite, rare enargite, electrum, native Au, barite, calcite</td>
<td>32.10</td>
<td>Shoshonitic to high-K calc-alkaline lavas and dykes and monzonites</td>
<td>32.7 to 32.2</td>
<td>Atanasov, 1959, 1962; Kolkovski et al., 1974; Breskovska and Tarkian, 1993; McCayd, 1995; Milev et al., 1996; Marchev and Singer, 2002</td>
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<td>Losen</td>
<td>Disseminated in subhorizontal layers</td>
<td>Quartz, galena, sphalerite</td>
<td>80 to 260</td>
<td>Rhyodacite-rhyolitic lavas and stocks, diorites</td>
<td>35?</td>
<td>Bogdanov, 1983; Breskovska and Gergelchev, 1988c</td>
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<td>Epithermal (enargite-gold) high-sulphidation</td>
<td>Perama Hill</td>
<td>Mushroom-shaped stockwork; (11 Mt at 3.8 g/t Au, 8.5 g/t Ag)</td>
<td>Quartz, pyrite, gold, Au-Ag telluride, bornite, enargite, luzonite, stannite, galena and tetrahedrite, barite</td>
<td>175 to 220; 2.5 to 5.6</td>
<td>Shoshonitic to high-K calc-alkaline mafic-intermediate-acid lavas and dykes</td>
<td>21.9 to 31.8</td>
<td>Arikas and Voudouris, 1998; McAlister et al., 1999; Scarplis et al., 1999; Lescuyer et al., 2003; Melfos et al., 2003; Peckay et al., 2003</td>
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<td>Sappes</td>
<td>Stockwork; (1.5 Mt at 15.7 g/t Au, 8.6 g/t Ag)</td>
<td>Quartz-barite veins with chalcopyrite, pyrite, galena, sphalerite, enargite, luzonite, tetrahedrite-tennantite, tellurides, native gold</td>
<td>Quartz 260 to 315; 1.7 to 1.8; barite 160 to 220; 4.2 to 5.5</td>
<td>Calc-alkaline to high-K calc-alkaline andesitic to rhyodacitic lavas and pyroclastic rocks</td>
<td>21.9 to 31.8</td>
<td>Michael et al., 1995; Bridges et al., 1997; Arikas and Voudouris, 1998; Shawh and Constantinides, 2001; Melfos et al., 2003; Voudouris et al., 2003; Peckay et al., 2003</td>
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<td>Epithermal sediment-hosted</td>
<td>Ada Tepe; Surnak; Sinap</td>
<td>Massive subhorizontal tabular body and E-W veins; (6.15 Mt ore at 4.6 g/t Au)</td>
<td>Electrum, pyrite, Au-Ag tellurides</td>
<td>Silicification, chlorite, pyrite, adularia-sericite, carbonates, clay minerals</td>
<td>150 to 2007 (150 to 240; 0.7 to 2.1; 240 to 270; 0.5 to 1.4)</td>
<td>High-K calc-alkaline andesites, rhyolitic and latitic dykes</td>
<td>35? to 31.8</td>
<td>Christova, 1996; Kunev et al., 1999; Marchev et al., 2003, 2004b</td>
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<td>Stremitsi</td>
<td>Stockwork; (6.07 Mt ore at 2.3 g/t Au)</td>
<td>Electrum, pyrite, small amount base metals</td>
<td>Silicification, adularia, sericite, carbonate</td>
<td>Quartz 90 to 270; 0.9; adularia 220 to 310; 2.2</td>
<td>High-Ka trachybasalts to latites</td>
<td>33.1 to 32.8</td>
<td>Stamatova, 1996; Marchev et al., 2004a, 2004b; Nokov et al., 1992; Christova, 1995, 1996; Marchev et al., 2003</td>
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<td>Rosino</td>
<td>Stockwork; (6.07 Mt ore at 2.3 g/t Au)</td>
<td>Electrum, small amount galena, sphalerite, chalcopyrite, carbonates and quartz</td>
<td>Silicification, carbonate-pyrite</td>
<td>35.94</td>
<td>Bimodal rhyolite-absarokite dykes</td>
<td>29.27</td>
<td>Christova, 1995, 1996; Mladenova, 1998</td>
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<td>Sedefche</td>
<td>Stockwork; (6.07 Mt ore at 2.3 g/t Au)</td>
<td>Chalcedony, quartz, pyrrhotite, arsenopyrite, pyrite, marcasite, sphalerite, galena, chalcopyrite, tetrahedrite, Pb-Sb-Sb-sulphosalts, stibnite, barite</td>
<td>Silicification, argillic</td>
<td>220 to 270; 4.9</td>
<td>Rhyolitic dykes, andesites</td>
<td>31.9 to 31.13</td>
<td>Christova, 1995, 1996; Mladenova, 1998</td>
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dominated by quartz–adularia and carbonate, which is consistent with the slightly lower temperature of homogenization for fluid inclusions of the quartz–sulphide assemblage (Petrov, in Breskovska and Gergelchev, 1988a). There are no direct age determinations, but crosscutting relationships with precisely dated fresh equivalents of high-silica rhyolite suggest that mineralization is younger than 32.8 Ma (Marchev et al., 2003).

4.2. Epithermal ore deposits in calc-alkaline to shoshonitic complexes

In the Eastern Rhodopes, epithermal deposits are mainly hosted by differentiated calc-alkaline, high-K calc-alkaline and shoshonitic volcanoes, sometimes associated with low-grade porphyry Cu–Mo occurrences in monzonitic to granitic stocks intruded in the volcanic rocks. They variably exhibit characteristics of low-, intermediate-, and high-sulphidation deposits (Hedenquist, 1987; Hedenquist et al., 2000; Sillitoe and Hedenquist, 2003), previously known as adularia–sericite and acid sulphate deposits (Heald et al., 1987).

Intermediate-sulphidation epithermal Pb–Zn–Cu ± Ag–Au deposits are located within major Palaeogene shoshonitic to high-K calc-alkaline volcano-intrusive centres of the Bulgarian Eastern Rhodopes (e.g., Spahievo in the Borovitsa complex; Zvezdel; Madjarovo), or more rarely within acid volcanoes (e.g., Losen; Fig. 3). Based on their well-expressed vertical zonation and their sulphide mineralogy, including Fe-poor sphalerite, high barite content and elevated fluid salinity, they are clearly of intermediate-sulphidation character (Hedenquist et al., 2000; Sillitoe and Hedenquist, 2003). Most of them are base-metal rich, and for about 40 years until 1995 more than 16.5 Mt of Pb–Zn ore (Table 5) was extracted from Spahievo, Zvezdel and Madjarovo (Milev et al., 1996). At present, only the Pcheloyad mine from the Zvezdel
ore field is in production as a Pb–Zn mine. Gold is present in all deposits, but only ca. 0.3 Mt containing 2 to 3 g/t Au was extracted from the upper parts of two base metal veins of Madjarovo ore field. A new gold mine at Chala in the Spahievo ore field will be opened by GORUBSO, based on ca. 15 t of gold reserves (A. Kestebekov, pers. comm., 1998).

Mineralization in all ore fields is closely associated with dyke swarms that fed the magmatic activity within the large volcanic centres. Epithermal mineralization in Madjarovo ore field is hosted in a crudely radial set of fractures (Atanasov, 1959), locally filled by coarse-porphyritic trachytic dykes (Fig. 6). Over the years, about 140 well-defined radial veins have been identified, the largest of which are 3 to 4 km long and locally up to 30 m thick. The Spahievo ore field is situated at the eastern end of the Borovitsa volcanic area (Figs. 3 and 7). Faults striking E–W to E–NE, radially from the eastern ring fault of the Borovitsa caldera, control both rhyolitic dyke intrusion and base-metal–Au mineralization (Maneva, 1988; Singer and Marchev, 2000). Mineralized breccia zones and veins are up to 1.4 km long and 20 to 30 m thick. Mineralization in the central part of the Zvezdel–Pcheloyad ore field is hosted predominantly by large veins (up to 2 to 3 km long and up to 2 m thick) (Breskovska and Gergelchev, 1988b) and linear stockwork-like bodies in the northern part (Obichnik), whereas in Losen ore is disseminated in subhorizontal layers and in steep zones or veins (Breskovska and Gergelchev, 1988c).

A large variety of minerals are present in the volcanic-hosted intermediate-sulphidation epithermal systems, dominated by galena, sphalerite, chalcopyrite and pyrite with minor marcasite, tennantite and bornite (Table 5). The paragenesis at Madjarovo includes up to six stages (Atanasov, 1962, 1965; Kolkovski et al., 1974, Breskovska and Tarkian, 1993). Early mineralization stages with quartz–sulphide were followed by quartz–carbonate phases at Spahievo (Dimitrov and Dimitrov, 1974), and by quartz–chalcedony with tetrahedrite–tennantite and Ag–Sb and Pb–Sb sulphosalts, and a final carbonate

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Fig. 7. Schematic geological maps of the Borovitsa volcanic area and Spahievo and Laki ore districts, with locations of veins and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the host rocks and alteration. Geology after Ivanov (1972), ages after Marchev and Singer (2002).
stage in the Zvezdel–Pcheloyad ore field (Breskova and Gergelchev, 1988).

Most of the deposits exhibit vertical and lateral zonation. Atanasov (1962), Gergelchev et al. (1977) and Bogdanov (1983) describe Cu, Pb and Zn in the central and lower part, and Au, Ag, sulphosalts and barite in the uppermost part and periphery of the Madjarovo and Losen systems, as in current models of epithermal mineralization (Berger and Eimon, 1983; Buchanan, 1981). A similar zonality seems to have existed in the Spahievo vein system before it was truncated by the Borovitsa caldera fault (Singer and Marchev, 2000). Chalcopyrite–galena–sphalerite–quartz mineralization in the Saje deposit, which is closer to the caldera rim and deeply eroded, was later replaced by quartz–specularite–adularia and Au mineralization that dominates in the Chala deposit, 4 km from the caldera rim. A massive cap of low-temperature silica (~150 °C), inferred from the quartz–kaolinite isotope geothermometers, implies a greater degree of meteoric input (McCoyd, 1995). This cap is more resistant to erosion than the other alteration and might be the reason for preservation of the Chala deposit (Singer and Marchev, 2000).

The alteration mineralogy and zonation in the Eastern Rhodopean deposits have been studied by many authors; e.g., Radonova (1960), Velinov et al. (1977), Velinov and Nokov (1991) and McCoyd (1995) in Madjarovo; Radonova (1973a), Kunov (1991a, b) and Velinov et al. (1990) in Spahievo; Radonova (1973b) and Kunov et al. (2000) in Zvezdel–Pcheloyad. The alteration accompanying sulphide mineralization commonly overprints previous advanced argillic (lithocap), potassic or district-wide propylitic alteration associated with shallow intrusions (e.g., in Madjarovo: Radonova, 1960; Marchev et al., 1997). A generalized sequence of alteration assemblages deduced from Madjarovo and Spahievo base- and precious metal veins (Kunov, 1991a; Velinov and Nokov, 1991; McCoyd, 1995; Marchev et al., 1997) includes (1) an inner quartz–adularia–sericite (illite) envelope around large quartz–sulphide veins or breccia zones containing up to 13 wt.% K₂O, mostly as adularia; (2) an intermediate quartz–sericite zone and (3) an outer propylitic alteration, with calcite, chlorite, albite, pyrite and subordinate epidote or sercite, extending tens to hundreds of m away from veins or vein swarms.

Fluid inclusion studies (Table 5) have been performed mostly on quartz, calcite and, more rarely, on sphalerite in most of these deposits (Atanasov, 1965; Dimitrov and Krusteva, 1974; Bogdanov, 1983; Breskovska and Tarkian, 1993; Nokov and Malinov, 1993; McCoyd, 1995; Christova, 1996). The major mineralization occurred at 210 to 280 °C, although ore deposition may have started at temperatures >300 °C and have finished at 80 to 105 °C (Bogdanov, 1983). The hydrothermal mineralization precipitated from aqueous Na–K–Ca–Cl solutions of 2 to 4 eq. wt.% NaCl.

Hydrothermal activity in the Spahievo and Madjarovo ore fields has been dated using ⁴⁰Ar/³⁹Ar (Singer and Marchev, 2000; Marchev and Singer, 2002). Surprisingly, ages of adularia from Au mineralization of the Chala gold deposit (32.10 Ma) and of an alteration halo of Pb–Zn–Au veins at Madjarovo (32.06 Ma) suggest that the two deposits formed almost simultaneously. However, whereas intermediate-sulphidation mineralization and preceding advanced argillic and potassic alteration occurred within less than 200,000 years at Madjarovo, these processes at Spahievo were separated by more than 700,000 years.

High-sulphidation (enargite–gold) mineralization occurs largely in recently discovered gold-bearing prospects in the southeastern Rhodopes in Greece (Michael et al., 1995, Bridges et al., 1997; Arikas and Voudouris, 1998; Scarpelis et al., 1999; Shawh and Constantinides, 2001; Melfos et al., 2003; Lescuyer et al., 2003; Voudouris et al., 2003).

Estimated reserves at Perama Hill include 11 Mt of oxide ore grading at 3.8 g/t Au and 8.5 g/t Ag (McAlister et al., 1999). Total reserves in the Sappes deposit include 1.2 Mt of ore with 18.4 g/t Au and 9.4 g/t Ag (Shawh and Constantinides, 2001).

Epithermal mineralization is hosted in calc-alkaline to high-K calc-alkaline volcanic rocks ranging in composition from andesitic to rhodacitic (Arikas and Voudouris, 1998). The deposits show close spatial relationships with Cu–Mo porphyry systems (Arikas and Voudouris, 1998; Voudouris et al., 2003). Mineralization in Perama Hill comprises a mushroom-shaped stockwork body in weathered sandstones and hydrothermally altered andesite breccia, which host oxide and refractory sulphide mineralization, respectively (Lescuyer et al., 2003). Ore at Sappes occurs in three prospects, which are divided by normal faults.
and hosted in subhorizontal brecciated zones between andesite lava flows.

Early hypogene ore at Perama Hill (Lescuyer et al., 2003) consists of quartz, pyrite and minor Au, Au–Ag tellurides, enargite, luzonite, stannite, galena and tetrahedrite. High-grade gold mineralization is associated with barite (Melfos et al., 2003) and Fe oxyhydroxides (Lescuyer et al., 2003) in the upper oxidized part. Mineralization was preceded by pervasive silicification, argillic and advanced argillic alteration (Scarpelis et al., 1999; Lescuyer et al., 2003). According to Voudouris et al. (2003), there is evidence for temporal transition from high- to intermediate sulphidation quartz–barite vein mineralization. Ore mineralization at Sappes is associated with stockwork veinlets within silicic, advanced argillic and sericitic alteration. Mineralization is represented by quartz and barite veins, with chalcopyrite, pyrite, galena, sphalerite, tetrahedrite–tennantite, enargite, luzonite and tellurides. Native gold occurs in the oxidized (quartz–barite) and hypogene (sulphide and sulphosalt) ores. Fluid inclusion studies by Scarpelis et al. (1999) show a salinity decrease of the hydrothermal solutions from silicic alteration to gold-bearing quartz–barite veins. The temperature of the fluids ranges from 175 to 220 °C.

Temperatures and salinities measured in the milky quartz and barite from the mineralized zones in Sappes vary between 160 and 315 °C and 1.2 and 5.5 eq. wt.% NaCl, being rather different in both minerals (Shawh and Constantinides, 2001).

Absolute age determinations of high-sulphidation epithermal mineralization in Greece are not available, but the emplacement age of the igneous rocks in the Petrota graben provides a maximum age constraint of ca. 27 Ma. A large range of reported K–Ar ages from the host rocks (32 to 22 Ma; Pécskay et al., 2003) may suggest overlapping Early Oligocene and Miocene volcanic phases that are difficult to relate to the Au mineralization.

4.3. Sediment-hosted gold deposits

In the Eastern Rhodopes, a somewhat unusual type of gold deposits formed in close association with extensional core complexes. These low-sulphidation epithermal Au deposits, exemplified by the Ada Tepe prospect (Box 2–2; Marchev et al., 2005, this volume; Marchev et al., 2003, 2004b) is hosted by syndetachment Maastrichtian to Palaeocene sediments, which overly the north-eastern closure of the Kessebir metamorphic core complex. Gold mineralization at Ada Tepe has two types of occurrence: (1) as a massive, tabular orebody located along and immediately above the detachment fault, and (2) as open-space filling ore within conglomerate and sandstone that was brecciated along predominantly E–W-oriented subvertical listric faults within the hanging wall of the detachment. Several other nearby prospects (Sinap, Surnak, Skalak) are close to or within the same detachment. The major ore-hosting structure in the Rosino deposit is a NNE-trending steep fault limiting the western end of an E–W-elongated graben within the upper plate of the detachment system in the centre of the Biala reka–Kechros dome (Figs. 2 and 3; Marchev et al., 2003; Bonev et al., in press). Host rocks consist of sandstone and conglomerate derived from the Variegated Complex and low-grade Mesozoic rocks. Similar mineralization at Sremtsi is hosted by Palaeogene sandstone and conglomerate overlying metamorphic basement rocks of the Variegated Complex. In contrast, Plofka and Sedefche South are located in limestones, and Sedefche North is hosted by volcano-clastic sediments and limestones, which unconformably overlie generally unmineralized metamorphic basement rocks.
Apart from its unusual structural setting and lack of obvious relationships with the local magmatism, the sediment-hosted mineralization exhibits many features that are typical of the adularia class of epithermal deposits, including banded veins of variably crystalline silica with adularia, bladed carbonates (occurring locally at Rosino, but commonly at Ada Tepe), and locally visible gold in some veins, giving rise to bonanza grades of up to 50 to 60 g/t over 10 to 20 m. The deposits are typically very base-metal-poor (Stremtsi, Ada Tepe), except for a small amount of galena, sphalerite and chalcopyrite at Rosino (Stamatova, 1996; Marchev et al., 2003). Sedefche is another exception, having a higher content of base metals along with Pb–Ag–Sb sulphosalts and stibnite (Mladenova, 1998). Visible Au has not been established, but Mladenova (1998) suggested that it was concentrated in the early pyrrhotite and arsenopyrite. These features (invisible gold, Sb mineralization and carbonate-rich host sediments) are very similar to ore deposits described in southern Tuscany, in the peripheral zones of the active geothermal fields of Larderello, Monte Amiata and Laterra (Lattanzi, 1999 and references therein).

Gold mineralization at Ada Tepe (Marchev et al., 2004b) and Stremtsi (Stamatova, 1996) consists mainly of electrum, associated with a small amount of pyrite or iron oxide (goethite). Traces of Au–Ag tellurides have been found in Ada Tepe. Electrum tends to occur on the margins of opaline quartz–adularia bands (in Ada Tepe) or in quartz–adularia aggregates and veinlets (at Stremtsi and Rosino). Unlike Ada Tepe, Au at Stremtsi shows highly variable composition and morphology. Gold in Rosino occurs as small intergrowths and inclusions along the grain boundaries of sulphides precipitated at the margins of thin (mm to cm) quartz–adularia–ankerite– siderite veinlets.

Alteration at Ada Tepe and Stremtsi is represented by quartz, adularia, sericite, pyrite, chlorite, carbonates and clay minerals in variable proportions. Massive silicification is characteristic of the tabular body of Ada Tepe and the limestone of Sedefche, which is converted into jasperoid quartz.

Fluid inclusions have been studied only in the Rosino deposit (Nokov et al., 1992; Christova, 1995, 1996) and at Surnak and Sinap (Christova, 1995, 1996; Kunov et al., 1999). The homogenization temperatures of fluid inclusions in quartz from Rosino are slightly lower than those in adularia (Table 5). Cryometric analyses in the adularia (Christova, 1995, 1996) indicate low salinity with a variable component of Mg or Ca chloride. Mineralization at Sarnak and Sinap precipitated from very dilute Na–K–Cl solutions at low temperatures. Temperature and pressure conditions in the Ada Tepe and Sedefche deposits have been roughly estimated on the basis of geological and mineralogical data, which indicate low temperatures and a shallow depth (<200 m) for the deposition of the bonanza Au bands at Ada Tepe. It probably resulted either from decompression, causing boiling and a temperature drop, or from mixing with cooler meteoric groundwater (Marchev et al., 2004b). Mineralization at Sedefche seems to have occurred at slightly higher temperatures.

5. Discussion

5.1. Space–time relationships between mineralization, magmatism, metamorphism and tectonic deformation

The origin of the Madan base metal mineralization has been related by several authors to the spatially associated Tertiary rhyolitic dykes (Ivanov, 1983; Kolkovski et al., 1996). Recently obtained \(^{40}\text{Ar}/^{39}\text{Ar}\) total fusion ages of adularia (Marchev et al., 2003) show that the mineralization at Ada Tepe and Rosino formed at 35 and 36 Ma, respectively (Marchev et al., 2003). Detrital muscovite separated from a gneiss clast within the alteration halo at Rosino yielded a much older age of 42 Ma (R. Spikings, pers. comm., 2004). This age difference between muscovite and adularia in the alteration zone of the Rosino deposit implies that muscovite was not heated to a temperature above its closure temperature (i.e., was not thermally reset) during hydrothermal activity.

The origin of the Madan base metal mineralization has been related by several authors to the spatially associated Tertiary rhyolitic dykes (Ivanov, 1983; Kolkovski et al., 1996). Recently obtained \(^{40}\text{Ar}/^{39}\text{Ar}\) data on hydrothermal muscovites and U–Pb zircon and Rb–Sr ages of regional magmatism and metamorphism (Peytcheva et al., 1993; Arkadakskiy et al., 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004) reveal the general timing of these processes in the Central Rhodopes, as summarized in Fig. 5. \(^{40}\text{Ar}/^{39}\text{Ar}\) ages of sericite in the sulphide veins in the Madan field (Kaiser-Rohrmeier et al., 2004) are ca. 0.5 to 1.0 million years younger than the U–Pb
zircon ages of nearby Perelic ignimbrites and a rhyolite dyke, but have an age identical to the Kotili–Vitinia ignimbrites (Ovtcharova et al., 2003 and unpubl. data). The mineralization in the Laki ore field (~29.3 Ma; Kaiser-Rohrmeier et al., 2004) is significantly younger than post-caldera volcanism of Borovitsa (~31.8 Ma; Singer and Marchev, 2000), but could still potentially be related to late-stage crystallization of deeper intrusive rocks. Ages of pre-ore muscovite (36 to 35 Ma; Kaiser-Rohrmeier et al., 2004), close to zircon ages of migmatite and pegmatite formation at 36 to 37 Ma (Peytcheva et al., 1993; Arkadakskiy et al., 2000; Ovtcharova et al., 2003), are 4 to 5 million years older than the age of the mineralization in all districts and are more closely related to the immediately preceding metamorphic history of the dome.

The 40Ar/39Ar studies of Singer and Marchev (2000) and Marchev and Singer (2002) have demonstrated that the volcanic-hosted intermediate-sulphidation epithermal deposits in the Eastern Rhodopes show a direct relationship to specific magmatic events. For example, mineralized veins in Chala and Madjarovo (~32.1 Ma) share fault zones with rhyolitic and trachytic dykes intruded less than 200,000 years before mineralization (Table 5). Similar time relationships have been established in other precisely dated epithermal systems in the world; e.g., Sleeper and Round Mountain, Nevada (Conrad and McKee, 1996; Henry et al., 1997). The only major difference between the Chala and Madjarovo systems is that mineralization at Madjarovo tends to occur at the end of magmatic activity, whereas that in Chala (Spahićevo ore field) formed ca. 200,000 to 300,000 years prior to the collapse of the large (30 × 15 km) Borovitsa caldera. Guillou-Frottier et al. (2000) show that pre-caldera epithermal mineralization is characteristic only of large calderas, where emplacement of a large silicic magma chamber may create significant extensional stress in the brittle upper crust. Radial veins to the east of the eastern caldera fault of Borovitsa caldera seem to confirm such a mechanism.

Precisely dated rhyolitic dykes from Kessebir and Biała Reka Domes (31.8 and 32.8 Ma; Marchev et al., 2003) and intraplate alkaline basalts (28 to 26 Ma; Marchev et al., 1998b) are distinctly younger than adularia of the sediment-hosted deposits Ada Tepe and Rosino (35 and 36 Ma, respectively) and they cannot be related to the low-sulphidation mineralization. Mineralization of the Ada Tepe deposit could be coeval with ca. 35 Ma lavas of the Iran Tepe palaeovolcano located 4 km to the north-east of the deposit (K–Ar; Lilov et al., 1987; Z. Pecska, pers. comm., 2002), but their stratigraphic position above the Upper Priabonian to Lower Oligocene marl–limestone formation suggests that Iran Tepe lavas are younger than 34 Ma. In addition, overlying Upper Eocene to Oligocene sedimentary rocks, which cover the northern part of the deposit, are not affected by hydrothermal alteration. On the other hand, the close association of high-grade gold mineralization with the detachment fault indicates an intimate association of Ada Tepe and similar deposits with metamorphic core-complex formation. Bonev et al. (in press) argue that ore deposit formation at ca. 35 Ma in the hanging wall of the detachment fault coincides with late-stage brittle extension after cooling of the basement rocks to temperatures <200 °C.

5.2. Source of metals and fluids

Comparing the available Pb and Sr isotopic analyses of sulphides and gangue minerals to the igneous and metamorphic rocks constrains the source of metals and fluid pathways in the hydrothermal systems (Figs. 8 and 9). Sulphides have a rather uniform Pb isotope composition with elevated 207Pb/204Pb and 208Pb/204Pb for a given 206Pb/204Pb, compared with the average crustal growth curve of Stacey and Kramers (1975). The homogeneity of the Pb isotope composition of sulphides from hydrothermal deposits from such a large area and hosted in such different rock types is rather surprising. Kalogeropoulos et al. (1989) and Nebel et al. (1991), who also pointed out the uniformity of the Pb isotope composition for ore and igneous rock lead in the Greek parts of the Rhodopes and Serbo-Macedonian Massif, suggested that it is the result of extensive reworking of Palaeozoic crust in Mesozoic to Tertiary times.

Most Pb isotope data of sulphides from the Central and Eastern Rhodopes fall within the ratios for the underlying metamorphic basement rocks (Fig. 8A). The simplest interpretation is that the ore Pb is derived from the metamorphic rocks through leaching by fluids of any origin. However, separate considera-
tion of the Pb isotopes in dome-related vein and replacement-type Pb–Zn–Ag deposits (Fig. 8A) and the volcanic-hosted epithermal systems (Fig. 8B) reveals some differences. Madan and Laki from the former group show very limited ranges and the highest $^{207}\text{Pb}/^{204}\text{Pb}$ and lowest $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, entirely overlapping the composition of metamorphic rocks. Sulphides from Popsko show slightly higher $^{206}\text{Pb}/^{204}\text{Pb}$ and lower $^{208}\text{Pb}/^{204}\text{Pb}$. Sulphides from the volcanic-hosted intermediate-sulphidation epithermal systems show a wider range in $^{206}\text{Pb}/^{204}\text{Pb}$ values, Madjarovo being the most radiogenic, and a regular decrease from east to west through the Zvezdel and Spahievo ore fields (Breskovska and Bogdanov, 1987). Lead isotope compositions of sulphides from each district have very limited ranges, the $^{206}\text{Pb}/^{204}\text{Pb}$ values being indistinguishable from the compositions of the spatially associated intermediate and acid igneous rocks, except for a slight enrichment in thorogenic and uranogenic Pb isotopes towards the metamorphic basement compositions. The overlap of the sulphides from each ore field with the compositional fields of the magmatic rocks suggests a largely magmatic origin of Pb in the mineralization. However, the general overlap with the metamorphic rocks suggest that crustal Pb is also present in the hydrothermal fluids, having been leached directly or inherited indirectly from the crustal contamination of the magmas.

Strontium isotope data (Fig. 9) throw additional light on the contribution of different possible sources to the hydrothermal fluids. Limited Sr isotopes for the barite and carbonates from Madan, Popsko, Zvezdel, Madjarovo and a hydrothermal apatite from Chala show that metamorphic-hosted vein- and replacement
Pb–Zn–Ag deposits (Madan, Popsko) are more radiogenic than the local igneous rocks. Strontium compositions are closer to or within the metamorphic range, consistently with a significant contribution from the basement rocks. In the volcanic-hosted epithermal deposits, small variations in the Sr isotope values of the gangue minerals lie within the magmatic range (e.g., Chala and Zvezdel) or show only slight 87Sr enrichment relative to host igneous rocks (Madjarovo). These data are consistent with the Sr contribution coming entirely from the igneous source with little or no input from the local metamorphic basement. A detailed Sr isotope study of barite from veins of variable thickness in the Madjarovo intermediate-sulphidation system (Marchev et al., 2002) demonstrated larger variations of the isotopes in thinner veins and almost constant isotopic compositions in the large veins. These values are more radiogenic than those of the host or associated magmatic rocks but lower than those of the metamorphic basement. Strontium isotope data were interpreted by Marchev et al. (2002) to derive from a crystallizing granite pluton through exsolution and expulsion of magmatic water, followed by limited interaction of the fluid with more radiogenic metamorphic and less radiogenic volcanic rocks.

Studies of stable isotopes (O and D) in silicates, sulphides, sulphates and carbonates from alteration and ore veins from Madjarovo, Drumche, Pcheloyad, Sphatievo and Luky (McCoyd, 1995) and inclusion fluids in galena from Madan (Bonev et al., 1997) confirm a contrasting origin of fluids in typical volcanic-hosted epithermal systems and metamorphic-hosted systems. According to McCoyd (1995), fluid responsible for the epithermal systems of Madjarovo and Drumche deposits may contain a significant component (up to 60%) of magmatic water, in addition to meteoric waters, whereas the mineralizing fluid in Laki is derived predominantly from exchanged meteoric water. The stable isotope characteristics of fluids directly determined in galena-hosted fluid inclusions from Madan (Bonev et al., 1997) also indicate a predominantly meteoric origin of these ore fluids, consistent with inclusion chemistry and thermal modelling by Kostova et al. (2004).
Limited measurements of Pb-isotope composition of pyrite and whole rock Pb in the Ada Tepe deposit (Fig. 8B) fall within the range of ratios for feldspars in the Zvezdel volcano as well as the field of the Rhodope metamorphic rocks (Marchev et al., 2004b) and do not allow any discrimination between a metamorphic and an igneous origin of Pb in the hydrothermal fluid. A significant contribution of the basement to the ore-forming fluid of the sediment-hosted Au deposits is apparent from the Sr isotope systematics of the Ada Tepe and Rosino deposits (Marchev et al., 2003, 2004b). Bulk rock and carbonate Sr isotope data from Ada Tepe and Rosino lie in the lower range of present-day $^{87}$Sr/$^{86}$Sr isotopic ratios for gneisses in the Eastern Rhodopes (Peytcheva et al., 1992; Peytcheva, 1997) but are much higher than the Sr isotopic values of the local, probably younger magmatic rocks from Iran Tepe and Zvezdel. These data have been interpreted by Marchev et al. (2004b) to represent a mixture of metamorphic and a small amount of old magmatic source (see below) isotopically similar to the Iran Tepe and Zvezdel magmas.

5.3. Magmatic influence on metal content of the Rhodope ore deposits

In style and composition, the Tertiary ore deposits in the Rhodope Massif exhibit significant geographic variations. The most striking feature is the increase in Cu and Au and the decrease in Pb, Zn and Ag, from the Central Rhodopean vein and metasomatic deposits, through the Eastern Rhodopean intermediate-sulphidation and high-sulphidation deposits. This difference is noticeable even for ore deposits of the same class. For example, the metamorphic-hosted vein deposit at Popsko is characterized by a much higher content of Cu and Au compared to its Central Rhodope counterpart. Except for the sediment-hosted epithermal Au deposits, changes in style and composition of the Central and Eastern Rhodopean ore deposits may be related to the changes in the chemical and isotopic composition of local magmatic rocks and to the nature of the host rocks.

Vein and replacement Pb–Zn deposits of the Madan and Biala Reka domes are spatially and temporally related to high-silica rhyolitic dykes and contemporaneous large ignimbrite deposits situated nearby. In the vicinity of the Popsko vein, magmatism is bimodal, rhyolites being cut by later absarokite-like bodies. Most Eastern Rhodopan epithermal intermediate-sulphidation deposits are spatially and temporally related to typical shoshonitic suites, with or without subordinate high-K calc-alkaline or ultrahigh-K varieties, and can be referred to as deposits related to alkaline rocks (Richards, 1995; Jensen and Barton, 2000; Sillitoe, 2002). The most distinctive characteristics of these deposits are elevated contents of tellurides and fluorite, vanadian mica (roscoelite), intense and widespread potassic alteration and deficiency of quartz gangue. From all these characteristics, the Eastern Rhodopean deposits possess only extensive potassic (adularia–sericite) alteration. They also differ from typical alkaline-related deposits in having elevated Ag and base-metal sulphides, which are more typical of the intermediate sulphidation class of epithermal deposits (Hedenquist et al., 2000), except for the subordinate presence of carbonates. In an attempt to explain the predominance of Pb–Zn over Au in the Rhodopes, Mitchell (1992, 1996) called on more saline fluids, or on the availability at depth of a Pb, Zn and Ag-rich source in the older basement. Available salinity data for the metamorphic-hosted Pb–Zn veins and volcanic-hosted intermediate-sulphidation deposits are both less than 5 eq. wt.% NaCl, but 2 to 3 eq. wt.% NaCl is adequate to transport ore-forming concentrations of Pb and Zn (Kostova et al., 2004). Leaching from old strata-bound Pb–Zn mineralization in deformed marbles, discovered in deep boreholes, has also been suggested as a potential metal source (Kolkovski et al., 1996). High-sulphidation mineralization at Perama Hill and Sappes on the Greek side of the Rhodopes is hosted in predominantly calc-alkaline to high-K calc-alkaline rocks (Table 5; Fig. 3). Such a spatial association between high-sulphidation deposits and calc-alkaline magmas has also been demonstrated earlier at other deposits (Arribas, 1995; Hedenquist et al., 1996). Perama Hill seems to be an exception to this rule, being associated with rhyolites, dacites and shoshonites, but closer examination of the volcanic evolution shows that the youngest igneous rocks, which are temporally closer to the mineralization, are high-K calc-alkaline mafic to intermediate magmas (Marchev et al., unpubl. data).

An explanation contributing to the differences between the metal proportions of the Rhodopean ore deposits can be derived from variations in the isotopic
composition of the magmatic rocks. Sr and Pb isotope compositions of the igneous rocks reflect an increasing amount of crustal components, from the SE Rhodopes towards the Central Rhodopes, and thus an increasing proportion of acid rocks coinciding with an increase in crustal thickness (Marchev et al., 1989; 1994). Therefore, crustal contamination could have diluted original mantle magmas containing Cu and Au with an increasing contribution of Pb from a continental basement source (Taylor et al., 1980; Dickin, 1981). Pb-rich deposits are typical in other areas with thick crust, such as those in Central Honduras, a convergent margin underlain by more than 40 km of continental crust (Kesler, 1997). Kesler (1978) previously pointed out that the most Au-rich ore deposits in Central America occur in areas with more primitive and/or thinner crust.

Sr and Pb data for the metamorphic-hosted and sediment-hosted deposits show some additional contribution from metamorphic rocks, consistent with hydrothermal convection through the Palaeozoic metamorphic basement after the fluids had been released by metamorphic core-complex formation or from deep-seated magma chambers. A similar model has been suggested by Arribas and Tosdal (1994) for the genesis of the polymetallic vein and manto deposits in the Betic Cordillera, Spain.

The metal source for the sediment-hosted low-sulphidation deposits is the most enigmatic. The relationship of the Ada Tepe deposit with the nearby Iran Tepe volcano is doubtful, not only because volcanic activity seems to be younger than the Ada Tepe mineralization but also because there is no hydrothermal activity in the volcano itself. Marchev et al. (2003, 2004b) and Bonev et al. (in press) emphasize the close spatial and temporal association of mineralization to the formation and cooling of the core complex, but they do not exclude a contribution from a deep-seated magma chamber, as suggested for other low-sulphidation deposits (Matsuhisa and Aoki, 1994; Simmons, 1995; cf. Heinrich et al., 2004). A close association between the formation of metamorphic core complexes and magmatic processes has been emphasized by many authors (e.g., Lister and Baldwin, 1993; Hill et al., 1995; Gans and Bohrson, 1998). It is believed that igneous rocks intruding the lower crust transfer heat and modify its thermal and mechanical properties, enhancing deformation and strain localization in an extensional environment (see Corti et al., 2003 and references therein). The process can be accompanied by elevated heat flow and hydrothermal activity (Gans and Bohrson, 1998).

Recently Marchev et al. (2004b) suggested that volcanism in the Eastern Rhodopes was probably preceded by accumulation of magma at greater depths. Findings from a series of ultramafic–mafic xenoliths (Marchev, unpubl. data), brought to the surface by the Krumovgrad alkaline basalts, suggest that large masses of alkaline ultramafic magmas formed layered intrusions in the uppermost mantle and lower and middle crust. Rapid boiling of fluids dissolved from these mafic magmas could have produced bonanza Au veins from silica and Au colloids, similar to those described by Saunders (1994) and Marchev et al. (2004b). Such a mechanism for deposition of bonanza low-sulphidation gold deposits in rift settings has been accepted recently by Sillitoe and Hedenquist (2003). Future age and isotopic studies of the xenoliths, local magmatism and mineralization are necessary to clarify the relationship between these processes.

6. Summary and conclusions

Hydrothermal ore deposits in the Rhodopes were formed during the final extensional stage of Cretaceous to Tertiary orogenic collapse, which led to the formation of metamorphic core complexes, block faulting, metamorphism and silicic to intermediate magmatism. The style and composition of the deposits show significant geographical variations, from Pb–Zn–Ag veins and replacement base-metal deposits in the Central Rhodopes, through intermediate-sulphidation epithermal base and precious metal-hosted deposits and detachment-related Au deposits in sedimentary basins in the Bulgarian part of the Eastern Rhodopes, to high-sulphidation epithermal deposits in the Greek part of the Rhodopes.

The ore-metal composition of the deposits shows a systematic correlation with the composition of spatially associated magmatic rocks. Metamorphic-hosted hydrothermal deposits (Madan, Laki, Davidkovo) are spatially related to silicic dykes in the metamorphic core complexes and ignimbrites in the nearby depressions, whereas intermediate-sulphidation base- and precious metal-hosted deposits (Chala and Madjarovo)
are structurally related to evolved silicic dykes within highly oxidized and water-rich shoshonitic volcanic rocks. High-sulphidation Au–Cu–base-metal systems in Greece are spatially associated with less oxidized and less water-rich calc-alkaline and high-K calc-alkaline magmas. An interesting type of sediment-hosted low-sulphidation epithermal Au deposit (e.g., Ada Tepe and Rosino) is related to detachment faults.

Close spatial and temporal relationships between the ore deposits and local magmatism indicate that a rapid succession of magmatic and hydrothermal processes resulted from a thermal disturbance of the crust and probably the underlying mantle by large-scale late orogenic extension. Magmatic fluid input was likely in the polymetallic and high-sulphidation Cu–Au deposits, and possibly in the Madan-type Pb–Zn deposits. The sediment-hosted deposits, including Ada Tepe, were formed during late-stage brittle extension, after cooling of the basement rocks in metamorphic core complexes by fluids that may be of metamorphic or deep magmatic origin.

Sr and Pb isotope compositions of sulphides and gangue minerals of ore deposits show an increase of \( ^{206}\text{Pb} / {^{204}\text{Pb}} \) and a decrease of \( ^{207}\text{Pb} / {^{204}\text{Pb}} \) and \( ^{87}\text{Sr} / {^{86}\text{Sr}} \) ratios from west to east, correlating with a similar pattern in magmatic rocks. These variations reflect a decreasing input to the hydrothermal systems of Palaeozoic or older crustal material from the much thicker continental crust in the Central Rhodopes and an increase of mantle contributions towards the Eastern Rhodopes, which are underlain by thinned crust.

In contrast to deposits in the Eastern Rhodopes, hydrothermal minerals in deposits of the Central Rhodopes have more radiogenic \( ^{87}\text{Sr} / {^{86}\text{Sr}} \) and \( ^{207}\text{Pb} / {^{204}\text{Pb}} \) isotope compositions than those of associated silicic magmas. This reflects an additional radiogenic basement input of Sr and Pb to the hydrothermal fluids, consistent with a possible metamorphic fluid contribution from the core complex, or large-scale circulation of mixed magmatic and meteoric fluids through the extensionally fractured gneisses.

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