

# 40Ar/39Ar single crystal laser dating of early volcanism in the Upper Rhine Graben and tectonic implications

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# $^{40}\text{Ar}/^{39}\text{Ar}$ single crystal laser dating of early volcanism in the Upper Rhine Graben and tectonic implications

by Jörg Keller<sup>1</sup>, Michael Kraml<sup>1,2</sup> and Friedhelm Henjes-Kunst<sup>2</sup>

## Abstract

$^{40}\text{Ar}/^{39}\text{Ar}$  single crystal laser fusion ages on amphibole phenocrysts have been obtained for the presumably earliest manifestation of graben-related volcanic activity in the Upper Rhine Graben. We report an isochron age of  $60.9 \pm 0.6$  Ma for the olivine-melilitite dike of Trois Epis (Colmar, Vosges) previously dated at  $102.5 \pm 7.6$  Ma by K/Ar method of a whole rock sample. This casts doubt on other pre-Tertiary K/Ar dates for the early graben magmatism, which were also measured on whole rocks. With the new laser  $^{40}\text{Ar}/^{39}\text{Ar}$  age the duration of pre-rift volcanism has shrunk considerably. With a Paleocene age, the onset of graben volcanism was contemporaneous with the onset of major Alpine crustal shortening and initial phases of the North Atlantic Tertiary Province.

*Keywords:* Upper Rhine Graben,  $^{40}\text{Ar}/^{39}\text{Ar}$  dating, amphibole, alteration, olivine melilitite dike.

## 1. Introduction

Rift-related magmatism associated with the Upper Rhine Graben (URG) occurs mainly on the graben shoulders. About 30 outcrops of primitive alkali basaltic rocks (olivine nephelinites, olivine melilitites) are known from the southern part and more than 50 occurrences, including some evolved volcanic rocks, appear in the northern part of the URG. Most of these occurrences were dated during the sixties and seventies with conventional K/Ar analyses on whole rocks (LIPPOLT et al., 1963, 1974, 1975, 1976; HORN et al., 1972; BARANYI et al., 1976; LIPPOLT, 1982). The oldest model ages date back to the Early/Late Cretaceous boundary. This has led to the view that volcanism predates Eocene onset of graben formation by more than 50 Million years (ILLIES, 1981; ZIEGLER, 1992). However, these volcanic rocks are commonly altered as shown by their mineralogical and chemical composition and may therefore have a disturbed K/Ar system. Moreover, they generally lack K-bearing phenocrysts. However, in one occurrence (olivine melilitite dike of Trois Epis, Vosges) amphibole phenocrysts were found. These unaltered amphiboles provided the

possibility to redate this key occurrence by the laser Ar/Ar method on single crystals. The large discrepancy between the new single crystal age and the existing whole rock K/Ar date for the same dike (BARANYI et al., 1976) is caused by an age-modifying alteration effect. The new precise Ar/Ar data reported in this paper shed new light on the age relationship between graben formation and mantle processes.

## 2. Geological setting of the Upper Rhine Graben (URG)

As the central part of the larger European Cenozoic rift system (ECRIS; ZIEGLER, 1992, 1994; PRODEHL et al., 1995) the URG extends 300 km from Basel to Frankfurt (Fig. 1). The graben is on average 35–40 km wide and shows 5–6 km horizontal extension (ILLIES, 1977, 1981).

First indications of rift valley subsidence with basin sedimentation are found in mid-Eocene times (Lutetian; ILLIES, 1977; LUTZ and CLEINTUAR, 1999). Hence, an age of ca. 45 Ma is indicated for the beginning of rifting associated with N–S compression in a strike-slip regime (LARROQUE

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and LAURENT, 1988; ZIEGLER, 1992; SISSINGH, 1998). However, major initial rifting started in late-Eocene times (Priabonian; SCHUMACHER, 2002).

The main subsidence occurred during E–W extension in the Oligocene (LARROQUE and LAURENT, 1988), during which sediment thickness in the graben reached more than 2000 m. In the southern sector, faulting reached its highest intensity in latest Chattian time and was followed by

uplift of the southern graben segment and the adjacent highs in the latest Aquitanian and Burdigalian (LUTZ and CLEINTUAR, 1999). This Miocene N–S compression phase (LARROQUE and LAURENT, 1988) coincides with the updoming of the Moho beneath the Black Forest-Vosges area (Fig. 1) and the emplacement of the Kaiserstuhl Volcanic Complex 18–16 Ma ago (LIPPOLT et al., 1963; KRAML et al., 1999).

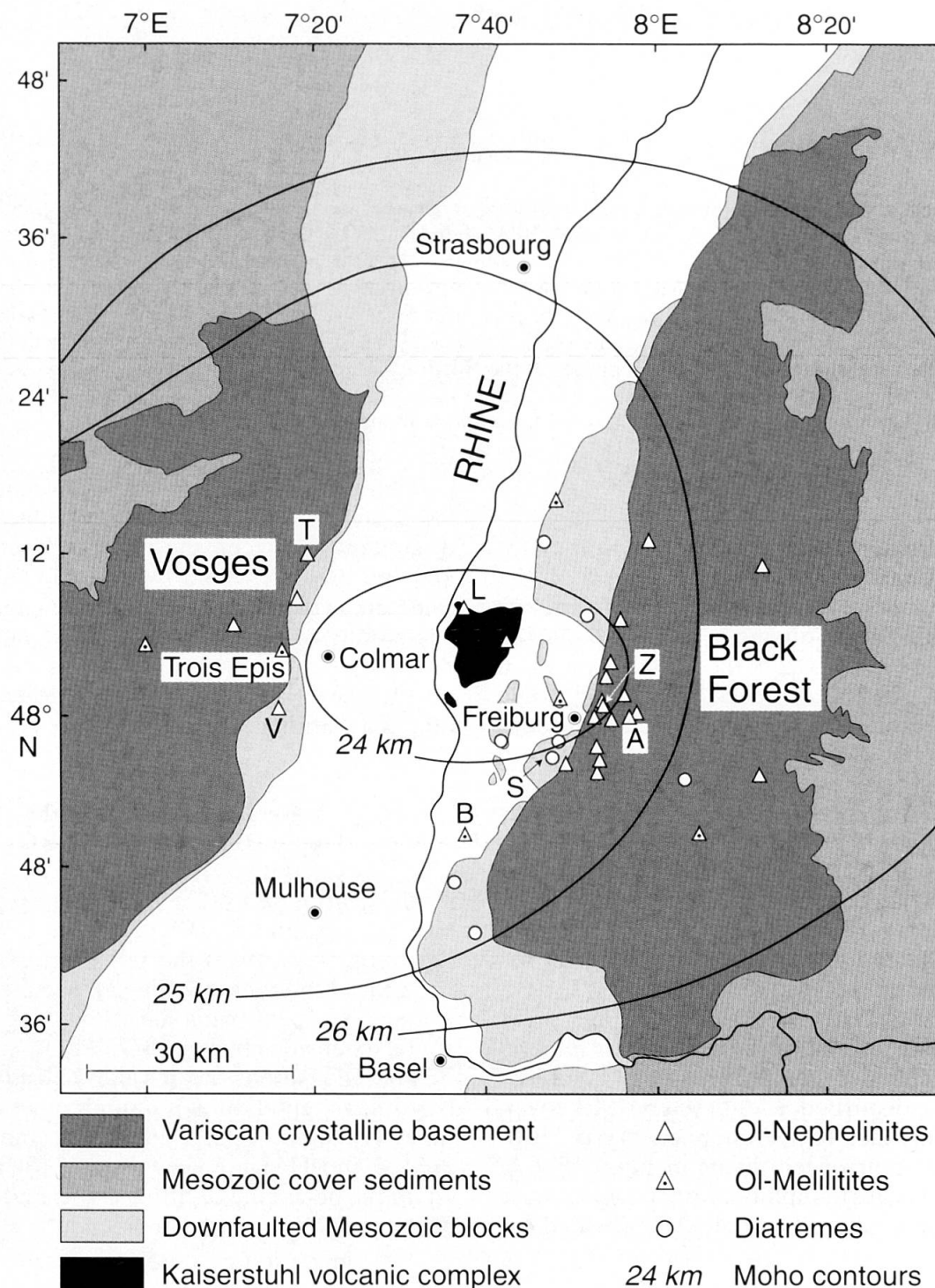


Fig. 1 Southern part of the Upper Rhine Graben with occurrences of rift-related volcanic rocks. A – Attental, B – Buggingen, L – Limberg/Lützelberg, S – Schönberg, T – Tannenbach, V – Vordermarbach, Z – Zähringen Reutebach/Uhlberg.

### 3. Volcanism of the Upper Rhine Graben

Graben-related magmatic activity takes the form of dikes, plugs and necks, and diatreme pipes (WIMMENAUER, 1952; KELLER et al., 1990). The known occurrences along the 300 km URG are concentrated in two sectors.

About 30 outcrops are situated in the southern Black Forest-Vosges Dome, which also marks the maximum up-doming of the graben shoulders. The Miocene Kaiserstuhl Alkaline Complex, the only differentiated volcanic field in the graben, is located in the centre of this dome (Fig. 1).

In the northern graben sector more than 50 dikes and necks of this Tertiary basic volcanism are concentrated between Heidelberg and Frankfurt and situated mostly in the Odenwald crystalline basement and its surroundings.

Primary magma compositions in this province, particularly during the early phases of the graben evolution, are highly-undersaturated, mafic, alkali-basaltic magmas, dominantly olivine nephelinites and olivine melilitites (WIMMENAUER, 1970; KELLER et al., 1990). Their primary nature is revealed by high Mg#, high Ni and Cr contents, and mantle xenoliths picked up by the melts during their rapid ascent to the surface. The geochemical systematics of these primitive olivine nephelinites and olivine melilitites indicates their origin as low-percentage partial melts from a dominantly asthenospheric source (PATTERSON et al., 1996; DUNWORTH and WILSON, 1998; WEDEPOHL and BAUMANN, 1999). Tomographic evidence for a source in the lower mantle down to 2000 km depth is presented by GOES et al. (1999).

Most volcanic occurrences cut through the crystalline basement or its Mesozoic cover. There is very little biostratigraphic evidence bracketing the geological age of emplacement. From Schönberg near Freiburg, HAHN et al. (1974) report the stratigraphic relationship of a volcanic tuff from a nearby diatreme pipe with Middle Eocene sediments. There, an Eocene age for the volcanic activity is clearly documented. In the potash salt mines of Buggingen several N-S oriented dikes are dated as post-middle Oligocene by their intrusive relationships (BRAITSCHE et al., 1964; ESSLINGER, 1976). On the younger end, the olivine nephelinite lavas from Limberg-Lützelberg, Kaiserstuhl, are related to Burdigalian lacustrine sediments (TOBIEN, 1959). Also in the northern part of the URG a few outcrops permit the timing of magmatic activity by biostratigraphic bracketing. Boulders of alkali basaltic rocks are found in middle Oligocene sediments of the Mainz basin, demonstrating their pre-middle Oligocene age (evidence from various sources compiled by LIPPOLT

et al., 1975). Hence these examples show volcanic activity extending from the Middle Eocene to the Middle Miocene, i.e. from about 45 to 15 Ma using the time scale of BERGGREN et al. (1995).

The URG might be classified as a low-volcanicity rift since the volume of volcanic material is comparatively small. Nevertheless, the Tertiary phases of graben tectonics were accompanied by basic magmas of a typical alkaline rift-valley volcanism.

### 4. Experimental methods

For laser Ar/Ar analysis, amphibole crystals (grain size 200–500  $\mu\text{m}$ ) were selected, ultrasonically cleaned, dried at  $<100^\circ\text{C}$ , wrapped in Al-foil and filled between two standards in a quartz glass ampoule. The ampoule was evacuated to ca.  $7 \times 10^{-3}$  Pa and sealed.

Neutron irradiation with 1mm Cd-shield was done in the 5 MW research reactor FRG-1 Geesthacht (Germany) for 96 hours (fast n-dose of ca.  $10^{18}$  n/cm<sup>2</sup>). The international irradiation monitor HD-B1 biotite (HESS and LIPPOLT, 1994) was intercalibrated against TCR sanidine (27.92 Ma; DUFFIELD and DALRYMPLE, 1990), and the resulting total age of 24.29 Ma was used for HD-B1 standard (WIJBRANS et al., 1995; KRAML, 1997). We fused 2 multigrain aliquots of each monitor position. There was a slight irradiation gradient (1.4%) in between the 5 mm distance of the two standards bracketing the amphibole sample. Therefore we used an interpolated J-value determined with a precision of about 0.4% ( $1.4405 \pm 0.0061 \times 10^{-3}$ ), which is included in the internal  $1\sigma$  analytical uncertainty quoted throughout the paper. Interfering Ar isotopes from K and Ca were corrected with the following factors ( $^{40}\text{Ar}/^{39}\text{Ar}$ )<sub>K</sub>:  $1.20 (\pm 0.12) \times 10^{-2}$ , ( $^{39}\text{Ar}/^{37}\text{Ar}$ )<sub>Ca</sub>:  $7.36 (\pm 0.74) \times 10^{-4}$  and ( $^{36}\text{Ar}/^{37}\text{Ar}$ )<sub>Ca</sub>:  $2.95 (\pm 0.10) \times 10^{-4}$ . The intensities of radioactive isotopes  $^{37}\text{Ar}$  (and  $^{39}\text{Ar}$ ) were corrected for decay.

Argon was analysed with the Ar/Ar laser probe in the BGR, Hannover (Germany). The laser probe consists of a 12 W YAG-Nd laser system (Baasel Lasertech), a stainless steel ultra-high vacuum line for gas extraction and purification, and a VG Micromass 3600 mass spectrometer (KRAML et al., 1996). An extended description of the instrument and its characteristics is given in KRAML (1997).

Discrimination correction is based on regular analyses of pipettes with atmospheric argon ( $[\text{Ar}]_{\text{atm}} = 287.9 \pm 2.4$ ). Line blanks were measured before every sample and used for blank correction. The differently-sized grains had high



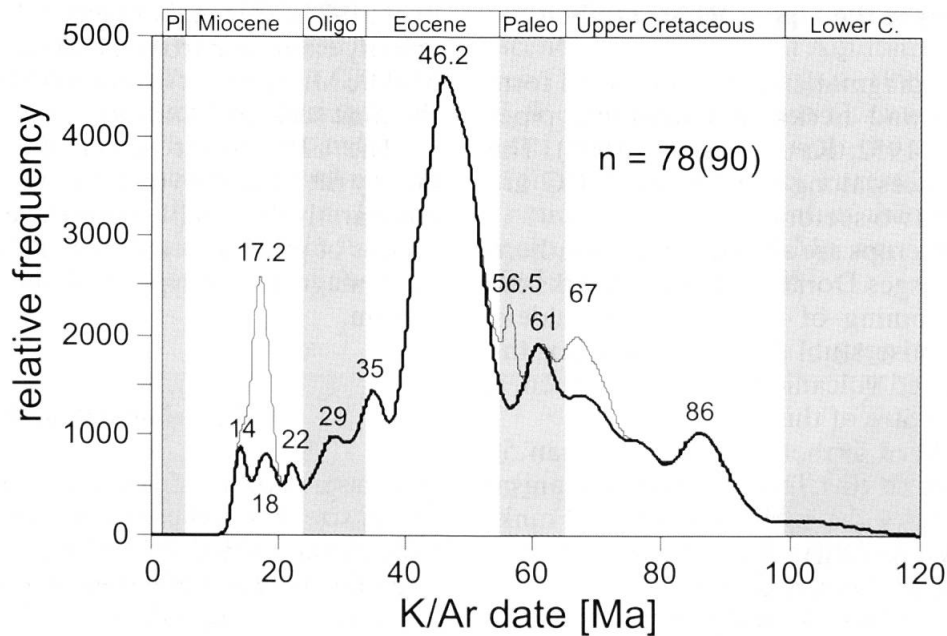


Fig. 2 Relative frequency of K/Ar dates of rift-related volcanic rocks from the entire Upper Rhine Graben (data from: LIPPOLT et al. 1963, 1975; HORN et al. 1972; BARANYI et al. 1976). If error bars were not given by the original authors, we assumed them to be identical to comparable analyses of the same laboratory. The thick line represents primitive-, and the thin line evolved-magma compositions.

radiogenic yields ( $> 89\%$   $^{40}\text{Ar}^*$ ) and  $^{40}\text{Ar}$ ,  $^{39}\text{Ar}$ ,  $^{37}\text{Ar}$  and  $^{36}\text{Ar}$  of total fusions were about 100–1100, 200–1500, 15–170 and 2–12 times their respective blank correction.

The IR laser ( $\lambda = 1064$  nm) was operated in continuous mode. Total-fusion analyses were done with a beam diameter of ca. 200  $\mu\text{m}$  and pre-heating of the multigrain aliquot with a beam diameter of ca. 1 mm.

### 5. Discussion of previously-published K/Ar ages

In several papers since 1963, Lippolt and co-workers provided a considerable number of K/Ar ages for the rift-related magmatic rocks in the area under discussion (LIPPOLT et al., 1963; BARANYI et al., 1976; HORN et al., 1972; LIPPOLT et al., 1974, 1975, 1976; LIPPOLT, 1982). Their model ages range from Cretaceous to Miocene and show pronounced peaks during the Eocene and Mio-

cene (Fig. 2). All quoted ages are recalculated with the constants recommended by STEIGER and JÄGER (1977), which raised the original values by up to 3 Ma.

Table 1 summarises the oldest whole rock K/Ar dates obtained in the southern Rhine Graben area. The four olivine-nephelinite samples of Zähringen/Reutebach/Uhlberg refer to a group of two closely related parallel dikes with identical petrographic characteristics (Keller unpublished). The oldest model age ( $119.9 \pm 2.5$  Ma) was withdrawn from further discussions by Lippolt and co-workers, because of possible contamination by basement inclusions. On the basis of the remaining model ages of 83–103 Ma, magmatism preceded rifting by more than 50 Ma, as argued in discussions of the rift evolution to support a  $>50$  Ma period of pre-rift magmatism (ILLIES, 1981; ZIEGLER, 1992). This evidence is entirely based on total rock K/Ar data. However, especially the older volcanic occurrences along the Rhine

Table 1 Oldest K/Ar dates from southern Rhine Graben magmatic rocks.

Locality	Rock type	K/Ar date $\pm 1\sigma$ [Ma]	Reported sample quality	Author & year
Trois Epis, Vosges	ol-melilitite	$102.5 \pm 7.6$	"unfresh"	BARANYI et al. 1976
Vordermarbach, Vosges	ol-nephelinite	$88.0 \pm 4.6$	"very unfresh"	BARANYI et al. 1976
Attental, Black Forest	ol-nephelinite	$82.7 \pm 2.6$	"fresh"	HORN et al. 1972
Zähringen, Black Forest	ol-nephelinite	$119.9 \pm 2.5$	"unfresh"	BARANYI et al. 1976
Zähringen, Black Forest	ol-nephelinite	$90.6 \pm 2.8$	"unfresh"	BARANYI et al. 1976
Reutebach, Black Forest	ol-nephelinite	$88.0 \pm 2.2$	"unfresh"	BARANYI et al. 1976
Uhlberg, Black Forest	ol-nephelinite	$85.3 \pm 2.1$	"unfresh"	BARANYI et al. 1976

Table 2 XRF analysis of the olivine melilitite from Trois Epis, Vosges.

Major Element [wt%]	[wt%] Trace element [ppm]			
	volatile free			
SiO <sub>2</sub>	34.02	38.03	Ni	174
TiO <sub>2</sub>	2.55	2.85	Cr	202
Al <sub>2</sub> O <sub>3</sub>	10.09	11.28	V	213
Fe <sub>2</sub> O <sub>3</sub> tot	11.63	13.00	Sc	18
MnO	0.17	0.19	Rb	84
MgO	11.31	12.64	Sr	1406
CaO	14.01	15.66	Ba	786
Na <sub>2</sub> O	3.05	3.41	Zr	265
K <sub>2</sub> O	1.40	1.57	Nb	101
P <sub>2</sub> O <sub>5</sub>	1.22	1.36	Y	22
CO <sub>2</sub>	8.43			
SO <sub>3</sub>	0.85			
L.O.I. (-CO <sub>2</sub> )	1.25			
sum	99.98	100.00		
Mg# (0.15)		68.6		

Graben are altered and therefore do not fulfil the requirements of whole-rock K/Ar dating as defined e.g. by MANKINEN and DALRYMPLE (1972). This refers particularly to the samples in the southern sector, i.e. the Black Forest-Vosges dome area (Table 1). Therefore, for example the 88 Ma age of Vordermarbach is called "problematic" by its authors (BARANYI et al., 1976). Alteration is evidenced by complete olivine transformation, hydration and oxidation of groundmass glass and infiltration of carbonates. Major element analyses show an unsystematic scatter in both Na<sub>2</sub>O and K<sub>2</sub>O, and high loss of ignition values due to secondary alteration (Keller, unpublished data). Therefore, the reliability of these Cretaceous K/Ar model ages has to be questioned.

## 6. The Trois Epis dike

The dike of Trois Epis, first described by COUTURIER et al. (1967), is one of 6 known volcanic necks and dikes that cut through the western graben shoulder of the Variscan basement (Vosges) and its cover (Fig. 1). The dike is about 50 cm wide and cuts with a NW-SE strike through granitic gneisses of Trois Epis at an elevation of 660 m. Petrographically, it is a nepheline- and hauyne-bearing olivine melilitite, with chemical features of a primary melt composition, like most other mafic volcanic rocks of the URG. Its chemical composition is given in Table 2. The freshest samples have preserved olivine phenocrysts, in contrast to those described by BARANYI et al. (1976). However, the chemical composition shows a loss of ignition (L.O.I. = H<sub>2</sub>O + CO<sub>2</sub>) of about 10 wt%, a clear indication of secondary altera-

Table 3 Microprobe analyses of amphibole phenocrysts found in the olivine melilitite from Trois Epis, Vosges.

grain number of measurements	amph1 n=4	amph5 n=3	amph6 n=3	amph8 n=5
SiO <sub>2</sub>	38.49	38.76	38.81	40.14
TiO <sub>2</sub>	4.21	3.88	4.03	3.77
Al <sub>2</sub> O <sub>3</sub>	14.06	13.94	14.15	14.35
FeO	10.95	11.84	11.07	7.61
MnO	0.06	0.09	0.09	0.04
MgO	13.25	12.81	13.30	15.31
CaO	11.85	11.76	11.72	11.73
Na <sub>2</sub> O	2.35	2.29	2.38	2.17
K <sub>2</sub> O	2.06	2.18	2.08	2.27
Total	97.28	97.57	97.62	97.39
Ferrous Form				
Si	5.77	5.82	5.80	5.89
Al	2.48	2.47	2.49	2.48
Ti	0.47	0.44	0.45	0.42
Mg	2.96	2.87	2.96	3.35
Fe	1.37	1.49	1.38	0.93
Mn	0.01	0.01	0.01	0.01
Ca	1.90	1.89	1.88	1.85
Na	0.68	0.67	0.69	0.62
K	0.39	0.42	0.40	0.43
Sum	16.05	16.06	16.05	15.97

tion. A special feature of the Trois Epis melilitite is that it contains amphibole macrocrysts. These are scarce, unresorbed, single crystals of homogeneous and unzoned pargasite (Fig. 3) up to 15 mm in length. From crystal to crystal they differ in their Mg/(Mg+Fe) ratio only, grading from pargasite to ferroan pargasite (LEAKE et al., 1997; Fig. 3). Microprobe analyses are given in Table 3. They show an average K<sub>2</sub>O content of 2 wt%.

## 7. Dating results and discussion

Figure 4 and Table 4 give the results of our new <sup>40</sup>Ar/<sup>39</sup>Ar analyses obtained by single crystal laser fusion on separated amphibole phenocrysts.

All total-fusion analyses yield a weighted mean age of 60.9 ± 0.5 Ma, identical to the isochron age of 60.9 ± 0.6 Ma. The isochron (Fig. 5) was calculated without analysis 6b, because this grain had virtually no atmospheric argon due to preheating. The initial <sup>40</sup>Ar/<sup>36</sup>Ar ratio (291 ± 37) of the isochron is in agreement with the atmospheric value of 295.5, which suggests the absence of an excess Ar component. As an additional check for the presence of excess Ar, eventually masked within error of the initial <sup>40</sup>Ar/<sup>36</sup>Ar ratio, we preheated at the lowest possible laser power (no visible glowing ⇒ below 600 °C) a single crystal (analysis TE 6a) and a multigrain separate

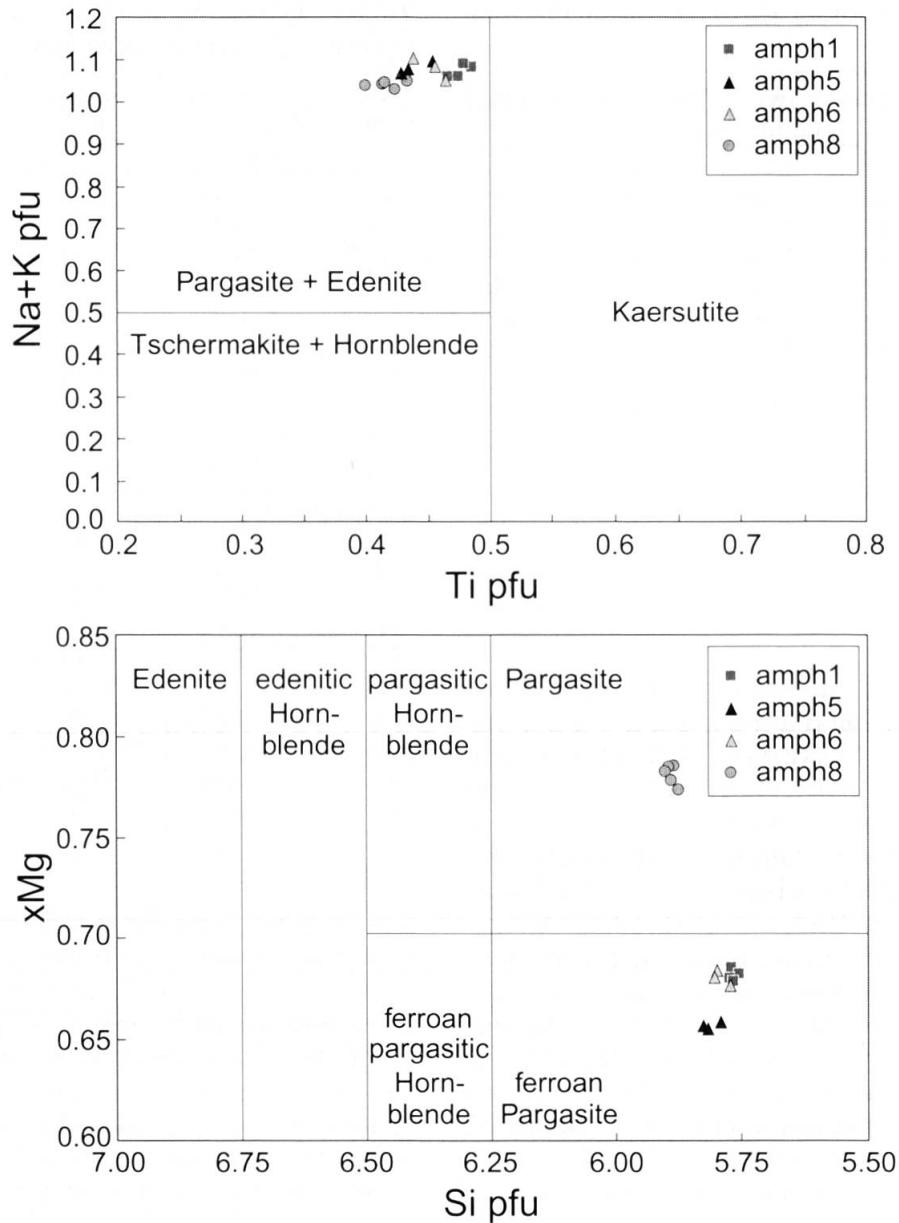


Fig. 3 Composition of rare amphibole phenocrysts of olivine-melilitite from Trois Epis, Vosges.

(analysis TE 8). The gas amount of analysis 6a was negligible, hence the age information is insignificant. The second preheating analysis (TE 8) was carried out on a large number of crystals to release a reasonable sample gas volume. It is evident that a small excess Ar component is present in the low temperature gas of the grains, either from decrepitated fluid inclusions (CUMBEST et al., 1994) and/or from nanoscale filling of cleavage planes with secondary minerals such as halloysite (VILLA et al., 1996). However, this has a negligible influence on the total fusion dates, as can be seen from the result of preheated grain TE 6b (Table 4). We rejected an incremental heating experiment on this multigrain separate because WARTHO et al. (1991) demonstrated that a possible concentration gradient of Ar cannot be

revealed due to the breakdown of the water-bearing mineral lattice *in vacuo* at temperatures above 750 °C.

We interpret the date of  $60.9 \pm 0.6$  Ma as the intrusion age of the olivine melilitite magma. This mineral age is 40 Ma younger than the whole-rock K/Ar age given by BARANYI et al. (1976) for the same dike. This large discrepancy can be explained by significant amounts of excess Ar-bearing minerals such as hauyn (LIPPOLT et al., 1990) and additional excess Ar-uptake and K-loss during alteration of the total rock (open system). Also BARANYI et al. (1976) mentioned a slightly (but not significantly) higher age for the intensely altered, outer part (1.05% K;  $31.9 \pm 3.0$  Ma) than for the less-altered inner part (1.33% K;  $28.1 \pm 2.8$  Ma) of one sample from Tannenbach (Vos-

Table 4 Laser  $^{40}\text{Ar}/^{39}\text{Ar}$  analyses of Trois Epis amphibole (single crystals of 500  $\mu\text{m}$  grain size except noted). Ages were calculated with a standard age of 24.29 Ma for HD-B1 biotite.

Sample	$^{40}\text{Ar}/^{36}\text{Ar}$	$1\sigma$	$^{39}\text{Ar}/^{36}\text{Ar}$	$1\sigma$	$^{37}\text{Ar}/^{39}\text{Ar}$	$1\sigma$	Ca/K	$^{40}\text{Ar}/^{39}\text{Ar}$	$1\sigma$	$^{40}\text{Ar}^*/^{39}\text{Ar}$	$1\sigma$	$^{40}\text{Ar}^*$ [%]	Date [Ma]	$1\sigma$	Note
TE 1	2856.20	243.52	106.90	9.16	2.32	0.04	4.64	26.72	0.39	23.95	0.43	89.7	61.2	1.1	4 grains#
TE 2	2715.74	36.39	101.87	1.59	4.10	0.06	8.20	26.66	0.38	23.76	0.36	89.1	60.7	0.9	12 grains#
TE 3	5069.68	411.51	203.36	16.59	2.33	0.04	4.66	24.93	0.36	23.48	0.36	94.2	60.0	0.9	
TE 4	6745.79	771.39	269.24	30.86	2.76	0.04	5.53	25.05	0.36	23.96	0.37	95.6	61.2	1.0	
TE 5	5792.69	258.85	230.57	10.47	2.26	0.03	4.51	25.12	0.36	23.84	0.35	94.9	60.9	0.9	2 grains
TE 6a	446.21	210.14	9.53	4.56	3.97	0.33	7.93	46.80	3.84	15.81	14.66	33.8	40.6	37.2	preheating
TE 6b	$^{50}\text{Ar}$		$^{50}\text{Ar}$		2.32	0.04	4.63	23.89	0.35	23.89	0.39	$^{50}\text{Ar}$ 100.0	61.0	1.0	fusion
TE 7	8568.49	1237.66	345.59	50.00	2.23	0.03	4.46	24.79	0.36	23.94	0.37	96.6	61.2	1.0	
TE 8	466.79	5.72	5.73	0.09	2.67	0.04	5.33	81.44	1.20	29.88	1.00	36.7	76.0	2.5	preheating multigrain#
Mean age													61.2	0.5	weighted mean all
Pooled mean													60.9	0.5	without 6a+8
Isochron age													60.9	0.6	without 6a,b+8

$^{50}\text{Ar}$  below detection limit.

# 200-300  $\mu\text{m}$  grain size.

ges). Additional evidence for anomalously old K/Ar dates of Tertiary whole-rock samples was presented by RITTMANN and LIPPOLT (1998) for comparable rocks from the ECRIS north of Frankfurt (Hessian Depression). These authors give three possible explanations for the elevated K/Ar dates: (i) excess Ar of mafic phenocrysts and (ii) excess Ar from hydrothermal overprint, or (iii) inherited Ar from crustal contamination. In addition we explain the elevated Trois Epis whole-rock date by meteoric water circulation through the Variscan crystalline basement with significant uptake of  $^{40}\text{Ar}$ , formation of alteration products (e.g. zeolites) in voids of the alkali basaltic rock with excess Ar-signature and K-loss from the matrix.

With this new Paleocene Ar/Ar date the time span for pre-rift magmatism in the URG area has shrunk drastically. This is in accordance with other peri-Alpine rift systems with European Asthenospheric Reservoir (EAR) magmatism, as defined by WILSON and DOWNES (1991). GRANET et al. (1995) discussed the interaction between man-

tle and crustal processes in Cenozoic Europe and compiled the dating results for the magmatic activity in the Massiv Central, France. There, the onset of pre-rift volcanism was also during the Paleocene, when small volumes of basaltic melts extruded as a consequence of lithospheric fracturing caused by Alpine compression (MICHON et al., 1999). Putting the Rhine Graben into a wider European context, we note that magmatic activity of the North Atlantic Tertiary Province also began during the Paleocene (ZIEGLER, 1990; TEGNER et al., 1998; LARSEN et al., 1999).

## 8. Conclusions

The precise  $^{40}\text{Ar}/^{39}\text{Ar}$  age by single-crystal laser fusion on amphibole phenocrysts places early graben-related volcanic activity in the Upper Rhine graben into the Paleocene. An age of  $60.9 \pm 0.6$  Ma was obtained for the olivine melilitite dike of Trois Epis, Colmar, Vosges. This dike was previously dated at  $102.5 \pm 7.6$  Ma by whole-rock K/Ar method (BARANYI et al., 1976; recalculated with constants recommended by STEIGER and JÄGER, 1977).

The new data indicate a considerably shorter duration of pre-rift volcanism, i.e. some 15 Ma before graben formation. The discrepancy between our single crystal date and the whole-rock date of BARANYI et al. (1976) casts doubt on all other Cretaceous K/Ar dates on early graben magmatism which were also measured on highly-altered whole rocks. We explain this discrepancy by uptake of excess Ar and K loss of the whole rock matrix during alteration.

The Paleocene age implies that the onset of Rhine graben volcanic activity within continental central Europe was contemporaneous with (i) the onset of major horizontal crustal shortening and

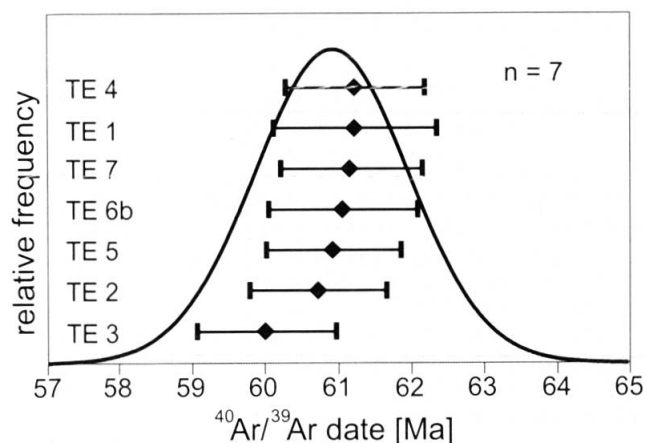


Fig. 4 Individual total-fusion analyses of Trois Epis amphibole ( $\pm 1\sigma$ ) with cumulative probability density function.



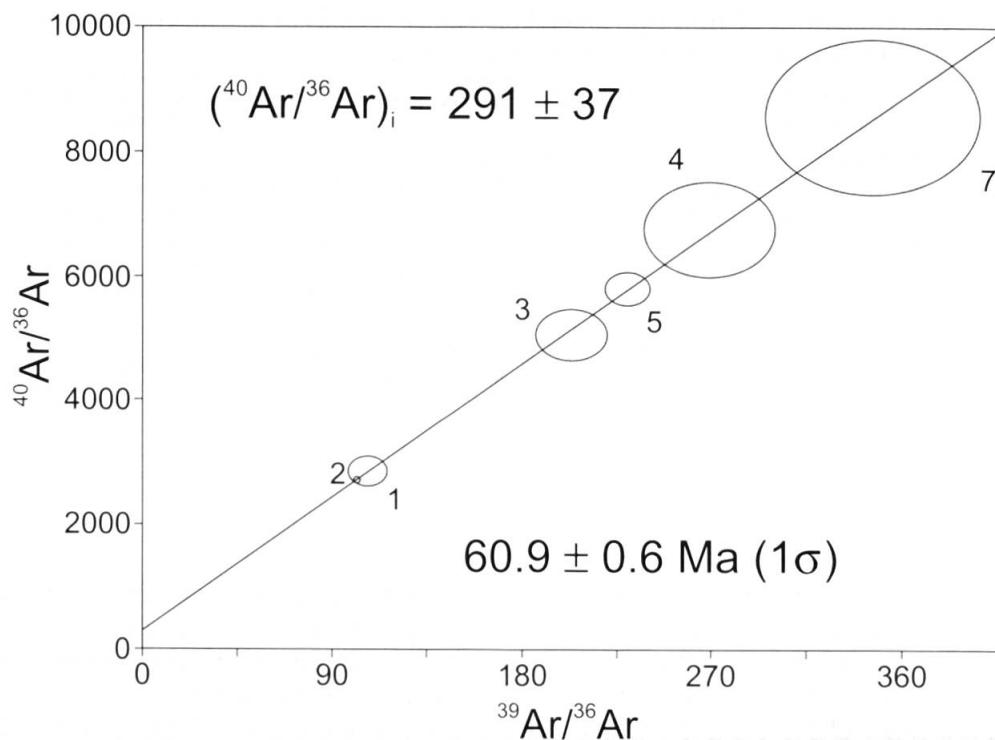


Fig. 5 Isochron of total-fusion analyses of Trois Epis amphibole. The number of the data points refers to the number of the analysed grain, or grain assemblage in the case of two, four and twelve grains. Note that the error correlation is not shown.

collision in the Western Alps (SCHMID et al., 1996; GEBAUER, 1999), (ii) a phase of major foreland compression (ZIEGLER, 1990; ZIEGLER et al., 1995) and (iii) the initial magmatic activity of the North Atlantic Tertiary Province at ~ 60 Ma (ZIEGLER, 1990; TEGNER et al., 1998; LARSEN et al., 1999).

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#### References

- BARANYI, I., LIPPOLT, H.J. and TODT, W. (1976): Kalium-Argon-Altersbestimmungen an tertiären Vulkaniten des Oberrheingraben-Gebietes: II Die Alters-traverse vom Hegau nach Lothringen. *Oberrhein. geol. Abh.* 25, 41–62.
- BERGGREN, W.A., KENT, D.V., SWISHER, C.C. and AUBRY, M.-P. (1995): A revised Cenozoic geochronology and chronostratigraphy. In: BERGGREN, W.A., KENT, D.V., AUBRY, M.-P. and HARDENBOL, J. (eds): *Geochronology, time scales and global stratigraphic correlations*. Soc. Econ. Paleontol. Mineral. Spec. Publ. 54, 17–28.
- BRAITSCH, O., GUNZERT, G., WIMMENAUER, W. and THIEL, R. (1964): Über ein Datolithvorkommen am Basaltkontakt im Kaliwerk Buggingen (Südbaden). *Beitr. Min. u. Petr.* 10, 111–124.
- COUTURIER, A., SIAT, A. and WEIL, R. (1967): Sur un filon d'ankaratrite dans le gneiss granitique des Trois Epis (Haut-Rhin). *Bull. Serv. Carte geol. Als. Lorr.* 20/1, 107–110.
- CUMBEST, R.J., JOHNSON, E.L. and ONSTOTT, T.C. (1994): Argon composition of metamorphic fluids: Implications for  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology. *Geol. Soc. Am. Bull.* 106, 942–951.
- DUFFIELD, W.A. and DALRYMPLE, G.B. (1990): The Taylor Creek Rhyolite of New Mexico: a rapidly emplaced field of lava domes and flows. *Bull. Volcanol.* 52, 475–487.
- DUNWORTH, E.A. and WILSON, M. (1998): Olivine melilitites of the SW German Tertiary Volcanic Province: mineralogy and petrogenesis. *J. Petrol.* 39, 1805–1836.
- ESSLINGER, G. (1976): Vorkommen und Tektonik der Basalte im Kalisalz-lager Buggingen (Südbaden). *Jh. Geol. Landesamt Baden-Württemberg* 18, 7–18.
- GEBAUER, D. (1999): Alpine geochronology of the Central and Western Alps: new constraints for a complex geodynamic evolution. *Schweiz. Mineral. Petrogr. Mitt.* 79, 191–208.
- GOES, S., SPAKMAN, W. and BIJWAARD, H. (1999): A Lower Mantle Source for Central European Volcanism. *Science* 286, 1928–1931.
- GRANET, M., WILSON, M. and ACHAUER, U. (1995): Imaging a mantle plume beneath the French Massif Central. *Earth Planet. Sci. Lett.* 136, 281–296.
- HAHN, W., MAUS, H. and SCHREINER, A. (1974): Eozäner Vulkanismus am Schönberg bei Freiburg i. Br.

- (Baden-Württemberg). *Jh. geol. Landesamt Baden-Württ.* 16, 41–49.
- HESS, J.C. and LIPPOLT, H.J. (1994): Compilation of K–Ar measurements on HD-B1 standard biotite – 1994 status report. In: ODIN, G.S. (ed): *Phanerozoic Time Scale*, Bull. Liais. Inform. Paris, IUGS Subcom. Geochronol. 12, 19–23.
- HORN, P., LIPPOLT, H.J. and TODT, W. (1972): Kalium-Argon-Altersbestimmungen an tertiären Vulkaniten des Oberrheingrabens I. Gesamtgesteinsalter. *Eclogae geol. Helv.* 65/1, 131–156.
- ILLIES, H. (1977): Ancient and Recent rifting in the Rhine graben. *Geol. Mijnbouw* 56, 329–350.
- ILLIES, J.H. (1981): Mechanisms of graben formation. *Tectonophysics* 73, 249–266.
- KELLER, J., BREY, G., LORENZ, V. and SACHS, P. (1990): Volcanism and petrology of the Upper Rhinegraben (Urach-Hegau-Kaiserstuhl). IAVCEI Int. Volc. Congress Mainz 1990. Pre- and post-conference excursion 2A + 2B Field Guide, 60 pp.
- KRAML, M. (1997): Laser- $^{40}\text{Ar}/^{39}\text{Ar}$ -Datierungen an distalen marinen Tephren des jung-quartären mediterranen Vulkanismus (Ionisches Meer, METEOR-Fahrt 25/4). Ph.D. thesis, university Freiburg, Germany.
- KRAML, M., KELLER, J. and HENJES-KUNST, F. (1996): Spot Fusion and Incremental Heating of Single Crystals from Kaiserstuhl Volcanic Rocks with the BGR  $^{40}\text{Ar}/^{39}\text{Ar}$  Laser Probe. V.M.Goldschmidt Conference March 31–April 4, 1996 Heidelberg, Germany, J. Conf. Abs. 1/1, 332.
- KRAML, M., KELLER, J. and HENJES-KUNST, F. (1999): Time Constraints for the Carbonatitic Intrusions of the Kaiserstuhl Volcanic Complex, Upper Rhine Graben, Germany. EUG 10 Strasbourg (France) 1999, J. Conf. Abs. 4, 322.
- LARROQUE, J.M. and LAURENT, P. (1988): Evolution of the stressfield in the south of the Rhinegraben from Eocene to present. *Tectonophysics* 148, 41–58.
- LARSEN, T.B., YUEN, D.A. and STOREY, M. (1999): Ultrafast mantle plumes and implications for flood basalt volcanism in the Northern Atlantic Region. *Tectonophysics* 311, 31–43.
- LEAKE, B.E., WOOLLEY, A.R., ARPS, C.E.S., BIRCH, W.D., GILBERT, M.C., GRICE, J.D., HAWTHORNE, F.C., KATO, A., KISCH, H.J., KRIVOVICHEV, V.G., LINTHOUT, K., LAIRD, J., MANDARINO, J., MARESCH, W.V., NICKEL, E.H., ROCK, N.M.S., SCHUMACHER, J.C., SMITH, D.C., STEPHENSON, N.C.N., UNGARETTI, L., WHITTAKER, E.J.W. and YOUZHI, G. (1997): Nomenclature of amphiboles – Report of the Subcommittee on Amphiboles of the International Mineralogical Association Commission on New Minerals and Mineral Names. *Eur. J. Mineral.* 9/3, 623–651.
- LIPPOLT, H.J. (1982): K/Ar Age Determinations and the Correlation of Tertiary Volcanic Activity in Central Europe. *Geol. Jb. D* 52, 113–135.
- LIPPOLT, H.J., GENTNER, W. and WIMMENAUER, W. (1963): Altersbestimmungen nach der Kalium-Argon-Methode an tertiären Eruptivgesteinen Südwestdeutschlands. *Jh. geol. Landesamt Baden-Württemberg* 6, 507–538.
- LIPPOLT, H.J., TODT, W. and HORN, P. (1974): Apparent Potassium-Argon Ages of Lower Tertiary Rhine Graben Volcanics. In: ILLIES, J.H. and FUCHS, K. (eds): *Approaches to Taphrogenesis*, E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 213–221.
- LIPPOLT, H.J., BARANYI, I. and TODT, W. (1975): Die Kalium-Argon-Alter der post-permischen Vulkanite des nord-östlichen Oberrheingrabens. *Aufschluß (Sonderband Odenwald)* 27, 205–212.
- LIPPOLT, H.J., HORN, P. and TODT, W. (1976): Kalium-Argon-Altersbestimmungen an tertiären Vulkaniten des Oberrheingrabens-Gebietes: IV. Kalium-Argon-Alter von Mineralien und Einschlüssen der Basalt-Vorkommen Katzenbuckel und Roßberg. *N. Jb. Miner. Abh.* 127/3, 242–260.
- LIPPOLT, H.J., TROESCH, M. and HESS, J.C. (1990): Excess argon and dating of Quaternary Eifel volcanism. IV. Common argon with high and lower-than-atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in phonolitic rocks, East Eifel, F.R.G. *Earth Planet. Sci. Lett.* 101, 19–33.
- LUTZ, M. and CLEINTUAR, M. (1999): Geological results of a hydrocarbon exploration campaign in the southern Upper Rhine Graben. *Bull. Appl. Geol.* 4, 3–80.
- MANKINEN, E.A. and DALRYMPLE, G.B. (1972): Electron microprobe evaluation of terrestrial basalts for whole-rock K–Ar dating. *Earth Planet. Sci. Lett.* 17, 89–94.
- MICHON, L., MERLE, O. and BERGER, E. (1999): Spatial and Temporal Distribution of Tertiary Volcanism in the Massif Central (France). paper presented at EUG 10 Strasbourg (France) 1999, J. Conf. Abs. 4, 339.
- PATERSON, R., WILSON, M. and KELLER, J. (1996): The Temporal Evolution of the European Asthenospheric Reservoir: Trace Element and Sr–Nd Isotopic Constraints from the upper Rhine Graben, Germany. V.M.Goldschmidt Conference March 31 – April 4, 1996 Heidelberg, Germany, J. Conf. Abs. 1/1, 448.
- PRODEHL, C., MUELLER, S. and HAAK, V. (1995): The European Cenozoic rift system. In: OHLSEN, K.H. (ed.): *Continental Rifts: Evolution, structure, tectonics*. Development In Geotectonics 25, 133–212.
- RITTMANN, U. and LIPPOLT, H.J. (1998): Evidence for distortion of Tertiary K/Ar ages by excess argon – example given by three alkali olivine basalts from Northern Hesse, Germany. *Eur. J. Mineral.* 10, 95–110.
- SCHMID, S.M., PFIFFNER, O.A., FROITZHEIM, N., SCHÖNBORN, G. and KISSLING, E. (1996): Geophysical-geological transect and tectonic evolution of the Swiss-Italian Alps. *Tectonics* 15/5, 1036–1064.
- SCHUMACHER, M.E. (2002): Upper Rhine Graben: The role of pre-existing structures during rift evolution. *Tectonics*, in press.
- SISSINGH, W. (1998): Comparative Tertiary stratigraphy of the Rhine Graben, Bresse Graben and Molasse basin: correlation with alpine foreland events. *Tectonophysics* 300, 249–284.
- STEIGER, R.H. and JÄGER, E. (1977): Subcommittee on Geochronology: Convention on the Use of Decay Constants in Geo- and Cosmochronology. *Earth Planet. Sci. Lett.* 36, 359–362.
- TEGNER, C., DUNCAN, R.A., BERNSTEIN, S., BROOKS, C.K., BIRD, D.K. and STOREY, M. (1998):  $^{40}\text{Ar}$ – $^{39}\text{Ar}$  geochronology of mafic intrusions along the East Greenland rifted margin: Relation to flood basalts and the Iceland hotspot track. *Earth Planet. Sci. Lett.* 156, 75–88.
- TOBIEN, H. (1959): Miozän. In: Geologisches Landesamt Baden-Württemberg (ed), *Erläuterungen zur Geologischen Exkursionskarte des Kaiserstuhls*, 21–23.
- VILLA, I.M., GROBÉTY, B., KELLEY, S.P., TRIGILA, R. and WIELER, R. (1996): Assessing Ar transport paths and mechanisms in the McClure Mountains hornblende. *Contrib. Mineral. Petrol.* 126, 67–80.
- WARTH, J.-A., DODSON, M.H., REX, D.C. and GUISE, P.G. (1991): Mechanisms of Ar release from Himalayan metamorphic hornblende. *Am. Mineral.* 76, 1446–1448.
- WEDEPOHL, K.H. and BAUMANN, A. (1999): Central European Cenozoic plume volcanism with OIB charac-

- teristics and indications of a lower mantle source. *Contrib. Mineral. Petrol.* 136, 225–239.
- WIJBRANS, J.R., PRINGLE, M.S., KOPPERS, A.A.P. and SCHEVEERS, R. (1995): Argon geochronology of small samples using the Vulkaan argon laserprobe. *Proc. Kon. Ned. Akad. v. Wetensch.* 98/2, 185–218.
- WILSON, M. and DOWNES, H. (1991): Tertiary–Quaternary Extension-Related Alkaline Magmatism in Western and Central Europe. *J. Petrol.* 32/4, 811–849.
- WIMMENAUER, W. (1952): Petrographische Untersuchungen an einigen basischen Eruptivgesteinen des Oberrheingebietes. *Neues Jb. Mineral. Abh.* 83/2/3, 375–432.
- WIMMENAUER, W. (1970): Zur Petrologie der Magmatite des Oberrheingebietes. *Fortschr. Miner.* 47, 242–262.
- ZIEGLER, P.A. (1990, 2nd edition): *Geological Atlas of Western and Central Europe*. Shell Internationale Petroleum Maatschappij B.V. Geol. Soc. London, Publishing House, 239 pp.
- ZIEGLER, P.A. (1992): European Cenozoic rift system. In: ZIEGLER, P.A. (ed.): *Geodynamics of rifting*. Vol. 1., Special Issue *Tectonophysics* 208, 91–111.
- ZIEGLER, P.A. (1994): Cenozoic rift system of western and central Europe. *Geol. Mijnbouw* 73, 99–127.
- ZIEGLER, P.A., CLOETINGH, S. and VAN WEES, J.D. (1995): Dynamics of intra-plate compressional deformation: the Alpine foreland and other examples. *Tectonophysics* 252, 7–59.

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