Mineralium Deposita (2002) 37: 669–677
DOI 10.1007/s00126-002-0278-3

ARTICLE

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Small-scale variations of ^{87}Sr/^{86}Sr isotope composition of barite in the Madjarovo low-sulphidation epithermal system, SE Bulgaria: implications for sources of Sr, fluid fluxes and pathways of the ore-forming fluids

Received: 19 January 2001 / Accepted: 19 December 2001 /

Abstract The Madjarovo ore district is located in the volcanic rocks of the Oligocene Madjarovo shield volcano and underlying Precambrian(?) and Palaeozoic high-grade metamorphic rocks of the Rhodope Massif, Bulgaria. It is situated in the eastern part of a large Tertiary magmatic–metallogenic belt, which resulted from the Cretaceous collision of Serbo-Macedonian and Rhodope Massifs with the Pelagonian microplate. The low-sulphidation base and precious metal mineralisation at Madjarovo (~32.1 Ma) formed shortly after the cessation of the shoshonitic and high-K calc-alkaline volcanic and intrusive activity (32.6–32.2 Ma), and is spatially and temporally related to late monzonite–trachyte intrusions. The strontium isotope composition of five barite samples hosted in the volcanic sequence is used to characterise the source(s) of Sr in associated base and precious metal mineralisation and to infer fluid fluxes and pathways of the ore-forming fluids. The ^{87}Sr/^{86}Sr compositions for barite samples from ore veins fall in the range 0.70854–0.70955 with the lowest and highest values found in the smaller brecciated veins. Barite from a thin vein in the basal latite lava flow has the most radiogenic ^{87}Sr/^{86}Sr isotope composition, likely reflecting the involvement of more radiogenic metamorphic basement rocks. The least radiogenic composition was determined for barite from a similar vein high in the volcanic pile, 500–600 m above the metamorphic basement. Barites from large veins taken from different stratigraphic positions in the host lavas have almost identical isotopic compositions in the range 0.70883–0.70899. The ^{87}Sr/^{86}Sr values for barite within the deposit are higher than those for host magmatic rocks (0.70775–0.70863), but lower than those of the metamorphic basement (0.7110–0.7278). It is concluded that strontium in the fluids is a mixture of predominantly magmatic strontium and a variable amount of more radiogenic Sr from the metamorphic basement rocks. The ore-bearing fluid may have been derived from a shallow (1–4 km) silicic pluton with an initial ^{87}Sr/^{86}Sr value ~0.7080. Because of the short distance to the site of deposition, the fault-focused ore fluids maintained homogeneous strontium, predominantly magmatic strontium isotope ratios, with slight contribution(s) of more radiogenic strontium from the metamorphic basement rocks. Larger variations in the small brecciated veins can be explained by more extensive fluid–rock interaction with local host metamorphic or volcanic rocks.

Keywords Barite · Bulgaria · Madjarovo · Rhodope · Strontium isotopes

Introduction

Strontium isotopes have been used either independently or combined with other isotopic systematics to infer the sources of metals in hydrothermal fluids in different types of ore deposits, including epithermal ores (Richards et al. 1991; Arribas et al. 1995; Alderton et al. 1998) or polymetallic, barite-bearing quartz veins (Polliand and Moritz 1999). These studies demonstrate that strontium isotopes in hydrothermal systems are sensitive indicators of fluid–wall rock interaction and reflect the signatures of the source(s) from which fluids were generated and the rocks through which they passed.

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The Madjarovo ore district in the Rhodope Massif, Bulgaria, shows an unusually close and clear spatial relationship between particular magmatic bodies, potassium-silicate and advanced argillic alteration, and low-sulphidation epithermal vein deposits (Marchev et al. 1997). Similar relationships are typical of other ore districts in the Rhodope Massif (e.g. Spahievo, Kassiteres and Konos (Georgiev et al. 1996; Arikas and Voudouris 1998, Singer and Marchev 2000), but are less common worldwide (Aoki et al. 1993; Thompson et al. 1994; Love et al. 1998). The clear spatial relationship between volcanism, intrusive magmatism and alteration-mineralisation in the Madjarovo district allows for an excellent opportunity to study the temporal relations and source of fluids and metals in intrusion-related low-sulphidation systems. Previously, McCoyd (1995) and Amov et al. (1979, 1985) applied O, H and Pb isotopic studies to infer and characterise the source of fluids and metals in the Madjarovo vein mineralisation. On the basis of oxygen and hydrogen isotopes in the silicate and sulphate minerals, McCoyd (1995) concluded that the hydrothermal water in the Madjarovo epithermal system had a mixed magmatic–meteoric origin, and Amov et al. (1979, 1985) interpreted the Pb isotope composition of galena in favour of a magmatic origin for lead in the Madjarovo ores. The timing and duration of magmatic activity and hydrothermal processes in the Madjarovo district have been dated precisely by laser-fusion ^{40}Ar/^{39}Ar (Marchev and Singer 2000).

In this study, which is a part of a larger Rhodope project in the framework of the European programme GEODE, we present the first Sr isotopic data on barite from the low-sulphidation epithermal veins in the Madjarovo district. These data are compared with Sr isotopic data for unaltered magmatic (intrusive and extrusive) and metamorphic basement rocks in order to place constraints on the relative contribution of these sources to the ore system and on flow pathways.

Regional geology

The Madjarovo ore district is located within the Palaeogene Madjarovo volcanic centre of the Eastern Rhodope Massif, which is a part of the large Macedonian–Rhodope–North-Aegean magmatic belt (Harkovska et al. 1989; Marchev et al. 1989b). This arcuate belt, which is about 500 km long and 130 to 180 km wide (Fig. 1), resulted from the Cretaceous collision of the Serbo-Macedonian and Rhodope Massifs with the Pelagonian microplate, a fragment of the African platform (Ricou 1994). Collision caused large-scale intra-crustal deformation and thickening of the crust, which was followed by post-Palaeocene–Eocene extension that

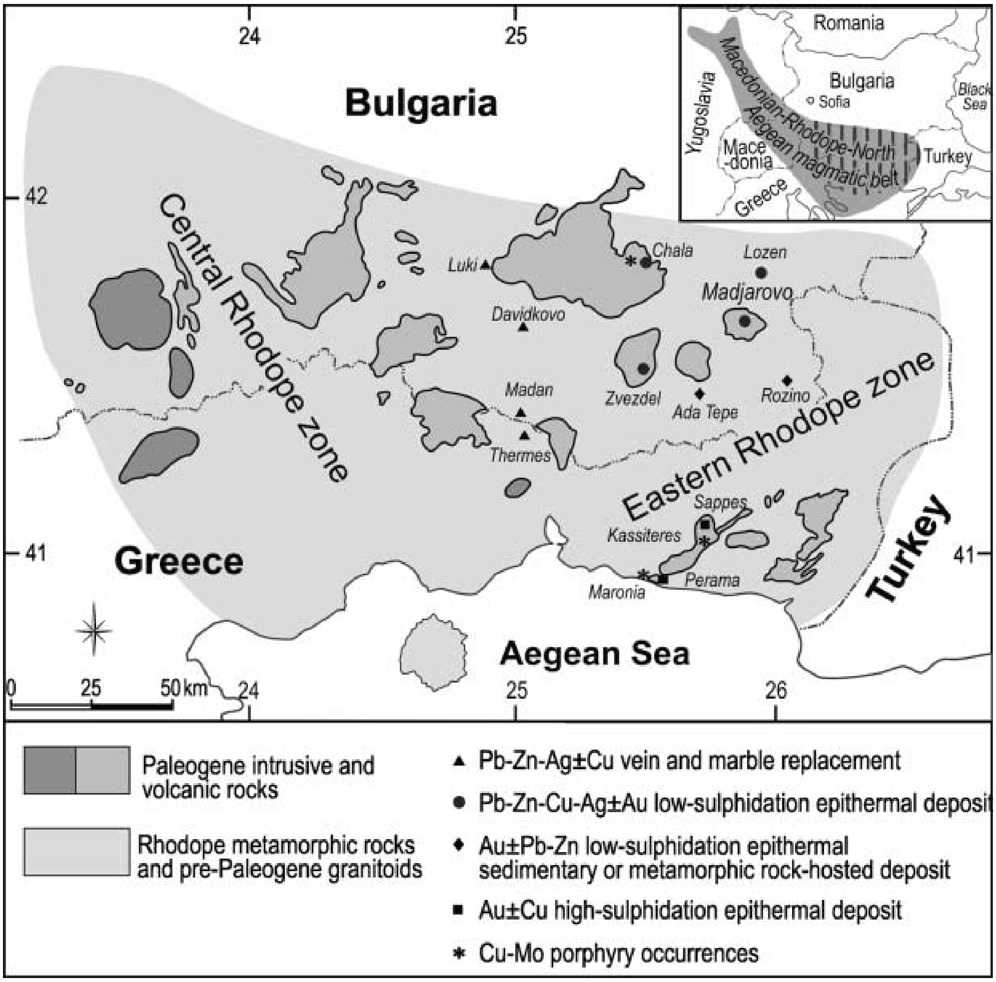


Fig. 1 Simplified geologic map of the Rhodope Massif, showing the distribution of Paleogene magmatic rocks and major ore deposits. *Inset* shows the Palaeogene Macedonian–Rhodope–North-Aegean magmatic belt. *Hatched area* is the Rhodope Massif. Serbo-Macedonian Massif is to the west of the Rhodope Massif

resulted in continued strong deformation, uplift and exhumation. Extension was accompanied by development of NNW–SSE-trending fault-bounded basins filled with continental clastics and intermediate to acid volcanics (Ivanov 1960, 1963; Kharkovska 1984; Harkovska et al. 1989; Jones et al. 1992).

The eastern part of the magmatic belt is occupied by the Rhodope Massif, which is divided approximately along the 25th meridian into the Central and Eastern Rhodope zones. Basement of the Rhodope Massif consists of high-grade Precambrian(?) and Palaeozoic meta-igneous and metasedimentary rocks (gneisses, migmatites, amphibolites, eclogites, mica-schists and marbles), which were intruded by Late Cretaceous granitoids. Seismic refraction studies and gravity models, summarised by Shanov (1998), indicate that the crust of the Eastern Rhodope zone is comparatively thin, varying between 30 and 38 km. The crust in the Central Rhodope zone is of highly variable thickness, being about 32 km to the south and 50 km in the north.

Major localities of Eocene–Oligocene magmatism in the Rhodope Massif are shown in Fig. 2. Magmatic rocks include calc-alkaline and shoshonitic basalts, andesites, dacites and rhyolites, and their intrusive equivalents (Ivanov 1963, 1964, 1968; Harkovska et al. 1989, 1998; Christofides et al. 1998; Marchev et al. 1998a; Yanev et al. 1998a), as well as alkaline basalts (Marchev et al. 1998b). A distinct south to north enrichment (from Greece to Bulgaria) in K_2O and LILE was established in the Eastern and Central Rhodope zones (Harkovska 1990; Marchev and Shanov 1991; Marchev et al. 1998a), with magmatism younging from north (39–35 Ma) to south (23.5 Ma) and the climax of volcanic activity between 33–30 Ma (Innocenti et al. 1984; Christofides et al. 1998; Marchev et al. 1998a, Yanev et al. 1998b).

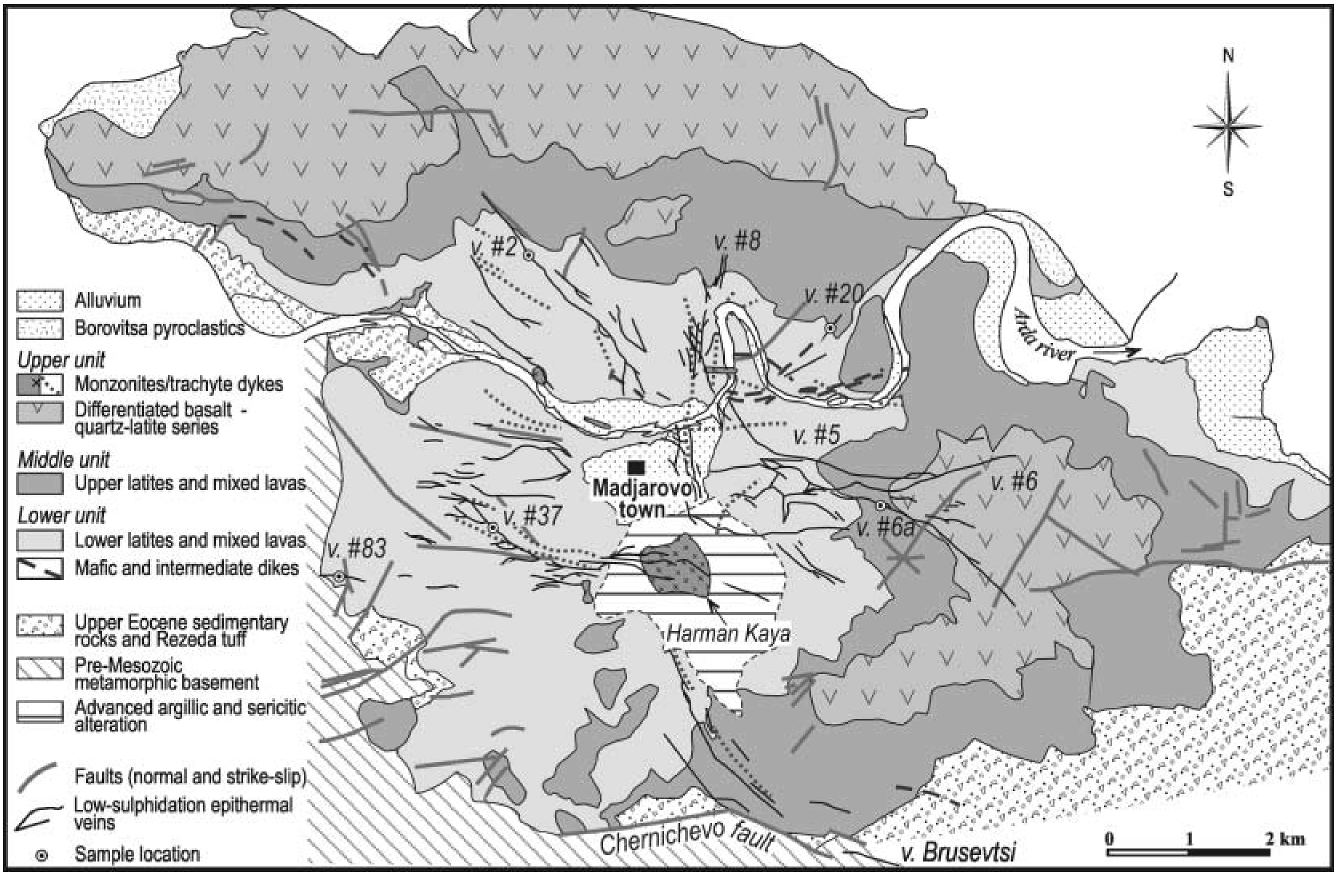
The magmatic activity in the Rhodope Massif was accompanied by the formation of abundant economic and subeconomic mineral deposits, which form the Rhodope metallogenic province (Stoyanov 1979). Based on metal association, mineralisation style and spatial relationships with magmatic systems, Tertiary ore deposits in the Rhodope Massif can be divided into:

1. Pb–Zn–Ag ± Cu vein and marble-replacement deposits hosted by the metamorphic basement rocks of the Central Rhodope zone and associated with silicic dyke swarms;
2. Pb–Zn–Cu–Ag ± Au low-sulphidation epithermal vein deposits hosted by differentiated, high-K calc-alkaline and shoshonitic central volcanoes or silicic dyke swarms in the Eastern Rhodopes zone;
3. Au ± Cu high-sulphidation epithermal deposits hosted by typically high-K calc-alkaline volcanic rocks located exclusively in the Greek part of the Eastern Rhodope zone;
4. Small and low-grade porphyry Cu–Mo deposits associated with monzonite–monzodiorite, diorite and granite porphyritic stocks within or outside volcanic centres;
5. Sedimentary or metamorphic rock-hosted gold deposits formed distal to dyke swarms or intrusions of the large volcano-plutonic systems;
6. Fluorite- and uranium-rich deposits and occurrences hosted by volcanic and metamorphic rocks (not shown in Fig. 1).

District geology

The Madjarovo district of south-eastern Bulgaria is situated approximately 200 km south-east of Sofia (Fig. 1) in the centre of the Oligocene Madjarovo Volcano. It is one of the best studied Bulgarian mining districts, but most of the information is in Bulgarian journals. The district is located in the Eastern Rhodope zone, which is characterised by an abundant low-sulphidation epithermal base

Fig. 2 Simplified geologic map of the Madjarovo ore district, showing sample locations (modified from unpublished map by Marchev et al. 1999)



and precious metal (Pb–Zn–Cu–Ag–Au) deposits and subeconomic porphyry Cu–Mo deposits (Mavroudchiev et al. 1996; Arikas and Voudouris 1998). In more than 45 years of mining, more than 10 million tons (t) of base metal ore have been extracted from the Madjarovo deposit, with 6.5 million t of reserves remaining unused because of changes in the Bulgarian economy. An extensive exploration program for gold was performed between 1988 and 1996 by the Jambol Exploration Organisation in the upper parts of the base metal veins. Eight major veins were explored and resulting proven reserves are about 2 million t grading at 3.9 g/t Au. However, a feasibility study completed in 1995 by Euraust Mineral Developments indicated that the ore deposit is not economically viable for gold.

The oldest exposed rocks in the Madjarovo district are the amphibolite facies pre-Palaeozoic and Palaeozoic metasedimentary and meta-igneous basement rocks of the Rhodope Massif and a small area of Mesozoic low-grade metamorphic rocks of greenschists, diabases and breccia, located west of the mapped area in Fig. 2. Pre-Tertiary lithologies, which outcrop south of the Chernichevo fault, are overlain by Upper Eocene conglomerates, sandstones and coral limestones (Fig. 2). A Lower Oligocene tephrostratigraphic marker, the Rezeda pumice and ash-fall tuff (Ivanov and Kopp 1969), overlies the Upper Eocene sedimentary sequence and underlies the Madjarovo volcanic rocks (Fig. 2). The Arda River, exploiting a large east–west fault, exposes the deeper stratigraphic levels of the volcanic complex. Volcanism was predominantly fissure-fed and dominated by large sheet-like lava flows and subordinate epiclastic rocks that formed a shield volcano (Ivanov 1960). The unaltered mafic to intermediate volcanic rocks (Marchev et al. 1989) are shoshonitic or high-K calc-alkaline rocks, dominantly latites. Quartz latites are the youngest volcanic rocks.

On the basis of petrology and strontium and oxygen isotope compositions (Marchev and Rogers 1998), three volcanic units have been defined. The two lower (Lower and Middle) units are characterised by up to 150 m of latites capped by basalts. Less voluminous intercalated flows of basaltic andesites, shoshonites and andesites show petrographic and isotopic evidence for large-scale magma mixing between end-members (Marchev et al. 1994; Raicheva et al. 1998). The third (upper) unit includes three consecutive lava flows that range in composition from high-K, high-Al basalts through high-K latites to quartz latites. They have identical strontium isotope compositions and $\delta^{18}O$ values that increase slightly with SiO_2 content, reflecting simple closed-system fractional crystallization. The overall range of strontium and oxygen isotope compositions for the Madjarovo lavas reflects contamination of asthenospheric mantle-derived magma by 25–30% crustal material (Marchev and Rogers 1998).

Early volcanic rocks are intruded by numerous monzonite stocks and rare gabbro and syenite bodies, similar in composition to the volcanic rocks of the Upper unit. It is believed that the monzonite stocks coalesce at depth (Mavroudchiev 1959). The largest monzonitic body, Harman Kaya, outcrops over approximately 1.5 km^2 (Fig. 2) and was intersected at depth in many drill holes. Porphyritic trachytic dykes of identical composition to the monzonites and probably derived from the same magma, also outcrop in the central part of the volcano over an area of about 40–50 km^2. Geophysical studies (Iosifov et al. 1987) document a gravity minimum and magnetic anomaly in the centre of the volcano, interpreted to represent a syenite pluton between depths of 1 to 4 km. Intrusion of the monzonite–trachyte magma was accompanied and followed by extensive destruction of the central part of the volcano, suggesting that volcanic rocks and intrusions are comagmatic. Gergelchev (1974) postulated the existence of a caldera structure coinciding in size with the pluton, but our field observations did not confirm this interpretation.

Alteration and mineralisation

The central part of the Madjarovo volcano is extensively altered and contains several distinct styles of alteration and abundant veins with low-sulphidation (adularia–sericite) epithermal mineralisation, which define the Madjarovo ore district. Detailed studies on the various alteration styles and vein mineralisation have been published by Radonova (1960), Atanasov (1962), Velinov and Nokov (1991), Breskovska and Tarkian (1993), McCoyd (1995) and Marchev et al. (1997). Advanced argillic (quartz–alunite–pyrophyllite–diaspore), pervasive quartz–sericite–pyrite alteration and zones of silicification, forming a lithocap (Sillitoe 1995), are closely associated with Harman Kaya and other monzonite outcrops. Outwards from the volcanic centre, the hydrothermal alteration grades into propylitic alteration, termed ‘regional’ by Radonova (1960). Subjacent potassic alteration assemblages, showing a transition from porphyry to epithermal environments (Marchev et al. 1997), and skarn bodies of unknown size and economic potential (Breskovska et al. 1976), are also spatially related to the monzonitic intrusions. The latter, together with associated argillic and potassic alteration, are cut by base metal-bearing veins with a radial distribution (Fig. 2) in which the mineralised part and related quartz–adularia alteration tend to be peripheral to the acid-sulphate environment. Thus, Madjarovo is a typical intrusion-related low-sulphidation epithermal base and precious metal mineralisation (e.g. Sillitoe 1993).

The ore veins are hosted within a 700- to 800-m-thick sequence of volcanic rocks and basement metamorphic rocks, spatially associated with trachyte dykes. Brusevtsi is the only deposit hosted entirely within metamorphic rocks (Fig. 2). Mineralised bodies range from comparatively short (no longer than several hundred metres), narrow brecciated zones with quartz veinlets, to large (> 3 km in length), more than 25-m-thick massive veins. The latter occur along faults with displacements of as much as 200 m (e.g. veins #2, 6, 8; Atanasov 1959) or systems of several faults that coalesce at depth (e.g. vein #37). The largest faults and fractures contain the highest grade ore and different varieties of silica (quartz, chalcedony, amethyst, agate, opal). Most of the large veins show abundant evidence of brecciation and re-cementation, which suggests protracted tectonic activity during ore deposition.

The ore consists of variable amount of sulphide minerals (galena, sphalerite, chalcopyrite), Se–Bi–Pb–Ag–Sb sulphosalts and native gold and silver. The paragenesis is complex and six stages of mineralisation have been identified (Atanasov 1962; Breskovska and Tarkian 1993). A zonation in which base metals were deposited below precious metals, similar to other epithermal deposits (Buchanan 1981; Berger and Eimon 1983), has been established by Atanasov (1962) and Arnaudova et al. (1991). Jasperoid-like (carbonate replacement) rocks with elevated gold contents are also present distal to the monzonitic intrusion and are similar to those in Carlin-like deposits (Marchev et al. 1997; Metodiev and Georgiev 1999). Ore minerals were formed from near-neutral, low-salinity (2.0–4.5 equiv. wt% NaCl) and low-temperature (210–280 °C) fluids

(Breskovska and Tarkian 1993; McCoyd 1995). No inclusion evidence for boiling has been found, but the presence of hydrothermal breccias and adularia, and estimated temperature–depth boiling point curves, indicate that boiling may have occurred (McCoyd 1995).

Age of magmatic and hydrothermal activity

Timing and duration of the magmatic and hydrothermal events at Madjarovo have been precisely dated by single-crystal and step-heating laser-probe $^{40}Ar/^{39}Ar$ measurements of potassium-bearing minerals in the host rocks (K-feldspar and biotite) and in alteration zones adularia (Marchev and Singer 2000). Age determinations of the basal latite flow (32.69 ± 0.15 Ma) and the top quartz latite flow (32.23 ± 0.15 Ma) suggest that magmatic activity may have been bracketed within less than 500,000 years. These ages are confirmed by the ages of the Rezeda marker (32.53 ± 0.18 Ma) and Borovitsa tuff (32.16 ± 0.15), which underlie and overlie, respectively, the volcanic rocks of the Madjarovo volcanic complex. The age of trachyte dykes (32.23 ± 0.07 Ma) and probably of the Harman Kaya monzonite confirm isotopic data for the affiliation of this magma to the Upper unit of the volcanic sequence (see below). Ages of adularia from two different veins (32.15 ± 0.16 and 32.12 ± 0.23 Ma) and crosscutting relations between advanced argillic alteration and mineralised veins, constrain the period of hydrothermal activity to less than 200,000 years (most probably ~100,000 years) after the intrusion of trachytes.

Samples and analytical technique

Five barite samples of different textural types and mode of occurrence, as described in Table 1, were selected for strontium isotope measurements. The location of the samples is shown on the geologic map (Fig. 2).

Because of the intense faulting, just before and during ore deposition (Atanasov 1959), we could obtain barite samples from different elevations within the volcanic stratigraphy. Samples V2, V6a and V20 were located approximately 500–600 m above the metamorphic basement, whereas the samples V37 and V83 were less than 100 m above the metamorphic basement.

For strontium isotope determinations on barite, approximately 100 mg of the 0.1–0.15-mm fraction (at the Department of Geology, Royal Holloway, University of London) or of finely ground material (at the Department of Mineralogy, University of Geneva) was leached overnight in 6 N HCl at 100 °C. The solution was evaporated and the residue dissolved in 2.5 N HCl. Strontium was separated using a cation exchange column, and isotopic analyses were made on a VG354 and Finnigan MAT 262 thermal ionisation mass spectrometer at London and Geneva, respectively. Duplicate analyses of sample V6a in the two laboratories (Table 1) are just outside of the analytical uncertainty. The magmatic rocks were measured at SURRC, East Kilbride (six samples) and at Royal Holloway University of London (one sample) using standard ion exchange separation techniques. Rubidium and strontium concentrations were determined by isotope dilution at East Kilbride (Dempster et al. 1995) and by X-ray fluorescence (XRF) at London (Thirlwall 1991). The strontium isotope compositions were determined on a VG 54E (East Kilbride) and a VG354 (London) thermal ionisation mass spectrometers. $^{87}Sr/^{86}Sr$ ratios were normalised to $^{86}Sr/^{88}Sr = 0.1194$ to account for mass fractionation. During the period of analyses NBS987 gave $^{87}Sr/^{86}Sr = 0.71028 \pm 2$ (2 s; East Kilbride), whereas SRM 987 yielded $^{87}Sr/^{86}Sr = 0.710219 \pm 15$(2 s; London). Some reconnaissance Nd isotope data for selected igneous rocks were obtained at East Kilbride, following the analytical procedure of Dempster et al. (1995).

For the rubidium and strontium concentrations, the barite powders were dissolved in a mixed solution of disodium-ethylene-diaminetetra-acetate and NH_4OH and analysed by atomic absorption at the University of Geneva. The precision of the rubidium analyses is 20%, whereas for the strontium is 10–15%.

Results

Strontium isotope analyses for the five barites, Tertiary igneous host rocks and basement metamorphic rocks from the Madjarovo area are listed in Tables 1 and 2.

Table 1 The $^{87}Sr/^{86}Sr$ compositions for vein barite. *n.d.* Not determined

Sample	Location/description	Present-day $^{87}Sr/^{86}Sr$	Rb (ppm)	Sr (ppm)	Present-day $^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ at 32 Ma
V2	Vein 2, barite enclosed by quartz	0.708937 ± 13	10.0	5,254	0.0055	0.70893
V6a	Vein 6a, massive barite	0.708921 ± 11	16.4	4,980	0.0095	0.70892
V6a[a]	Vein 6a, massive barite	0.708990 ± 10	16.4	4,980	0.0095	0.70899
V37[a]	Vein 37, fine-grained quartz–barite intergrowth	0.708837 ± 11	15.7	2,959	0.0154	0.70883
V83	Vein 83, fine-grained quartz–barite intergrowth	0.709546 ± 11	n.d.	n.d.	–	–
V20[a]	Vein 20, crystals in brecciated zone	0.708538 ± 7	19.0	8,670	0.0063	0.70854

[a] Analyses done in Geneva; the rest of analyses done in London

Magmatic and metamorphic rocks are corrected to 32 Ma.

Tertiary igneous and pre-Mesozoic basement metamorphic rocks

The $^{87}Sr/^{86}Sr$ isotopic analyses of seven samples of unaltered volcanic rocks and one intrusive rock fall between 0.70775 and 0.70863 (Table 2, Fig. 3). The highest $^{87}Sr/^{86}Sr$ ratio was from the lowermost latite flow and the values decrease with stratigraphic height, being 0.70822–0.70832 in the lavas of the Middle unit and 0.70775–0.70784 in the Upper unit. A slightly propylitised to sericitised sample from the Harman Kaya monzonite has a slightly elevated $^{87}Sr/^{86}Sr$ value (0.70837) compared with the lavas of the contemporaneous Upper unit. However, the $^{143}Nd/^{144}Nd$ ratio for the Harman Kaya monzonite (0.512443) falls in the range of $^{143}Nd/^{144}Nd$ ratios of the latite and quartz latite lavas of the Upper unit (0.512447–0.512425). A similar increase of the $^{87}Sr/^{86}Sr$ isotopic ratio in altered rocks was noted by Richards et al. (1991) in the Porgera epithermal system, Papua New Guinea. They interpreted this to reflect slight modification of the original magmatic strontium isotopic ratio, whereas neodymium was immobile during alteration.

Plyusnin et al. (1988) measured the strontium isotopic composition of two biotite gneiss and one biotite–muscovite gneiss samples from the basement lithologies and found present-day isotopic ratios of 0.71170–0.73173 (Table 2). These data are within the range of present-day $^{87}Sr/^{86}Sr$ isotopic values (0.7088–0.7391) for metamorphic rocks elsewhere in the Rhodope Massif (Zagorchev and Moorbath 1986; Zagorchev et al. 1987; Del Moro et al. 1990; Kolocotroni and Dixon 1991) and are much higher than the highest values of the Madjarovo lavas.

Madjarovo barites

Strontium concentrations in the four analysed barites vary between 2 959 and 8 670 ppm at rubidium contents in the range 10.0–19.0 ppm. These values are within or close to the ranges of strontium and rubidium contents of barites in various ore deposits (e.g. Lieben et al. 1996; Valenza et al. 2000). Corrections made of the $^{87}Sr/^{86}Sr$ ratios, based on the rubidium and strontium contents of the barites for the age of 32 Ma are within the analytical error and the measured present-day $^{87}Sr/^{86}Sr$ ratios of the hydrothermal barite can be used to directly estimate the composition of the mineralising fluid.

Overall, the range in the $^{87}Sr/^{86}Sr$ ratios of the five barite samples is narrow (0.70854–0.70955) and lies between the isotopic compositions of the Tertiary igneous rocks and the pre-Mesozoic basement rocks. They are much closer to and partly overlap the igneous values (Fig. 3), indicating a predominantly magmatic origin for the strontium in the hydrothermal fluid.

Two important features can be distinguished within the barite data. First, four of the five samples, taken from the largest veins #2 (0.70893), #6a (0.70892–0.70899) and #37 (0.70883), have almost identical isotopic compositions. The homogeneity of the strontium isotope ratios of the barites from the large veins is independent of their distance above the metamorphic basement, suggesting that the isotopic composition of the fluid was determined before it entered the volcanic

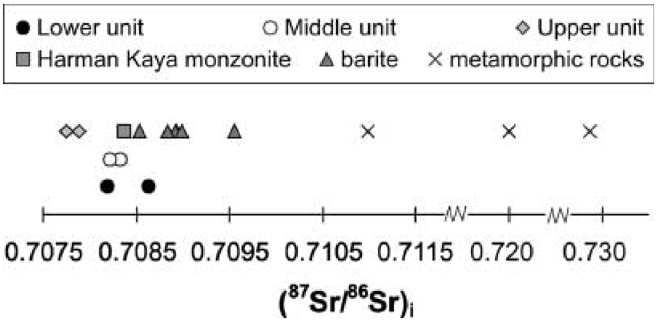


Fig. 3 The $^{87}Sr/^{86}Sr$ isotope ratios for barite from Madjarovo epithermal veins compared with Harman Kaya monzonite and host volcanics, and metamorphic basement rocks. Isotopic data are listed in Tables 1 and 2

Table 2 $^{87}Sr/^{86}Sr$ ratios of potential sources of strontium. All analyses for the magmatic rocks done in East Kilbride, except where specified; data for three gneiss samples from Plyusnin et al. (1988)

	Stratigraphic unit and rock type	Present day $^{87}Sr/^{86}Sr$	Rb (ppm)	Sr (ppm)	Present-day $^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ at 32 Ma
Oligocene volcanic rocks	Bottom latite lava (Lower unit)	0.709254 ± 36	194.6	407.8	1.3809	0.70863
	Mixed lava (Lower unit)	0.708390 ± 52	123.1	831.9	0.4282	0.70819
	Latite lava (Middle unit)[a]	0.709298 ± 12	277	373	2.1489	0.70832
	Mixed lava (Middle unit)	0.708765 ± 30	197.8	479.3	1.1941	0.70822
	Latite (Upper unit)	0.708839 ± 31	300.8	366.5	2.3749	0.70775
	Quartz latite (Upper unit) (Plagioclase)	0.707929 ± 46	79.8	1,124.4	0.2053	0.70784
	Harman kaya intrusion	0.709413 ± 36	274.9	347	2.2925	0.70837
Pre-Mesozoic metamorphic rocks	Biotite gneiss	0.72064 ± 35	107.0	252.5	1.184	0.72008
	Biotite–muscovite gneiss	0.73173 ± 24	566.8	157.7	8.231	0.72784
	Biotite gneiss	0.71170 ± 22	94.46	174.9	1.505	0.71099

[a] Analyses from London

sequence. Second, the $^{87}Sr/^{86}Sr$ compositions of the fluid in the small brecciated veins deviate from those in the large veins. Barite from the narrow brecciated zone #83 (0.70955) at the base of the volcanic stratigraphy is more radiogenic and probably influenced by directly underlying metamorphic rocks. In contrast, the barite from the small brecciated vein #20 high in the volcanic pile shows the lowest ratio of $^{87}Sr/^{86}Sr$ (0.70854), perhaps suggesting the influence of the volcanic host rocks.

Summary and conclusions

The strontium isotope data for barite from epithermal veins in the Madjarovo ore district constrain the source of strontium in the Pb–Zn–Au-depositing hydrothermal fluid and the degree of fluid–rock interaction from the source to the deposit and within the mineralised vein system. The $^{87}Sr/^{86}Sr$ ratios of the barites fall between those of the Tertiary magmatic (intrusive and extrusive) rocks and the underlying amphibolite facies metamorphic rocks, indicating that strontium is a mixture of predominantly magmatic source plus a subordinate amount of more radiogenic strontium from the metamorphic basement. Geophysical evidence and $^{40}Ar/^{39}Ar$ age data suggest a pluton located at a depth of 1–4 km as a plausible magmatic fluid source. Its estimated $^{87}Sr/^{86}Sr$ ratio is ~0.7080, as recorded by monzonite/trachyte stock and dykes, which are exposed at the present erosion level and closely associated in space and time with the ore veins.

The shift of the $^{87}Sr/^{86}Sr$ composition of the barites in the large veins from their inferred igneous source composition of 0.7080 toward a more radiogenic and homogenised composition of ~0.7089 is most easily explained by limited interaction of the fluid with at least 1 km of more radiogenic metamorphic rocks along major fluid channels. Passage of the fluid through the overlying 500–600-m-thick less radiogenic volcanic complex did not cause a noticeable modification of its strontium isotope signature, where the fluids remained focused in large veins. Larger strontium isotopic variations occur in the narrow veins in brecciated zones, where increasing interaction with either volcanic or the immediately underlying metamorphic rocks led to slight shifts towards lower or higher $^{87}Sr/^{86}Sr$ ratios, respectively.

Acknowledgements The isotopic work was made by P.M. during stays at the Scottish Universities Research and Reactor Center, East Kilbride, the Radiogenic isotope laboratories at Royal Holloway, at University of London and at the Department of Mineralogy of the University of Geneva through Europrobe and GEODE grants. A constructive comment by Antonio Arribas on an early draft helped to improve the manuscript. We appreciate very much the thought-provoking and helpful reviews of the journal reviewers H. Stein and I. Bonev. The comments and helpful suggestions by R. Goldfarb are greatly acknowledged. C. Heinrich and T. Pettke gave constructive advice. Thanks are due to Denis Fontignie and Pia Voldet (University of Geneva) for mass spectrometry analyses and rubidium and strontium determinations. Raya Raycheva is acknowledged for assistance with the figures.

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