ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • 34 • СОФИЯ • 1998 GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 34 • SOFIA • 1998

# New Rb-Sr data on the bottom and top lava flow of the Madjarovo volcano: Inferences for the age and genesis of the lavas

# Peter Marchev, Graeme Rogers

Abstract. Rb-Sr mineral isochrons have been obtained for the bottom and top flows of the Madjarovo volcano. The analysed whole-rock and mineral separates (plagioclase and biotite) from the bottom latitic flow form a good linear Rb-Sr array which is interpreted as an isochron yielding an age of  $31.6\pm1.2$  Ma and an initial  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of  $0.70862\pm5$ . The analysed phases of the top quartzlatite flow (plagioclase, clinopyroxene, sanidine and biotite) yield an age of  $32.3\pm0.6$  Ma and initial  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of  $0.70789\pm7$ . The Sr isotope data of these two lavas do not confirm an origin by simple fractional crystallization. Rather, they have suffered different degrees of crustal contamination.

Key words: Madjarovo Volcano, Rb-Sr, isochron, crustal contamination Address: P. Marchev - Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; G. Rogers - Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow, G750QF, Great Britain

Марчев, П., Г. Роджерс. 1998. Нови Rb-Sr данни от първия и последния лавов поток на Маджаровския вулкан: Изводи за възрастта и генезиса на лавите. - *Геохим., минерал. и петрол.*, 34, 91-96

Получени са Rb-Sr минерални изохрони за първия и последния потоци на Маджаровския вулкан. Анализираната обща скална проба и мономинерални проби от плагиоклаз и биотит от първия поток оформят добра Rb-Sr редица, която се интерпретира като изохрона даваща възраст от  $31,6\pm1,2$  Ма и начално отношение  $^{87}$ Sr/ $^{86}$ Sr  $0,70862\pm5$ . Анализираните фази на последния поток (плагиоклаз, клинопироксен, санидин и биотит) дава възраст от  $32,3\pm0,6$  Ма и начално отношение  $^{87}$ Sr/ $^{86}$ Sr  $0,70789\pm7$ . Изотопните данни на Sr в тези две лави не потвърждават формирането им чрез фракционна кристализация. По-скоро, те са претърпели различна степен на корова контаминация

Ключови думи: Маджаровски вулкан, Rb-Sr, изохрона, корова контаминация.

*Адрес:* П. Марчев - Българска академия на науките, Геологически инстититут, 1113 София, България; Г. Роджерс - Изследователски и ядрен център на шотландските университети, Ист Кълбрайд, Глазгоу, G750QF, Великобритания

#### Introduction

The age of the Madjarovo volcano is controversial. K-Ar ages (Lilov et al., 1987)

for 12 whole-rock samples range from 33.5 to 31.0 Ma. The thorogenic Pb model age of galenas from the base metal veins, (Amov et al., 1979) is  $50\pm10$  Ma. At the

same time, corals (Corallinacaea) from organogenic limestones at the base of the volcanic sequence in the southern part of the Madjarovo volcano were determined to be of Miocene age (Bakalova, 1980). An attempt to determine the age of the Madjarovo volcanics using the Rb-Sr whole-rock isochron method was made by Plyusnin et al., (1988). The age computed for nine lavas is 28.1±1.6 Ma with <sup>87</sup>Sr/<sup>86</sup>Sr 0.7078±2.

In the last few years, the Madjarovo volcano has been the subject of a large scale project including mapping on a scale of 1:10 000, and extensive petrological and geochemical studies. In this paper we report newly obtained Rb-Sr ages for the Madjarovo bottom and top lavas in order to determine the time span of volcanic activity and to discuss briefly the petrogenetic significance of the Sr isotopic data.

## **Geological setting**

The Madjarovo volcano covers an area of about 120  $\rm km^2$  in the Eastern part of the Eastern Rhodope volcanic district which represents a part of the Macedonian-Rhodope-North Aegean Magmatic Belt (MRNAMB; Harkovska et al., 1989; Marchev et al., 1989b). The basement rocks crop out south, west and east of the volcanic pile and belong to the Rhodope crystalline basement. The volcanic activity is of predominantly fissure type which formed a shield volcano (Ivanov, 1960). Although it is difficult to calculate the total volume of magma erupted due to uncertainties in erosional losses, particularly in the southern part, an estimate of  $60 \pm 10$  km<sup>3</sup> is reasonable. The Arda river, exploiting a large fault, flows from west to east and dissects the central part of the volcano. The erosion here provides about 700 m of vertical relief and access to the deep stratigraphical levels. Several drill holes in the central part provide an additional 100-200 m of vertical exposure.

The unaltered volcanic rocks (Marchev et al., 1989a) have the composition of high-K calc alkaline and shoshonitic basic to

intermediate varieties with latites being the most voluminous rock type. The most evolved rocks are of quartztrachyte composition. On the basis of O and Sr isotope ratios Marchev et al. (1997 and unpubl. data) distinguished two sharply distinctive periods in the evolution of the Madjarovo volcano. The first is characterized by alternating thick (up to 150 m) latitic lava flows (sheets) with 1 to 4-5 thinner more basic high-K basalts, basaltic andesites and andesites. During this stage the Madjarovo magma system evolved as an open-system dominated by the mixing of latitic and basaltic magmas. The second period includes the last 3 consecutive lava flows ranging in composition from high-K, high-Al basalts through high-K latites to quartzlatites. They evolved by almost closedsystem fractional crystallization processes. There is a notable increase in K in the second evolutionary period.

The dated rocks are from the bottom and top flows of the Madjarovo volcano. Following the discrimination diagram of Peccerillo and Taylor (1976), as modified by Marchev (1986), these rocks are termed latite and quartzlatite. The bottom flow has  $SiO_2$  59.6 wt. % and  $K_2O$  4.0 wt.%. It is a porphyritic rock, with phenocrysts and microphenocrysts of plagioclase as the most abundant phase. The plagioclase is zoned with a more calcic, strongly corroded core  $(An_{775-71})$  surrounded by a distinct, oscillatory zoned outer rim  $(An_{63-51})$  with a trend of decreasing calcium towards to outer rim. Rounded or irregular brown glass inclusions of various size occur within the cores of the plagioclase. Clinopyroxene (augite with Mg# 76.4-75.0), orthopyroxene (Mg# 72.2-69.9), titanomagnetite (TiO<sub>2</sub> 10-12% wt.% and MgO 1 wt.%), biotite (Mg# 69-68 and TiO<sub>2</sub> 4.9 wt.%), and amphibole (Mg# 65.6 and TiO<sub>2</sub> 3.26 wt.%) and apatite are subordinate. The groundmass contains the same phases which occur as phenocrysts with the exception of biotite. The glassy portion represents about half of the volume of the groundmass.

The top lava flow is the most acid rock in the Madjarovo volcano with  $SiO_2$  65.8 wt.% and  $K_2O$  4.5 wt.%. It is a coarsegrained, porphyritic rock. The phenocryst mineralogy is dominated by plagioclase  $(An_{58.5-41.2})$  with rare, strongly corroded cores of bytownite  $(An_{85.5})$  and sanidine  $(Or_{75.1-72.4} Ab_{22.1-24.8} An_1 Cn_{1.8-1.5})$ , associated with low- and high-Mg clinopyroxene (Mg# 79-75.4 and 86-81, respectively); rare orthopyroxene (Mg# 69.8-68.2), always jacketed by clinopyroxene (Mg# 74.5), biotite (Mg# 61 with TiO<sub>2</sub> 4.4-5.5 wt.%), titanomagnetite (TiO<sub>2</sub> 7 wt.%) and apatite. Zircon is an accessory mineral. The groundmass is glassy (perlitic) or holocrystalline, composed of plagioclase, sanidine, quartz and titanomagnetite dust.

#### **Analytical procedures**

The mineral separates were extracted using standard mineral separation techniques including heavy liquids, magnetic separator, and further purification by hand picking under alcohol until pure mineral fractions were obtained.

<sup>87</sup>Sr/<sup>86</sup>Sr ratios were determined on spiked samples at the Scottish Universities Research and Reactor Centre (SURRC) East Kilbride, Scotland. Rb and Sr were separated by standard procedures (Dempster et al., 1995). Rb and Sr were run on VG MM30 and VG 54E thermal ionization mass spectrometers respectively. <sup>87</sup>Sr/<sup>86</sup>Sr ratios were corrected for mass fractionation using <sup>86</sup>Sr/<sup>88</sup>Sr 0.1194. During the period of analysis NBS987 gave <sup>87</sup>Sr/<sup>86</sup>Sr 0.71028 ± 2 (2σ).

In the isochron calculations a precision of 0.7% ( $2\sigma$ ) was assigned to the <sup>87</sup>Rb/<sup>86</sup>Sr ratios whereas the measured  $2\sigma$  error was assigned to the <sup>87</sup>Sr/<sup>86</sup>Sr ratios.

#### **Results and discussions**

Table 1 gives the results of Rb-Sr mineral and whole-rock isotope data for the bottom



#### Madjarovo lower flow

Fig. 1. Rb-Sr isochron diagram showing the three-point-isochron of whole-rock, plagioclase and biotite from the bottom flow

Фиг.1. Rb-Sr изохронна диаграма показваща триточкова изохрона от валов състав, плагиоклаз и биотити на долния поток

### Madjarovo upper flow



Fig. 2. Rb-Sr errorchron diagram showing the four-point errorchron of plagioclase, clinopyroxene, sanidine and biotite from the top flow

Фиг.2. Rb-Sr ерохронна диаграма показваща четириточкова ерохрона от плагиоклаз, клинопироксен, санидин и биотит от горния поток

and the top flows obtained in this study. The analysed minerals (plagioclase and biotite) and the whole-rock of the bottom latitic flow form a good linear Rb-Sr array (Fig. 1) which is interpreted as an isochron yielding an age of 31.6±1.2 Ma and an initial  $\frac{87}{r}$  sr/ $\frac{86}{r}$  0.70862±5. The MSWD is low (2.4) indicating that the deviations of the samples from the isochron are small and may be attributed to analytical uncertainties. Thus, the first latite flow appears to have been isotopically uniform at the time of emplacement. The mineral separates (plagioclase, clinopyroxene, biotite) from sanidine and top the quartzlatite flow (Fig.2) yield an errorchron age of 32.3±0.6 Ma and initial <sup>87</sup>Sr/<sup>86</sup>Sr  $0.70789\pm7$  (MSWD 6.8). Although there is a little scatter of the data on the isochron diagram, these phases also seem to have been in isotopic equilibrium at the time of crystallization.

The results from this work define the age

relationships for the Madjarovo volcano. The mineral ages from the youngest and the oldest flows are within error of each other. These data show that the volcanic activity at the Madjarovo paleovolcano took place at about 32 Ma and lasted no more than 2 Ma. and most probably less than 1 Ma. Conventional K-Ar dates (Lilov et al., 1987) for 12 whole-rock samples (33.5-31.0 Ma) give an average 32.3 Ma. The Rb-Sr results are thus in excellent agreement with the K-Ar data not only in terms in their age but also in the respect of showing that the time span of emplacement is shorter than can be resolved by the data. An Rb-Sr age  $(28.1\pm1.6)$ Ma), obtained by Pljusnin et al. (1988), is 2-4 Ma younger than our mineral isochron data. The initial <sup>87</sup>Sr/<sup>86</sup>Sr of 0.7078±0.0002, estimated from the 9 whole-rock samples of Plyusnin et al. (1988), is similar to that of the quartzlatite flow given above. For the bottom latitic flow, these authors also found higher <sup>87</sup>Sr/<sup>86</sup>Sri (0.70834), although slightly Table 1

Rb-Sr data and Sr isotope ratios measured for the bottom and top Madjarovo lava flows

Таблица 1

Rb-Sr данни и изотопни отношения на Sr измерени в долния и горния лавов поток на Маджарово

Sample	Rb (ppm)	Sr (ppm)	87 <sub>Rb/</sub> 86 <sub>Sr</sub>	87 <sub>Sr/</sub> 86 <sub>Sr</sub>
Top Flow				
M88-268 Bi	642.9	20.2	92.1922	$0.75017 \pm 8$
M88-268 San	310.3	725.5	1.2374	$0.70848 \pm 3$
M88-268 Cpx	8.9	32.5	0.7936	$0.70799 \pm 4$
M88-268 Plag	79.7	1124.4	0.2050	$0.70793 \pm 5$
Bottom Flow				
M89-202 Bi	290.6	67.1	12.5293	$0.71422 \pm 13$
M89-202 WR	194.6	407.8	1.3811	$0.70926 \pm 4$
M89-202 Plag	12.5	1276.5	0.0284	0.70861 ± 4

lower than our value.

The relatively radiogenic strontium isotopic compositions of the Madjarovo lavas were interpreted by Plyusnin et al. (1988) as indicating that metasomatic fluids, introducing alkalies into the zone of melting at deep mantle levels, participated in the generation of the Madjarovo shoshonitic magmas. The difference between the latites and the 9 other samples was thought to reflect isotopic heterogeneity in the mantle melts.

It is not the aim of this paper to consider the genesis of Madjarovo lavas in detail. However, several important conclusions can be drawn.

1. The initial ratios of the two lava flows, as well the rest of the measured lavas (Marchev, Rogers, unpubl. data) are enriched relative to the OIB asthenospheric source beneath the Rhodope Massif (Marchev et al., 1998) as well as to the depleted lithospheric mantle in Bulgaria (Vaselli et al., 1997) and indicate the involvement of considerable amount of crustal component. In several consecutive works (Marchev et al., 1989; 1994) showed an impressive correlation between Sr, Nd, O and Pb isotope variations and the crustal thickness in the whole Rhodope Massif which was interpreted as reflecting an increasing addition of crustal material to mantle magmas in the areas of thicker crust. In these papers the Madjarovo lavas were estimated to have been contaminated by 25-30% crustal material.

2. It is noteworthy that among all 8 measured whole-rock samples of Marchev and Rogers (unpubl. data), the <sup>87</sup>Sr/<sup>86</sup>Sri ratio of the bottom flow has the highest value whereas the top flow is amongst the lowest measured values in the whole set of data. The difference between the initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the two flows is much larger than their  $2\sigma$  errors which suggests a real isotopic difference between them. This difference precludes an origin of the quartzlatites from the latites by simple fractional crystallization. Rather it indicates that (1) either the samples investigated originate from different parental magmas or (2) they have suffered different degrees of crustal contamination. The origin of these isotopic differences could be interpreted as reflecting two-stage contamination as suggested by Marchev et al.

(1995) for the neighbouring large Borovitsa volcanic area: (1) lower crustal MASH processes operating on magmas with an OIB-like Sr isotopic composition to produce a base level \$r isotopic signature of about 0.7079; (2) fractionation and additional assimilation of the ascending basic magmas in the upper crust leading to intermediate (latitic) compositions and small changes (0.7086) in the Sr isotopic composition of the first lava flow. Other workers (Myers et al., 1985) have also proposed that the amount of assimilation will be greatest during the early stages of the development of a magmatic plumbing system.

#### References

- Amov, B., V. Breskovska, Ts. Baldzhieva, S. Evstatieva. 1979. Lead isotopic composition of Madjarovo ore field and some conclusion on its age and genesis. C. R. Acad. bulg. Sci., 32, 9, 1271-1274.
- Bakalova, D. 1980. Calcareous algae of the family Corallinaceae in the area of Madjarovo, Southeastern Bulgaria. - Paleont., Stratigr. and Lithol., 12, 13-24 (in Bulgarian with English abstract).
- Dempster, T.J., N.F.C. Hudson, G. Rogers. 1995. Metamorphism and cooling of the NE Dalradian. - J. Geol. Soc. Lond., 152, 383-390.
- Harkovska, A., Y. Yanev, P. Marchev. 1989. General features of the Paleogene orogenic magmatism in Bulgaria. - *Geologica Balc.*, 19, 1, 37-72.
- Ivanov, R. 1960. Magmatism in the East-Rhodopean depression. I. Geology. - Trav. Geol. Bulgar., ser. Geochim., Mineral. and Petrogr., 1, 297-323 (in Bulgarian with German abstract).
- Lilov, P., Y. Yanev, P. Marchev. 1987. K/Ar dating of the Eastern Rhodope Paleogene magmatism. - *Geologica Balc.*, 17, 6, 49-58.
- Marchev, P. 1986. Extension of the subdivision and nomenclature of the shoshonitic rocks. - C. R. Acad. bulg. Sci., 39, 6, 69-71.
- Marchev, P., Z. Iliev, S. Nokov. 1989a. Oligocene volcano "Madjarovo". - Guide-book of Scientific Excursion E-2 (CBGA, XIV Congress, Sofia). Alpine magmatism and

related metalogeny in Srednogorie and Eastern Rhodopes, 97-103.

- Marchev, P., S. Nokov, R. McCoyd, D. Jelev. 1997. Alteration processes and mineralizations in the Madjarovo Ore Field - a brief review and new data. - Geochem., Mineral. and Petrol., 32, 47-58.
- Marchev, P., P. Larson, G. Rogers, O. Vaselli, R. Raicheva. 1994. Crustal thickness control on the Sr, Nd, and O isotopic variation in the Macedonian-Rhodope-North Aegean magmatic belt (MRNAMB). - Abstracts. Intern. Volcanol. Congress. IAVCEI, Ankara, 1994.
- Marchev P., P. Lilov P., B. Amov. 1989b. Major, trace element, and isotopic (Sr, Pb) zonality in the Eocene-Oligocene Macedonian-Rhodope Magmatic Zone: evidence for subduction processes and crustal influence. - In: IAVCEI Continental Magmatism Abstracts. Santa Fe, New Mexico, USA.
- Marchev, P., Y. Yanev, J. Quick, Z. Peckay. 1995. Evolution of Eocene-Oligocene Borovitsa Volcanic System, Bulgaria. - *Abstracts IUGG*. Boulder, USA.
- Marchev P., O. Vaselli, H. Downes, L. Pinarelli, G. Ingram, G. Rogers, R. Raicheva. 1998.
  Petrology and geochemistry of alkaline basalts and lamprophyres: implications for the chemical composition of the upper mantle beneath the Eastern Rhodopes (Bulgaria). Acta Vulcanologica (in press).
- Myers, J.D., A. K. Sinha, B.D. Marsh. (1984). Assimilation of crustal material by basaltic magma: strontium isotopic and trace element data from the Edgecumbe Volcanic Field, SE Alaska. - J. Petrol., 25, 1-26.
- Peccerillo, A., S. R.Taylor.1976. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area, northern Turkey. - Contrib. Mineral. Petrol., 58, 63-81.
- Pljusnin G.S., Marchev P., Antipin, V.S.,1988. Rb-Sr age and genesis of the shoshonite-latite Eastern Rhodopes series. - *Dokl. Akad. Nauk SSSR*, **303**, 719-724 (in Russian).
- Vaselli, O., Marchev, P., Downes. H., Coradossi, N., Ingram, G. 1997. Ultramafic xenoliths from Chatala and Kamuka volcanoes (Northern Bulgaria). - C. R. Acad. bulg. Sci., 50, 4, 75-78

Accepted May 21, 1998 Приета на 21 май, 1998 г.