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Achievements and Limitations of the K-Ar and $^{40}Ar/^{39}Ar$ Methods: What's in It for Dating the Quaternary Sedimentary Deposits?

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Abstract

Basic principles of the K-Ar and $^{40}Ar/^{39}Ar$ methods and particular analytical techniques are reviewed in light of its applicability and limitations for purpose of direct dating of Quaternary volcanic rocks and building up a reference time scale for calibration of methods commonly used for dating of sediments. It is shown that the major problem for K-Ar method is in the plausible inequality of initially trapped argon isotopic composition in minerals of volcanic origin to the atmospheric $^{40}Ar/^{36}Ar$ ratio of 295.5. Inverse isochron approach of the stepwise-heating technique in the $^{40}Ar/^{39}Ar$ method provides a possibility to reveal isotopic composition of the initially trapped argon and hence to yield accurate age. Additionally, $^{40}Ar/^{39}Ar$ laser fusion technique allows finding and dating of ultimately fresh mineral fractions, which are free of non-atmospheric argon contamination. Coupled application of the stepwise-heating and laser fusion techniques of the $^{40}Ar/^{39}Ar$ method is sufficient for calibration purposes from ca. 10 thousands to several millions years range.

Key words: K-Ar and 40Ar/39Ar dating

1. Introduction

Absolute chronology of sediments in lacustrine (and palaeolacustrine) environment is achievable via variable dating methods (Geyh and Schleicher, 1990 and references therein). Though arbitrary, commonly used methods can be classified by their principles: 1) dating on basis of cosmogenic isotopes (^{14}C, ^{10}Be, ^{26}Al methods), 2) uranium disequilibrium series chronology (^{230}Th-^{234}U and related methods), 3) annealing of radiation-induced defects in crystals (thermoluminescence (TL), optically stimulated luminescence (OSL), electron spin resonance (ESR) methods), 4) age estimations on basis of Milankovitch orbital tuning theory, 5) correlation with sections of known age on basis of ^{18}O and paleomagnetic records, and finally 6) K-Ar and $^{40}Ar/^{39}Ar$ dating among others classic daughter/parent isotope ratios methods. Peculiarity of the methods of groups 1 to 5 is in that they ought to be intercalibrated one against another. ^{14}C method has been precisely calibrated by dendrochronology back to the beginning of the Holocene (Stuiver et al., 1998a) and may be considered as the most accurate dating tool for the last 12 Ka. With less degree of precision calibration of ^{14}C method has been extended back to 20 Ka (Stuiver et al., 1998b). Cross calibration of other methods is possible due to overlapping of its applicability ranges (Fig. 1). The age calculation on basis of daughter/parent isotopic ratios is more straightforward. Recent analytical developments expanding the K-Ar and $^{40}Ar/^{39}Ar$ methods for dating Pliocene and Holocene deposits with sufficient precision makes them desirable for being reference for other methods mentioned above. Ability of the K-Ar isotopic chronometer for very recent eruptions is represented by the $^{40}Ar/^{39}Ar$ age of 1925 ± 94 years for the 79 AD Vesuvius eruption (Renne et al., 1997).

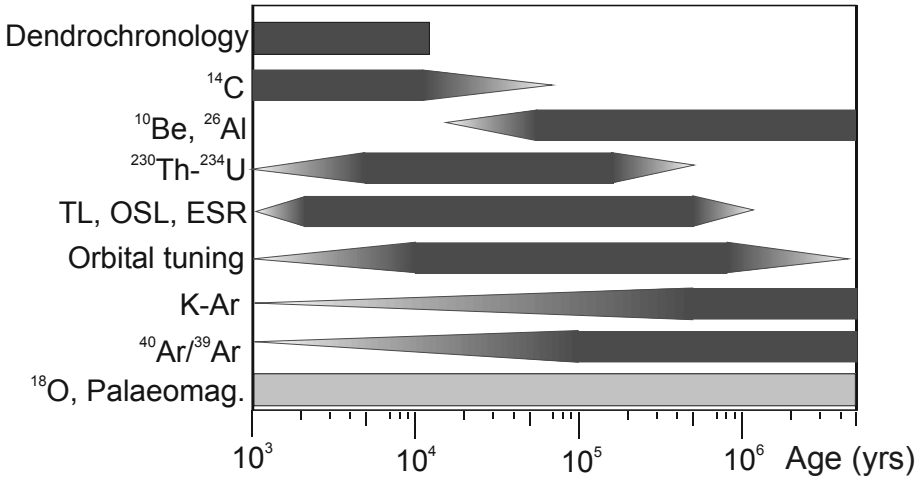

Fig. 1: Application ranges of the various dating methods (adapted after Geyh and Schleicher, 1990).

In this paper we review basic principles of the K-Ar and $^{40}Ar/^{39}Ar$ methods and consider major limiting factors to its application for dating of the Quaternary deposits. We restrict our consideration mainly for volcanic rock dating, because it was the common case study (Boven et al., 1998; Dalrymple and Lanphere, 1969; Ebinger et al., 1993; Gillot and Cornette, 1986; Guillou et al., 1996; Matsumoto and Kobayashi, 1995; Rasskazov et al., 2000a; 2000b; Singer et al., 1998; Villa, 1991; Wilch et al., 1999 etc.). For purpose of the calibration the volcanic rocks can be used in two ways. First, direct dating of volcanic horizons intercalated with sediments and ice (Rasskazov et al., 2000b; 2001; Wilch et al., 1999 etc.). Second, building up a calibrated palaeomagnetic and ^{18}O curves due to study of thick volcanic strata, sedimentary and ice cores (Guillou et al., 1996; Singer et al., 1998 etc.).

2. K-Ar Dating Method

^{40}K isotope is radioactive and decays to ^{40}Ca and ^{40}Ar. Because of branching decay the equation for K-Ar clock is the following: $t = 1/\lambda_{total} \times \ln(\lambda_{total}/\lambda_{Ar} \times {}^{40}Ar_{rad}/{}^{40}K + 1)$, where t is the age, λ_{Ar} and λ_{total} are respectively the decay constant of potassium to reach ^{40}Ar and total decay constant, the $^{40}Ar_{rad}/^{40}K$ is the ratio of radiogenic ^{40}Ar to present-day ^{40}K in a dated rock or mineral. There are three sets of potassium decay constants used in physical, chemical and geological studies, which, however, are statistically undistinguished from each other (Min et al., 2000). There is no difference in age calculations with using of any of potassium decays sets for 0 to *ca*. 25 Ma old samples. Hence the error in the age calculation for K-Ar clock is solely dependent on precision and accuracy of the $^{40}Ar_{rad}/^{40}K$ measurements.

Determination of $^{40}Ar_{rad}$ in young volcanic rocks (and minerals) is complicated due to low quantities of radiogenic argon in comparison to overwhelming amount of the atmospheric argon. To overcome the problem special analytical procedures such as unspiked K-Ar technique (Cassignol et al., 1978; Gillet and Cornette, 1986) and isotope dilution technique by the atmospheric argon (Brandt, 1965; Rasskazov et al., 2000b) have been developed. Isotope dilution by spike of argon-38 has also been routinely applied (e.g. Chernyshov et al., 2001). In the latter two techniques precision for determination of $^{40}Ar_{rad}$ is strongly dependent upon amount of the spike added. For optimal dilution a ratio of $^{40}Ar_{spike}/^{40}Ar_{rad}$ or $^{38}Ar_{spike}/^{40}Ar_{rad}$ should be equal to unity. In practice, precision for determining of $^{40}Ar_{rad}$ concentrations in the Pleistocene volcanic rocks of the Baikal rift system with isotope dilution by the atmospheric argon was 2-15 % using the double-collector MI-

1201 mass-spectrometer (Rasskazov et al., 2000b). In the unspiked, so-called, Cassignol technique the measured sample peaks are compared with isotopic composition of the atmospheric argon. Volumetric calibration of introduction line relies on analysis of reference age standard minerals. Precision for $^{40}Ar_{rad}$ determination in the Pleistocene volcanic rocks from Canary and Hawaii with using specially constructed 180°, 6 cm radius, 620 V accelerating potential mass-spectrometer was 0.7–2.7 %, and rise up to 50-150 % for the Holocene rocks of the same islands (Guillou et al., 1996; 1997).

Potassium content has to be determined in a separate aliquot by flame photometry or another suitable technique with a typical precision of 1-1.5 %. Large weight samples (> 1 g) are used to neglect possible inhomogeneous distribution of potassium (Guillou et al., 1996; 1997; Matsumoto and Kobayashi, 1995; Rasskazov et al., 2000b).

Measured amount of ^{40}Ar in a dated sample consists of radiogenic argon ($^{40}Ar_{rad}$), which was accumulated from ^{40}K since mineral crystallisation, and non-radiogenic argon ($^{40}Ar_{n\text{-}rad}$), which was initially trapped by the mineral during its crystallisation ($^{40}Ar_{ini}$) and impregnated after by the atmospheric pressure into intercrystalline defects ($^{40}Ar_{atm}$):

$$^{40}Ar = {}^{40}Ar_{rad} + {}^{40}Ar_{n\text{-}rad} = {}^{40}Ar_{rad} + {}^{40}Ar_{ini} + {}^{40}Ar_{atm}.$$

If magma erupted, completely degassed and crystallised in equilibrium with the atmosphere the initially trapped argon in all minerals must have an isotopic composition, which is identical to those of the atmosphere. Conventionally, concentration of $^{40}Ar_{rad}$ in a dated sample is simply calculated from measured abundance of ^{40}Ar and ^{36}Ar (rarely ^{38}Ar):

$$^{40}Ar_{rad} = {}^{40}Ar_{measured} - 295.5 \times {}^{36}Ar_{measured} = {}^{40}Ar_{measured} - 1580.925 \times {}^{38}Ar_{measured}, \text{ due to}$$

$$(^{40}Ar/^{36}Ar)_{atm} = 295.5 \text{ and } (^{36}Ar/^{38}Ar)_{atm} = 5.35.$$

Initial argon composition of volcanic rocks may, however, differ from those of the atmosphere. For instance, analysis of $^{40}Ar/^{36}Ar$ ratio in historic lavas revealed variations from 283.5 to 356.6 (Dalrymple, 1969). If initially trapped argon is characterised by $^{40}Ar/^{36}Ar > 295.5$ such argon is called extraneous argon. If the extraneous argon is incorporated in the sample in any other ways than *in situ* decay of potassium it is referred to as excess argon (Dalrymple and Lanphere, 1969).

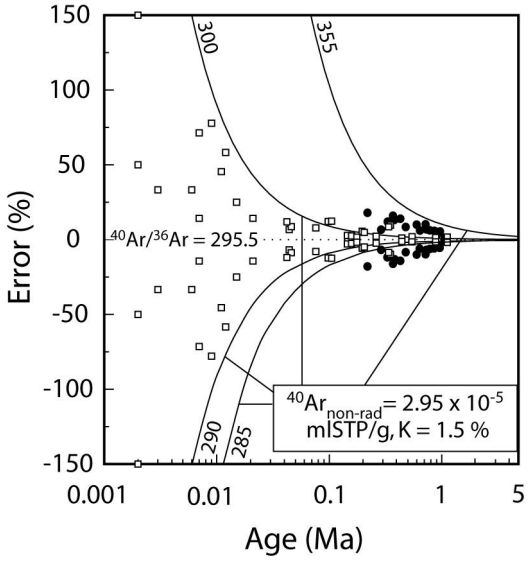

Fig. 2: Error for the conventional K-Ar age due to non-atmospheric initially trapped argon isotopic composition. Analytical errors for the unspiked K-Ar technique (open squares) and isotope dilution technique by the atmospheric argon (filled circles) are shown for comparison after Guillou et al. (1996, 1997), Gillet and Cornette (1986) and Rasskazov et al. (2000b). Note that the curves for various $(^{40}Ar/^{36}Ar)_{ini}$ can be quantitatively applied only for the case of K = 1.5 % and $^{40}Ar_{non\text{-}rad} = 2.95 \times 10^{-5}$ mlSTP/g.

Lower initial $^{40}Ar/^{36}Ar$ ratio in volcanic rocks is because of argon isotopic fractionation in subsurface magma chambers (Krummenacher, 1970; Kaneoka, 1980). If $(^{40}Ar/^{36}Ar)_{ini} > (^{40}Ar/^{36}Ar)_{atm}$ the measured age will be overestimated and vice versa. Shift of measured age from the true age is dependent on initial $^{40}Ar/^{36}Ar$ ratio, amount of non-radiogenic argon and potassium content in a dated sample. Uncertainty in the age estimation resulted from various $(^{40}Ar/^{36}Ar)_{ini}$ ratios is generally larger than analytical error (Fig. 2).

To overcome the problem of fractionated argon isotopic composition ($(^{40}Ar/^{36}Ar)_{ini} < 295.5$) the "mass-fractionation correction procedure" has been applied. In that procedure initial $^{40}Ar/^{36}Ar$ ratio is estimated from the stable $^{38}Ar/^{36}Ar$ ratio measured by the unspiked technique (Matsumoto and Kobayashi, 1995) (Fig. 3). Though resulting analytical error in age determination became 4-5 times larger, this procedure allows more accurate age determination in comparison to conventional K-Ar dating. Unfortunately, the "mass-fractionation correction procedure" is not applicable if extraneous argon presented in the sample.

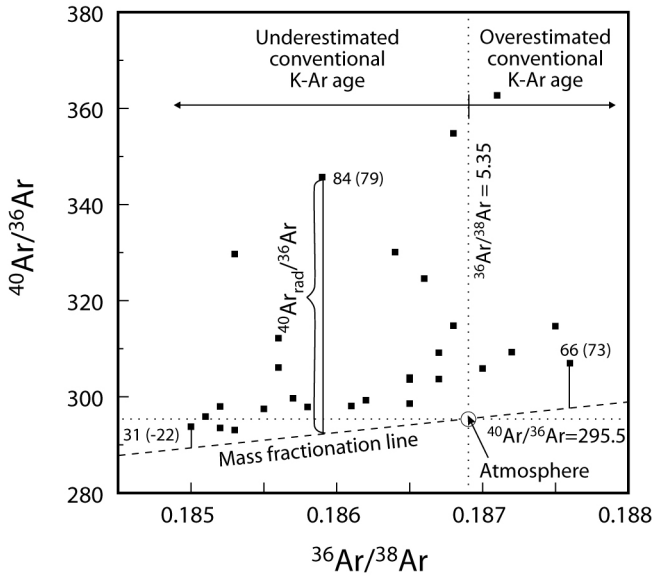

Fig. 3: Principle of the "mass fractionation correction procedure". Black squares are measured values after Matsumoto and Kobayashi (1995). Numbers close to the squares are "true" K-Ar ages, while those in brackets are erroneous conventional K-Ar ages in ka.

To minimise influence of extraneous argon on the K-Ar age determination it was suggested to avoid dating of glassy rocks, remove pheno-, mega- and xenocrystals and use holocrystalline rock matrix as dating material (Guillou et al., 1996; 1997; Matsumoto and Kobayashi, 1995; Rasskazov et al., 2000a; 2000b; Singer et al. 1998 etc.). However, such approach can not totally guarantee initial $^{40}Ar/^{36}Ar$ ratio of 295.5 in the matrix. For instance, among 5 matrix samples taken with stratigraphic position control at Loihi volcano (Hawaii) one has shown too high apparent age and another one appeared to be too young (Guillou et al., 1997). Reliability of K-Ar dating of feldspar mega- and xenocrystals was recently reconsidered by Rasskazov et al. (2000b). It was shown that some of the feldspars yielded K-Ar age in agreement with K-Ar matrix age, whereas some other did not. Another remarkable example is for dating of leucite-bearing volcanic rocks. It was observed through using the $^{40}Ar/^{39}Ar$ stepwise-heating technique (which will be discussed below) that leucites are usually characterised by the excess argon released at intermediate temperature steps (Boven et al., 1998; Rasskazov et al., 2000b; Villa, 1991). Karner et al. (2001) have found, however, leucites free of excess argon and suggested it as Quaternary age standard mineral. All these show that there are no strict criteria to reveal presence of extraneous argon by the K-Ar method. So, it remains the major limiting factor for dating young volcanic rocks.

3. $^{40}Ar/^{39}Ar$ Dating Method

The $^{40}Ar/^{39}Ar$ method differs from the conventional K-Ar method in that the determination of potassium is replaced by determinations of artificially created ^{39}Ar due to $^{39}K(n,p)^{39}Ar$ reaction with fast neutrons (Merrihue and Turner, 1966). For this purpose sample is irradiated in a nuclear reactor.

The quantity of the ^{39}Ar formed because of the neutron bombardment is proportional to ^{40}K with coefficient of proportionality referred to as J-factor: $^{40}K = {}^{39}Ar/J \times \lambda_{total}/\lambda_{Ar}$. The $^{40}Ar/^{39}Ar$ age equation is the following: $t = 1/\lambda_{total} \times \ln(J \times {}^{40}Ar_{rad}/{}^{39}Ar + 1)$.

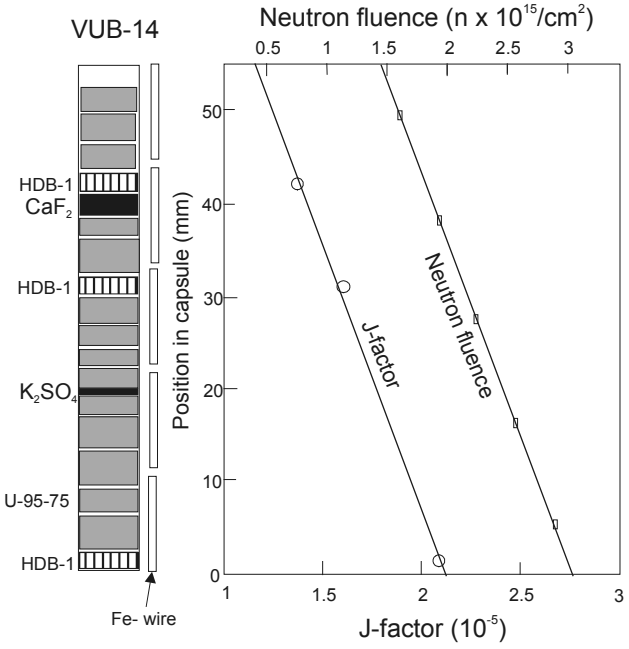

Fig. 4: J-factor and neutron fluence gradient monitoring by HDB-1 age standard and Fe-wire respectively. Position of the U-94-75 sample shown in Fig. 5 is also marked.

To determine the J-factor together with samples of unknown age a monitor, a standard sample with known K-Ar age, is irradiated (Fig. 4). Besides $^{39}K(n,p)^{39}Ar$ reaction McDougall and Harrison (1988) have listed fifteen more nuclear reactions on Ca, K, Ar and Cl among which five ($^{40}Ca(n,n\alpha)^{36}Ar$, $^{42}Ca(n,\alpha)^{39}Ar$, $^{40}K(n,p)^{40}Ar$, $^{35}Cl(n,\gamma)^{36}Cl \rightarrow \beta^- \rightarrow {}^{36}Ar$, $^{37}Cl(n,\gamma)^{38}Cl \rightarrow \beta^- \rightarrow {}^{38}Ar$) are considered as important for purpose of the $^{40}Ar/^{39}Ar$ dating. Amount of these argon isotopes depends upon neutron fluence and hence would vary from reactor to reactor and from irradiation to irradiation. To account for interfering argon isotopes produced from Ca and K pure CaF_2 and K_2SO_4 salts are irradiated together with samples (Fig. 4). Correction of chlorigenic ^{36}Ar is done from measuring ^{38}Ar. So, a routine procedure for determination of $^{40}Ar_{rad}/^{39}Ar$ ratio requires measurement of five argon isotopes.

$$\frac{{}^{40}Ar_{rad}}{{}^{39}Ar} = \frac{\frac{{}^{40}Ar}{{}^{39}Ar} - 295.5 \times \left(\frac{{}^{36}Ar}{{}^{39}Ar} - \frac{{}^{37}Ar}{{}^{39}Ar} \times \left(\frac{{}^{36}Ar}{{}^{37}Ar}\right)_{CaF_2} - \frac{{}^{38}Ar}{{}^{39}Ar} \times \frac{{}^{36}Ar}{{}^{38}Ar}\right) - \left(\frac{{}^{40}Ar}{{}^{39}Ar}\right)_{K_2SO_4}}{1 - \frac{{}^{37}Ar}{{}^{39}Ar} \times \left(\frac{{}^{39}Ar}{{}^{37}Ar}\right)_{CaF_2}}$$

$^{40}Ar/^{39}Ar$ age calculation includes two major sources of errors: 1) instrumental errors on peak measurements and blank corrections, and 2) errors on J-factor and Ca, K, Cl correction factors. For MAP-216 mass-spectrometer the instrumental precision for ^{40}Ar and for ^{36}Ar peaks is generally better than $\pm$ 0.1 % and $\pm$ 1 % respectively. At laboratory of argon isotope geochemistry of Vrije Universiteit Brussel (VUB) during routine

measurements peak/blank ratio of ca 10 and 100 were observed for induction and double-vacuum resistance extraction oven systems respectively. Prior each stepwise-heating oven extraction experiment three to five system blanks are routinely measured at high, intermediate and low temperatures to account for the blank correction (e.g. Ivanov et al., 2000). Laser extraction system is characterised by few orders lower blank value in comparison to double-vacuum resistance oven.

To calculate the J-factor for each sample a common procedure is to include into a vial, at least, three age monitors at the bottom, middle part and top of the vial (see Fig. 4). Control of the neutron fluence gradient can be done also by ^{54}Mn activity measurements of a Fe-wire placed along the irradiated vial (Boven et al., 2001). Errors, which results from K-Ar calibration of the age monitors, Ca and K correction factors, are systematic and often are not considered for the final error propagation in the $^{40}Ar/^{39}Ar$ age. However, for calibration of other methods these errors have to be accounted for. Complete algorithm of numerical error analysis has been recently developed for such purposes (Scaillet, 2000). Special studies on intercalibration of the age monitors were performed to reduce that source of systematic errors in $^{40}Ar/^{39}Ar$ dating (e.g. Baksi et al., 1996; Renne et al., 1998). "Artificial age" monitors are expected to be created in coming future (Beauvais et al., 1999).

$^{40}Ar/^{39}Ar$ method is advantageous in comparison to K-Ar method despite the more complex procedure. First of all, a $^{40}Ar/^{39}Ar$ ratio is measured from the same aliquot of a sample. It reduces problem of inhomogeneous distribution of potassium, which is one of the sources of uncertainty in K-Ar method. Secondly, there is no need for absolute concentrations of argon isotopes to be determined. It increases precision of the method and allows samples with small amount of argon be analysed. Third, as only isotopic ratios have to be known, it can be measured in fractions of gas released from a sample at different temperatures. These advantages have lead to development of stepwise-heating and laser fusion techniques.

In the stepwise-heating technique a sample is incrementally heated from a low temperature until its final melting. Each portion of gas released at several temperature steps is analysed separately. If studied sample had experienced neither argon losses nor redistribution of the potassium prior the analysis (in other words, the K-Ar isotopic system remained close) all temperature steps will yield equal $^{40}Ar_{rad}/^{39}Ar$ ratio and hence the same age. Measured $^{36}Ar/^{40}Ar$ and $^{39}Ar/^{40}Ar$ ratios are also analysed in the inverse isochron coordinates. In a case of good linear relation between measured values for different temperature steps the x-intercept yields $^{39}Ar/^{40}Ar_{rad}$ ratio (and hence the age), while the y-intercept provides an information on the $^{40}Ar/^{36}Ar$ ratio of initially trapped argon (upon a convention for a "good" isochron mean standard weighted deviation (MSWD) should be, at least, less than 2.5). If the requirements of closed isotopic system are fulfilled total fusion and isochron $^{40}Ar/^{39}Ar$ ages must be equal within analytical precision, and the $^{40}Ar/^{36}Ar_{ini}$ ratio, estimated from the inverse isochron diagram, must be 295.5. Such an example is represented in the Fig. 5 for an anothoclase megacrystal from the Udokan area (Rasskazov et al., 2000b).

The age obtained from the inverse isochron diagram is independent from the assumption of the atmospheric initially trapped argon isotopic composition. Theoretical consideration of the inverse isochron diagram has shown, however, that some care should be taken while interpreting scattered points regressing to a non-atmospheric y-intercept. Such data can be merely an analytical artefact due to wrong correction to the extraction system blank of non-atmospheric isotopic composition (Roddick, 1978). If a dated sample experienced $^{40}Ar_{rad}$ losses in geological history and/or ^{39}Ar losses in the nuclear reactor due to recoil effect the measured $^{36}Ar/^{40}Ar$ and $^{39}Ar/^{40}Ar$ values will yield curvilinear trend (Brandt et al., 2003). Hence, the inverse isochron approach gives additional control on both the analytical conditions and natural isotopic disturbances.

In the $^{40}Ar/^{39}Ar$ laser fusion technique gas is released by melting of the sample with a continuous wave laser (e.g. Kelley, 1995). For young ages a sample is usually fused out in one step. Total fusion $^{40}Ar/^{39}Ar$ age

does not differ in principle from the K-Ar age. The advantage of the $^{40}Ar/^{39}Ar$ total fusion technique is in that the very small samples, such as single crystals or individual grains of ultimately fresh rock matrixes, can be analysed and in that K and Ar will be determined in the same sample (Ebinger et al., 1993; Rasskazov et al., 2000a; Singer et al., 1998; Wilch et al., 1999 etc.). $^{40}Ar/^{39}Ar$ stepwise-heating by the laser system is also possible (Renne et al., 1997; Feng and Vasconcelos, 2001).

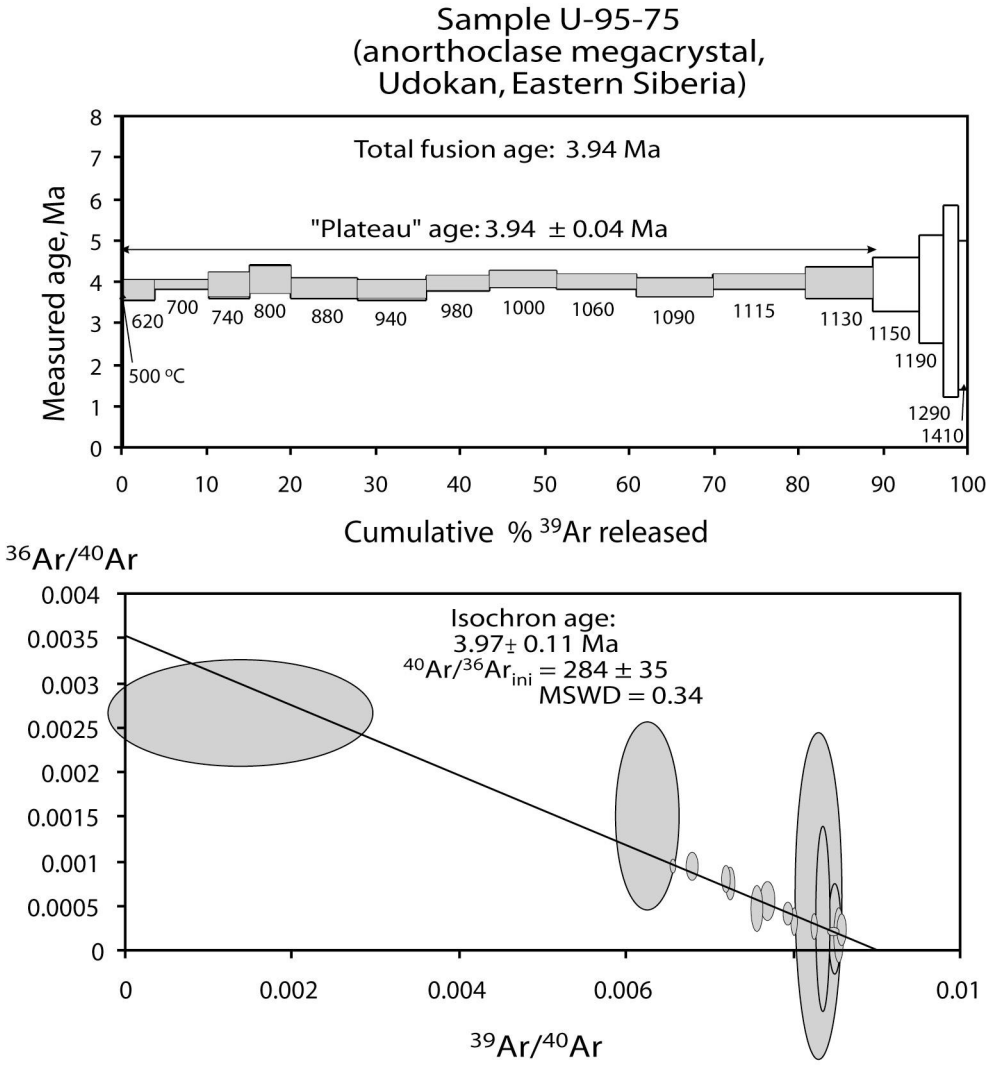

Fig. 5: Common presentation of the $^{40}Ar/^{39}Ar$ stepwise-heating data as the argon release and inverse isochron diagrams. Argon was extracted with induction oven system and analysed with MAP-216 mass-spectrometer at Vrije Universiteit Brussel, Belgium (measurements of A.V. Ivanov). Errors include statistical errors of the peak measurements and blank corrections as well as errors of J-factor and K and Ca correction factors. "Plateau" age is taken as the crystallisation age of the U-94-75 megacrystal. Note that this age agrees with the total fusion and isochron ages. Geological interpretation see in Rasskazov et al. (2000b).

An example of coupled application of $^{40}Ar/^{39}Ar$ stepwise-heating and laser total fusion techniques is shown in Fig. 6 for an alkali olivine basalt matrix from the Rungwe province (Eastern Africa). Laser fusion yielded three age clusters of 0.46±0.14, 1.28±0.17 and 3.5±0.8 Ma for different grains. Stepwise-heating of the same matrix sample revealed "plateau" age of 0.6±0.1 at relatively low temperature steps and elevated ages at intermediate and high temperature steps. These show that there are at least two different mineral phases with excess argon. The total fusion age of 0.8 Ma, which is an equivalent of conventional K-Ar age, is apparently high in comparison to the "plateau" age. The true crystallisation age is represented by younger

cluster of the $^{40}Ar/^{39}Ar$ laser total fusion ages with the mean of 0.46±0.14 (Fig. 6). This age confirms previous information that the most recent volcanic activity in the Rungwe province started at 0.6 Ma (Ebinger et al., 1993).

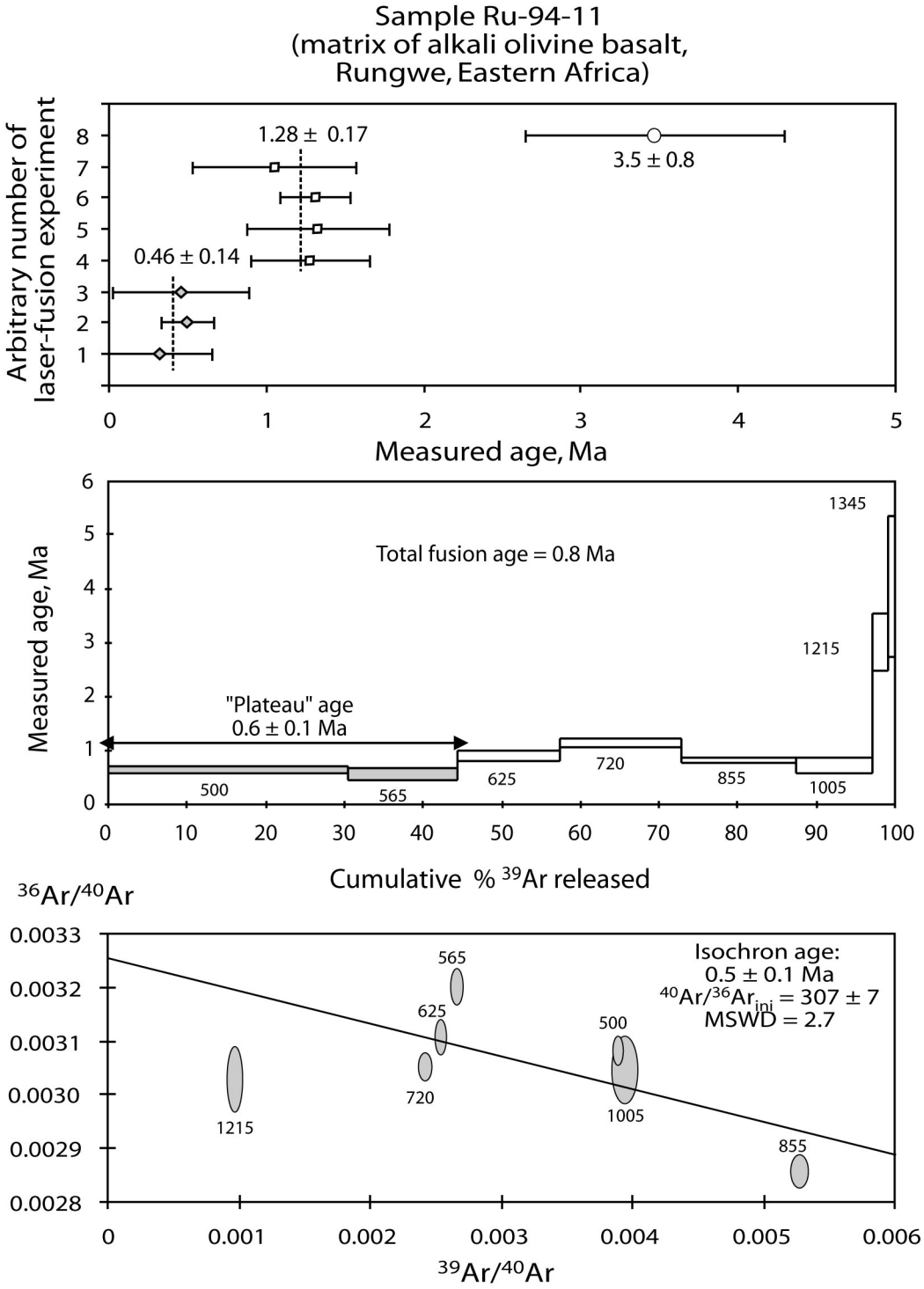

Fig. 6: An example of coupled application of the stepwise-heating and laser fusion $^{40}Ar/^{39}Ar$ techniques. Argon was extracted with double-vacuum resistance extraction system at Vrije Universiteit Brussel, Belgium (measurements by A.V. Ivanov) and continuous wave laser system at Menlo Park, USGS (measurements by A.A. Boven). Errors include statistical errors of the peak measurements and blank corrections as well as errors of J-factor and K and Ca correction factors. In both laboratories measurements were done with MAP-216 mass-spectrometer. Geological description and location of the sample see in Ivanov et al. (1998).

The $^{40}Ar/^{39}Ar$ was also used for dating authigenic (Kapusta et al., 1997 etc.) and weathering profile (Feng and Vasconcelos, 2001 etc.) minerals such as clays and cryptomelane respectively. Due to ^{39}Ar recoil losses from clay-structure minerals because of irradiation, dating of authigenic minerals by the $^{40}Ar/^{39}Ar$ method is unwarranted. Laser fusion and laser stepwise-heating $^{40}Ar/^{39}Ar$ dating of cryptomelane from eastern Australia weathering crust yielded geologically meaningful ages (Feng and Vasconcelos, 2001).

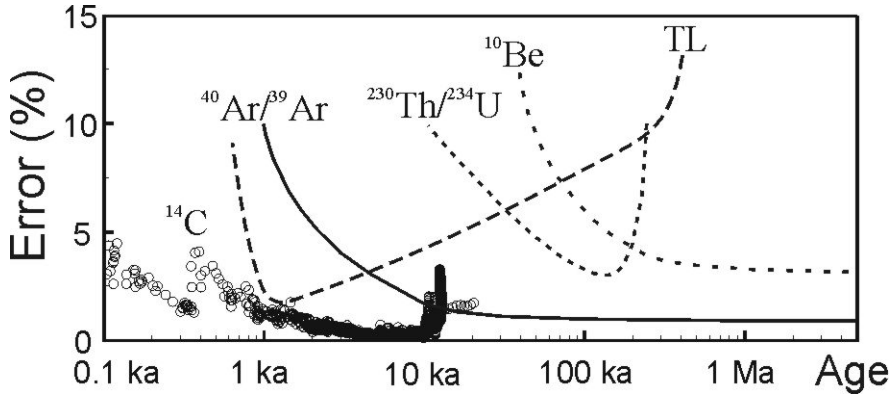

Fig. 7: Comparison of precision achievable by various geochronological methods. Errors for ^{14}C represent uncertainity of ^{14}C calibration (Stuiver et al., 1998b). Errors for TL, $^{230}Th/^{234}U$, ^{10}Be and $^{40}Ar/^{39}Ar$ should be viewed as the limits of the methods (Geyh and Schleicher, 1990).

4. Discussion and Conclusions

Inequality of the initially trapped argon isotopic composition in minerals of volcanic origin to the atmospheric $^{40}Ar/^{36}Ar$ ratio of 295.5 remains the main problem for dating the Quaternary deposits and is practically unresolvable for K-Ar chronology. In the $^{40}Ar/^{39}Ar$ method the initially-trapped isotopic composition of the argon is revealed through stepwise-heating experiment combined with inverse-isochron approach. Additionally, the $^{40}Ar/^{39}Ar$ laser-fusion technique provides an excellent possibility for finding and dating ultimately fresh mineral fractions, which are free of non-atmospheric argon contamination. Besides the volcanic rocks the $^{40}Ar/^{39}Ar$ dating is suitable for dating cryptomelane-bearing weathering crusts. The $^{40}Ar/^{39}Ar$ dating method is, at present, the most precise and accurate geochronological tool for a range from *ca.* 10 ka up to several Ma (Fig. 7). Hence, the $^{40}Ar/^{39}Ar$ method may provide a reference time-scale for calibration of other methods such as TL, $^{230}Th/^{234}U$, ^{10}Be etc., commonly used for dating of the Quaternary sediments. Decay constants of the calibrated radioisotope systems can be adjusted to ^{40}K decay constants. For instance, similar approach is used for some long-lived decay radioisotope systems with U-Pb system as a reference scale (e.g. Begemann et al., 2001).

5. Acknowledgements

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