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K/Ar AGES IN THE CASE OF CORRELATED K AND EXCESS Ar CONCENTRATIONS: A CASE STUDY FOR THE ALKALINE OLIVINE BASALT OF SOMOŠKA, SLOVAK - HUNGARIAN FRONTIER

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Abstract: K/Ar ages (prepared by magnetic and heavy liquid separation) were determined for different fractions of the alkaline olivine basalt of Somoška, located on the Slovak - Hungarian frontier. The K/Ar ages range from 7.27 Ma to 4.65 Ma and isochron ages show a similarly great scatter from 6.02 Ma to 4.31 Ma; the fit of the points to the straight lines is poor. It has been demonstrated, that a linear relation of K and Ar(ex) concentrations may cause erroneously old isochron ages. On the basis of correlation of K and Ar(atm) concentrations in the fractions of the Somoška basalt, similar relation between the K and Ar(ex) contents could not be excluded, thus, the reality of the K/Ar as well as the isochron ages remained questionable. However, by selecting fractions of similar Ar(atm) concentrations, very accurate isochron ages of 4.06±0.06 Ma and 4.08±0.03 Ma were obtained, which are interpreted in terms of the real age of Somoška basalt and in the same time demonstrate the use of Ar(atm) content for the evaluation of isochron ages.

Key words: Slovakia, Hungary, Somoška, basalt, K/Ar age, reliability, atmospheric Ar.

Introduction

Alkaline basalts represent the youngest products of volcanic activity in the Carpathians and Pannonian basin. One important basaltic region is located on both sides of the Slovak - Hungarian frontier (Fig. 1, Kuthan et al. 1964; Jugovics 1971; Vass et al. 1992). The first K/Ar studies were performed on the alkaline olivine basalts and nepheline basanites of the Cerová basalt formation (Vass & Kraus 1985) in the Cerová Vrchovina hills (Balogh et al. 1981; Kantor & Wiegerová 1981), in Slovakia. The K/Ar dating of the Cerová basalts provided ages (2.75 - 1.35 Ma) in accordance with the stratigraphic position, though they differed from the FT age of 7.3 Ma obtained for Hajnačka by Repčok (1981). Similar K/Ar ages (2.5 - 2.0 Ma) were measured for the basanites of Medves Magosa (Balogh et al. 1983), Hungary, and additional investigations (Balogh et al. 1986) suggested that basaltic volcanism in this region was restricted to a relatively short period. Although excess Ar was frequently observed, the real ages were regularly obtained by the isochron method. Since it was difficult to find basalt samples of remarkably different K contents in the individual lava flows, according to Fitch et al. (1976), different fractions of a single piece of rock were used to define the isochron ages. In the Hungarian portion of this field K/Ar dating was the only means for obtaining the age of volcanic activity, since the basalts here lie on eroded Miocene and Oligocene surfaces.

The alkaline olivine basalt of Somoška is located in the vicinity of the well dated Medves Magosa, and it was unreasonable to expect an older age for it. However, the first investigations (Balogh et al. 1989) resulted in K/Ar ages of 4.65 - 5.95 Ma and the $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ isochron age also proved to be older (4.24±0.57 Ma). A systematic study was undertaken to discover the causes of this bias. The main mineral composition of the fractions was measured by XRD analysis. The pyroxene and plagioclase contents varied from 30 to 64 % and from 22 to

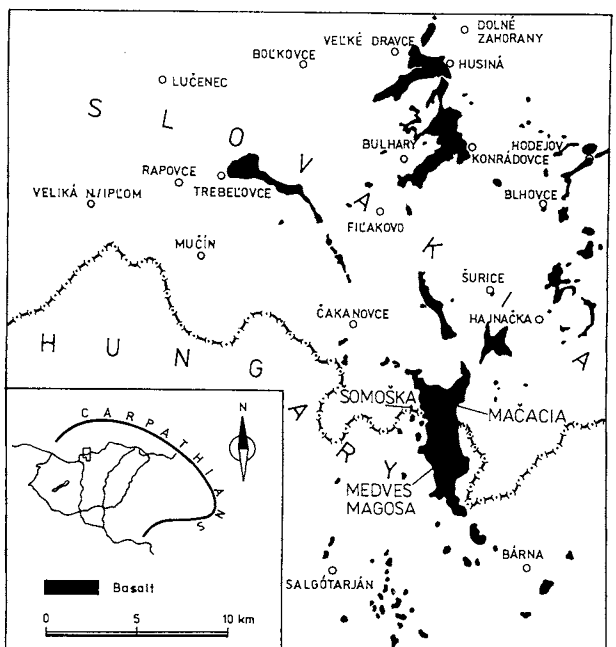

Fig. 1. Distribution of Cerová basalt formation (with its equivalents in Northern Hungary).

60 %, respectively, but no correlation was found between the ages and the pyroxene or plagioclase content. The sum of the plagioclase + pyroxene contents was 86 - 90 %, so 10 - 14 % remained for the groundmass and accessories (Balogh et al. 1989). The possible age increase due to the desorption of atmospheric Ar during baking the extraction line was calculated, and it has been shown that maximum 0.6 % of atmospheric Ar may appear as radiogenic due to the isotopic fractionation during desorption (Balogh et al. 1989). This was insufficient to explain the estimated bias, but it agreed well with the experimental value obtained by Gillot & Cornette (1986) on synthetic zeolite.

In the present work a special source of error in K/Ar isochron ages will be examined and the real age of the alkaline olivine basalt of Somoška will be presented.

Meanwhile the ongoing volcanologic study of the basalt forming the Somoška hill has proved that the Somoška basalt represents an individual basalt volcanic center separate from the Medves Magosa - Mačacia volcano lava flow complex (Konečný & Lexa in: Vass et al. 1992; L. Gaál, pers. comm.).

Experimental methods

The measurement of K/Ar ages was performed at the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary. The samples were first crushed, then a split of the crushed rock was selected and pulverized for K determination, when the measurement was performed on the whole rock sample. The majority of the measurements was performed on fractions prepared from the rock. First the crushed rock was split to fractions of different specific gravity by heavy liquids (mixture of bromoform and methylene iodide diluted with acetone for the lighter fraction) and then each fraction was further split by a magnetic separator of Cook type.

1 g of sample was used for Ar analysis. An argon extraction line and a mass spectrometer, both designed and built in the ATOMKI, were used for the Ar measurement. The rock was degassed by high frequency induction heating, and the usual getter materials (titanium sponge, SAES getter, CuO, zeolite and cold traps) were used for cleaning Ar. The ^{38}Ar spike was introduced to the system from a gas-pipette before degassing. The cleaned Ar was directly introduced into the mass spectrometer. The mass spectrometer was a magnetic sector type of 150 mm radius and 90° deflection, operated in the static mode. Recording and evaluation of Ar spectra was controlled by a microcomputer.

0.1 g of the pulverized material was digested in HF with the addition of some sulphuric and perchloric acids. The digested samples were dissolved in 100 ml 0.25 mol.l^{-1} HCl and diluted fivefold. 100 ppm Na and 100 ppm Li were added as buffer and internal standard. K concentration was measured with a digitized flame photometer of OE-85 type manufactured in Hungary.

The inter-laboratory standards Asia 1/65, HD-B1 and GL-O and atmospheric Ar were used for calibration. Details of the instruments, the applied methods and results of calibration have been described elsewhere (Balogh 1985; Odin et al. 1982).

Results of K/Ar dating

The results of the K/Ar measurements are summarized in Tab. 1. Ages were calculated according to the constants of Steiger & Jäger (1977). D_i characterizes the density of the samples; for grain sizes 0.1 - 0.15 mm $D_1 < 2.88\ g/cm^3 < D_2$, and for grain sizes 0.043 - 0.1 mm $D_1 < 2.79\ g/cm^3 < D_2 < 2.88\ g/cm^3 < D_3 < 2.98\ g/cm^3 < D_4$. M_i refers to the magnetic difference of the fractions and i increases with increasing magnetic susceptibility.

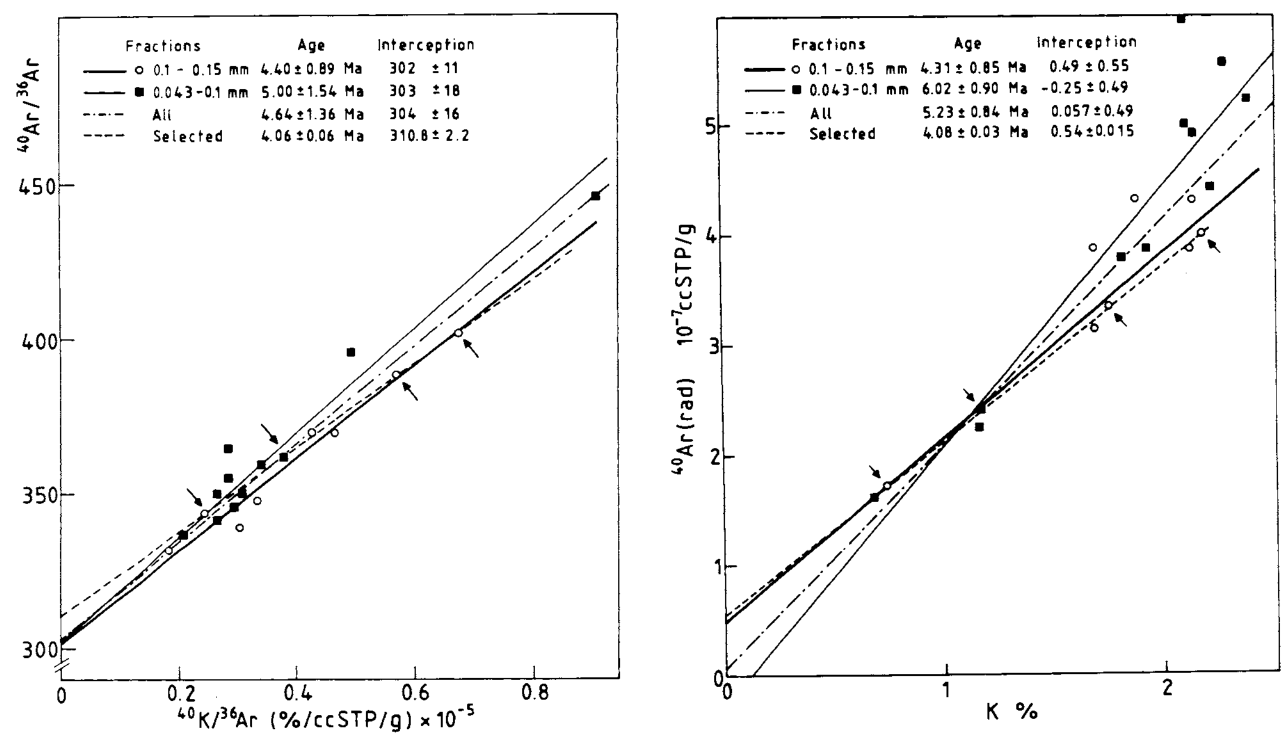

Fig. 2. $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ and ^{40}Ar(rad) - K diagrams and isochron ages for fractions of the Somoška basalt.

Table 1: K/Ar ages of fractions of the basalt from Somoška.

Fraction	K %	$^{40}Ar(rad)$ 10^{-7}ccSTP/g	$^{40}Ar(rad)$ / $^{40}Ar(tot)$	$^{40}Ar(atm)$ 10^{-6}ccSTP/g	^{40}Ar / ^{36}Ar	$^{40}K/^{36}Ar$ $\cdot 10^{-5}$	Age Ma
grain size: 0.1 - 0.15 mm							
D_1M_7	2.140	4.310	0.200	1.72	369.7	0.429	5.18±0.38
D_1M_5	2.182	4.001	0.265	1.11	402.0	0.678	4.72±0.28
D_1M_3	2.132	3.860	0.150	2.19	347.6	0.336	4.65±0.44
D_1M_1	1.884	4.317	0.110	3.49	332.0	0.186	5.89±0.75
D_2M_7	1.760	3.345	0.240	1.06	388.8	0.573	4.89±0.31
D_2M_4	1.689	3.881	0.170	1.90	339.7	0.307	5.80±0.49
D_2M_2	1.698	3.142	0.200	1.26	369.7	0.464	4.70±0.35
D_2M_1	0.743	1.723	0.140	1.06	343.6	0.242	5.96±0.60
grain size: 0.043 - 0.1 mm							
W.r.1.	1.819	3.782	0.156	2.05	350.1	0.306	5.35±0.48
W.r.2.	1.932	3.871	0.135	2.48	341.6	0.269	5.15±0.51
D_1M_3	2.389	5.227	0.178	2.41	359.5	0.342	5.62±0.45
D_1M_1	2.107	5.959	0.190	2.54	364.8	0.286	7.27±0.56
D_2M_3	2.223	4.428	0.146	2.59	346.0	0.296	5.12±0.47
D_2M_2	2,282	5.559	0.168	2.75	355.2	0.286	6.26±0.53
D_2M_1	2.145	4.942	0.123	3.52	336.9	0.210	5.92±0.67
D_3M_2	2.109	4.992	0.254	1.47	396.1	0.495	6.08±0.37
D_4M_3	1.173	2.404	0.184	1.07	362.1	0.378	5.27±0.38
D_4M_2	1.162	2.251	0.338	0.44	446.4	0.911	4.98±0.20
D_1M_1	0.678	1.625	0.156	0.88	350.1	0.266	6.16±0.53

The K/Ar ages range from 7.27 to 4.65 Ma, and are all older than 2.5 - 2.0 Ma, the value expected on the basis of previous K/Ar studies. The isochron plots and the calculated "ages" are shown in Fig. 2. The poor fit of the points to the straight lines shows that no isochrons were obtained. However, the calculated age values are also systematically older, and this contrasts with the experiences of previous datings, where in the presence of excess Ar geologically acceptable isochron ages were obtained.

The "isochron ages" are older and their errors are greater for samples of smaller grain size. This reflects the greater heterogenity of $^{40}Ar/^{36}Ar$ initial ratio and/or the Ar(ex) content of the smaller grained samples. The correlation coefficient between the atmospheric Ar and K concentrations is 0.85 for the smaller and 0.31 for the coarser grained fractions. The better correlation of Ar(atm) and K concentrations in the more heterogeneous smaller grains suggests that a similar correlation may exist between the Ar(ex) and K concentrations, thereby creating the isochron ages that appeared unrealistically old in view of previous studies.

Analysis of the reliability of K/Ar isochron ages

It is most difficult to recognize erroneous isochron ages if the same age is obtained with the $^{40}Ar(rad)$ - K and $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ methods and if the points fit well the defined straight line. Therefore, the important question is: under what conditions will the isochron ages be equal, and in the same time erroneously old?

Linear relation was assumed between the Ar and K contents in the following manner:

$$^{40}Ar(ex)_i = {}^{40}Ar(ex)_0 + C_1 * {}^{40}K_i \quad (1)$$

$$^{40}Ar(atm)_i = {}^{40}Ar(atm)_0 + r * C_2 * {}^{40}K_i \quad (2)$$

$$^{36}Ar(atm)_i = {}^{36}Ar(atm)_0 + C_2 * {}^{40}K_i \quad (3)$$

Indices i refer to the relevant concentrations in the i-th fraction, and o refers to the argon concentration if the K content is zero. C_1 and C_2 are coefficients and r denotes the $^{40}Ar/^{36}Ar$ ratio of atmospheric argon.

It follows from Eqs. (1 - 3) that the apparent age increase (the difference betweens the obtained isochron age and the real age) is

$$C_1 \quad (4a)$$

for the $^{40}Ar(rad)$ – K, and

$$C_1 - C_2 * [{}^{40}Ar(ex)_0]/[{}^{36}Ar(atm)_0] \quad (4b)$$

for the $^{40}Ar/^{36}Ar$ – $^{40}K/^{36}Ar$ methods, respectively. The erroneous isochron ages will be equal, if

$$C_2 * [{}^{40}Ar(ex)_0]/[{}^{36}Ar(atm)_0] = 0 \quad (5)$$

Table 2: Model calculations for correlated $^{40}Ar(ex)$ and K concentrations. Real age: 2.57 Ma; $r = ^{40}Ar(atm)/^{36}Ar(atm) = 300$.

Case I.: $^{40}Ar(ex)_i = C_1 * K_i$

$^{40}Ar(ex)_i = 0.5*10^{-7}K_i$ — ^{40}Ar (atm): random variable

i	K %	$^{40}Ar(rad)$ real	$^{40}Ar(ex)$	$^{40}Ar(rad)$ apparent	$^{40}Ar(atm)$	K/Ar age Ma	$^{40}Ar/^{36}Ar$	$^{40}K/^{36}Ar$ %/(cc STP/g) $*10^{-5}$
		10^{-7}(cc STP)/g						
1	0.5	0.5	0.25	0.75	5	3.86	345	0.35
2	1.0	1.0	0.50	1.50	7	3.86	3643	0.50
3	1.5	1.5	0.75	2.25	3	3.86	525	1.75
4	2.0	2.0	1.00	3.00	4	3.86	525	1.75
5	2.5	2.5	1.25	3.75	6	3.86	487.5	1.46

Case II.: $^{40}Ar(ex)_i = ^{40}Ar(ex)_0 + C_1 * K_i$; ($C_2 = 0 => Ar(atm) = const.$)

$^{40}Ar(ex)_i = 10^{-7} + 0.5\,K_i$; $^{40}Ar(atm) = 5*10^{-7}$(cc STP/g)

i	K %	$^{40}Ar(rad)$ real	$^{40}Ar(ex)$	$^{40}Ar(rad)$ apparent	$^{40}Ar(atm)$	K/Ar age Ma	$^{40}Ar/^{36}Ar$	$^{40}K/^{36}Ar$ %/(cc STP/g) $*10^{-5}$
		10^{-7}(cc STP)/g						
1	0.5	0.5	1.25	1.75	5	8.99	405	0.35
2	1.0	1.0	1.50	2.50	5	6.43	450	0.70
3	1.5	1.5	1.75	3.25	5	5.57	495	1.05
4	2.0	2.0	2.00	4.00	5	5.14	540	1.40
5	2.5	2.5	2.25	4.75	5	4.89	585	1.75

^{40}Ar (rad) apparent is the sum of ^{40}Ar (rad) real and ^{40}Ar (ex)

Equation (5') will be fulfilled, if $^{40}Ar(ex)_0 = 0$ or, if $C_2 = 0$, these possibilities will be referred to as case I and case II respectively. The relation of Ar(ex) and K concentrations will be described by

$$^{40}Ar(ex)_i = C_1 * ^{40}K_i \qquad (6)$$

for case I and by equation (1) for case II.

The Ar(atm) concentration is variable in case I and constant in case II. Model calculations (Tab. 2 and Fig. 3) show that in case I the analytical ages are uniform and the interceptions do not indicate the presence of excess Ar, while in case II the analytical ages are different and the interceptions correspond to the Ar(ex) concentration at zero K content. The isochron ages are always 3.86 Ma, i.e. uniform, but older than the real age of 2.57 Ma.

The excess age will be proportional to C_1, and the fit of the points depends on the correlation of the K and Ar(ex) concentrations. If this correlation is poor, the great age error will point to the unreliability of the obtained data. However, if the correlation is good, and there is no additional information on the age, the erroneously old isochron age likely will be accepted. The relation of Ar(atm) and K concentrations is an indicator of the relation of Ar(ex) and K concentrations.

The K content of a rock is determined by the chemical composition of the magma, while the Ar content depends on the conditions of solidification (Itaya et al. 1984; Itaya et al. 1989). Thus, it is unjustified to expect correlation of Ar and K, if whole rock samples are used for obtaining the isochron. However, when fractions of a single piece of rock are used, and K is incompatible with its minerals, the correlation of incompatible elements (K and Ar) is not surprising.

Discussion

In Fig. 4 the atmospheric Ar concentration is plotted against K content, and the slopes of the fitted straight lines are also indicated. In spite of the poor fit, an increase in ^{40}Ar content with increasing K concentration can be observed, suggesting that the reliability of the obtained old age data can be questioned. This offers a possible explanation for the K/Ar ages that appear unrealistically old in light of previous studies, but does not allow the determination of the real geological age. Successful determination of geological age might be tried by using whole rock samples of different K concentrations for obtaining the isochron ages, or by dating minerals in which K is a major constituent. Both of these possibilities may be impeded by the lack of suitable samples.

The great number of prepared fractions from the basalt of Somoška allowed an additional attempt to determine the geological age. According to Tab. 1, fractions of similar Ar(atm) concentration were selected, and it was hoped that their radiogenic Ar concentrations will also be similar. Fractions D_1M_5, D_2M_7, D_2M_1 and D_4M_3 were chosen in which the Ar(atm) contents were 1.11, 1.06, 1.06 and 1.07×10^{-6} cc STP/g, respectively. The isochron plots are shown in Fig. 5. The fit of the points to the straight lines and the agreement of isochron ages are excellent, and this is a strong argument for the validity of the obtained data. The K content in the selected fractions shows a great variation (from 0.743 % to 2.182 %), this is the basis of an additional support for the reality of isochron ages. Namely, in the course of crystallization the minerals with low K content crystallized first and K concentrated later in the groundmass. On the

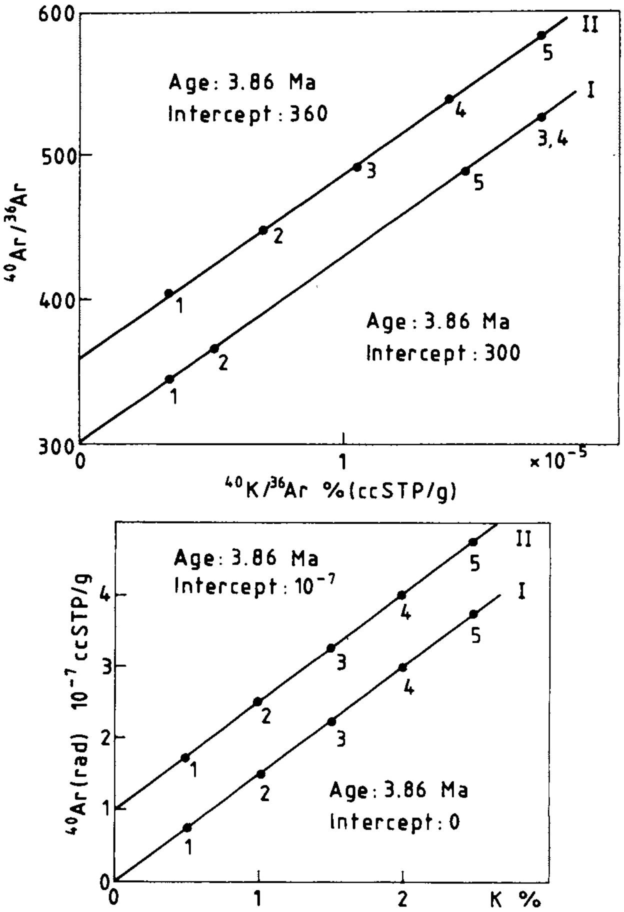

Fig. 3. Isochron diagrams and ages for case I. and case II. according to the model calculations in Table 2.

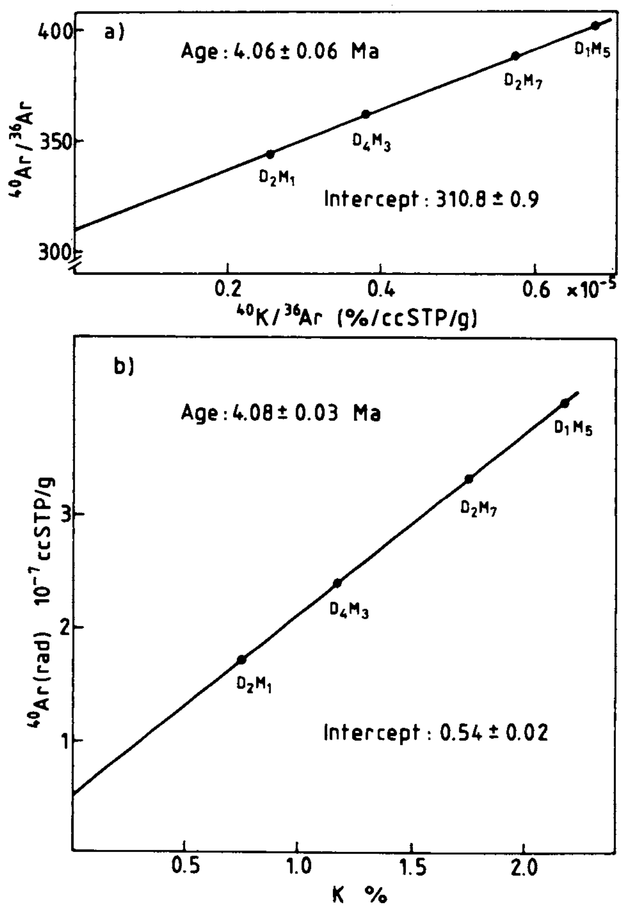

Fig. 5. Isochron diagrams and ages for fractions with similar Ar(atm) concentrations of the Somoška basalt.

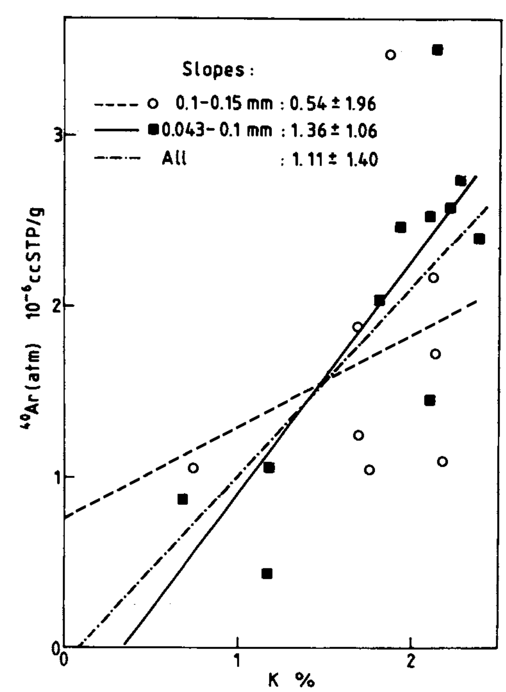

Fig. 4. Atmospheric Ar concentrations plotted against K concentrations for fractions of the Somoška basalt.

other hand, incorporation of excess and atmospheric Ar takes place in an environment where both Ar components are present and as crystallization proceeds only atmospheric Ar can be added to this environment. Thus, if the incorporated Ar(atm) is similar during the different phases of crystallization, the incorporated Ar(ex) has to be either similar too, or it has to decrease. However, there is no reason to assume a linear relation between the incorporated K content and the decrease of the $^{40}Ar/^{36}Ar$ ratio of the environment. On the basis of the considerations above, the accurate isochron ages can be interpreted only in terms of Ar incorporation with uniform concentration and $^{40}Ar/^{36}Ar$ ratio in the selected fractions. This implies the reality of isochron ages.

In Fig. 2 the true isochrons are shown with dashed lines, the selected fractions are marked with arrows. It can be seen in the $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ diagram in Fig. 2 that several additional points also fit the line well but these could not have been selected on the basis of uniform Ar(atm) content. Several fractions of 0.043 - 0.1 mm size lie above the isochron. These were crystallized in an environment with higher $^{40}Ar/^{36}Ar$ ratio. The lower initial $^{40}Ar/^{36}Ar$ ratio of fractions below the isochron can be explained by the incorporation of more Ar(atm) during or after crystallization. Similarly, in the ^{40}Ar(rad) - K diagram in Fig. 2 several additional points also fit the isochron. Only fraction D_4M_2 with exceptionally low Ar(atm) content lies below it. It can be seen that only fractions with a higher K content have higher initial ^{40}Ar(rad) concentrations.

Conclusions

1 – It has been demonstrated that $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ and $^{40}Ar(rad)$ - K isochron ages are equal, but older than the real geological age, if the $^{40}Ar(ex)$ and K concentrations are related through Eqs. (1) or (6), where $Ar(ex)_0$ is the Ar(ex) concentration when K = 0. The excess age is proportional to the C_1 coefficient. On the basis of geochemical considerations the proportionality of K and Ar concentrations is acceptable when minerals and/or fractions of a single piece of rock, in which K is incompatible with the minerals present in the rock, are used for defining the isochron.

2 - The atmospheric Ar content of the fractions indicates the possible correlation of Ar(ex) and K. Therefore reproducible baking of the argon extraction line is desireable.

3 - In the case of the Somoška basalt, fractions of nearly uniform Ar(atm) concentrations were selected, and these defined reliable isochron ages of 4.06±0.06 Ma and 4.08±0.03 Ma with the $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ and $^{40}Ar(rad)$ - K methods, respectively. This proves that basaltic volcanism in the study area started earlier than expected and lasted at least for 2.5 - 3.0 Ma.

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