OFFPRINT

A/

ACTA
VULCANOLOGICA

THE K/AR DATING METHOD: PRINCIPLE, ANALYTICAL TECHNIQUES, AND APPLICATION TO HOLOCENE VOLCANIC ERUPTIONS IN SOUTHERN ITALY

Pierre-Yves Gillot[*,1] · Anthony Hildenbrand[1] · Jean-Claude Lefèvre[1]
Claude Albore-Livadie[2]

1. *Géochronologie Multi-Techniques, UMR 8148 IDES Université Paris-Sud, Bâtiment 504, F 91405 Orsay, France*
2. *Centre Jean Bérard, Via F. Crispi 86, I 80121 Napoli, Italy;*
Centre Camille Jullian, GDR 1122 CNRS, F 13100 Aix-en-Provence, France

Abstract

The K/Ar geochronometer is appropriate to date geological materials ranging in age from several thousands to several billions of years. Two complementary techniques of the K/Ar method are classically used: 1. the K/Ar conventional technique, in which potassium and argon are measured separately from a homogeneous preparation of the sample, and 2. the $^{40}Ar/^{39}Ar$ technique, which consists in the combined measurement of radiogenic argon ($^{40}Ar^{\star}$), and argon produced from potassium ($^{39}Ar_K$) during irradiation of the sample in a fast neutron nuclear reactor. We here review the principle, the analytical procedures, the advantages and the limitations of the two techniques. More specifically, we focuss on the unspiked K/Ar Casignol-Gillot technique, which allows to detect tiny amounts of radiogenic argon (as low as 0.1%) and is thus especially suitable to date very recent volcanic products, even basic in composition. Applications of this technique to young volcanic eruptions in southern Italy are presented, including the Avelino sub-historical explosive event from Monte Somma-Vesuvius. Sanidines separated from a grey pumice layer sampled independently in the sites of Nola and Cava Novasche yield a mean age of 3840 ± 180 yr, in perfect agreeement with calibrated AMS radiocarbon ages achieved recently on charcoal fragments (Albore-Livadie *et alii* 1998). This demonstrates the effectiveness of the K/Ar method to date accurately volcanic episodes up to historical periods, with absolute uncertainties presently reaching a few centuries.

Keywords: K/Ar dating, Analytical techniques, Vesuvius, Avellino eruption

1. Introduction

Based on the natural decay of potassium to argon, the K/Ar geochronometer is suitable to date geological materials ranging in age from several thousands to several billions of years. It has been used to calibrate most of the Phanerozoical period of the Geological time-scale (Odin 1990, 1994) making the link between the various radio-isotopic dating methods commonly used in Earth Sciences (Fig. 1).

Two complementary techniques of the K/Ar method are classically used: 1. the K/Ar conventional technique, in which Potassium and Argon are measured separately from a homogeneous preparation of the sample, and 2. the $^{40}Ar/^{39}Ar$ technique, which consists in the combined measurement of radiogenic argon ($^{40}Ar^{\star}$), and argon produced from potassium ($^{39}Ar_K$) during irradiation of the sample in a fast neutron nuclear reactor. Since the early sixties, both techniques have been greatly improved and applied to a variety of geological topics. We here present the principle of the K/Ar method, the analytical techniques and main procedures, and their application to the dating of olocene volcanic eruptions in Southern Italy.

2. The K/Ar Geochronometer

2.1. *Principle*

Potassium occurs in the nature as three isotopes, ^{39}K, ^{40}K and ^{41}K, with relative abundances of 93.258%, 0.0117% and 6.730%, respectively (Table 1). Potassium 40 is radioactive and decays to produce ^{40}Ar at a half-life period of 1.25×10^9 years. Consequently, ^{40}K is presently about 1/12 of what it was at the time of Earth formation 4.5 Ga ago.

Isotope	Atomic abundance (%)
^{39}K	93.2581 ± 0.0029
^{40}K	0.01167 ± 0.00004
^{41}K	6.7302 ± 0.0029

Table 1. Isotopic abundances of potassium in nature (after Garner *et alii* 1975).

Argon belongs to the noble gas family constrained in the last column of the Mendeleiev classification. All the elements from this family are characterized by a saturated external electronic configuration and are chemically inactive. While other noble gases are rather scarce in nature, Argon accounts for about 1% (in volume) of the present composition of the Earth atmosphere. Specifically, the heaviest argon isotope ^{40}Ar is by far the most abundant (Table 2).

This abnormal distribution led Von Weizsäcker 1937 to propose that ^{40}Ar was produced by a nuclear reaction involving electron capture by the ^{40}K nucleus, accompagnied by a correlative emission of a gamma ray. Based upon this scheme, Aldricht an Nier (1948) elabo-
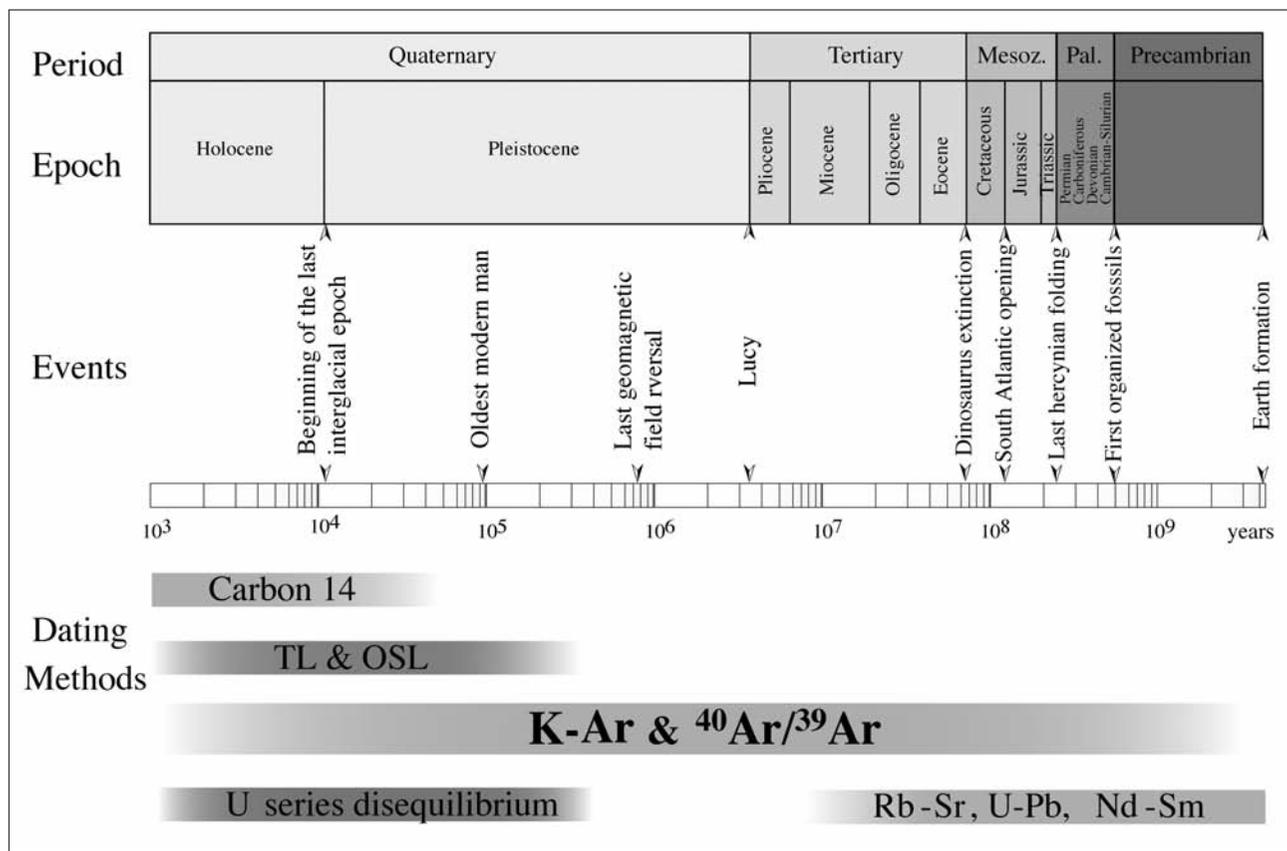
FIG. 1. Logarithmic scale of the geological times and range of application of the different radiometric methods.

rated the first principle of the K/Ar dating method. These authors shown that the decay of ^{40}K in fact produces both ^{40}Ar and ^{40}Ca, according to the scheme presented in Figure 2. The decay constants are $\lambda\beta = 4.962$ 10^{-10} yr^{-1} and $\lambda\varepsilon = 0.581$ 10^{-10} yr^{-1} for the ways producing ^{40}Ca and ^{40}Ar, respectively (Steiger and Jaeger 1977). In other terms, the decay of ten atoms of ^{40}K produces nine atoms of ^{40}Ca and one atom of ^{40}Ar.

Isotope	Abundance (atom%)
^{40}Ar	99.600
^{36}Ar	0.3364 ± 0.0006
^{38}Ar	0.0632 ± 0.0001

TABLE 2. Isotopic composition of atmospheric argon (after Nier 1950).

Theoretically, the measurement of ^{40}Ca thus should be more suitable for sake of dating. Practically, however, the scheme involving the decay of ^{40}K into ^{40}Ar is much more appropriate, due to the contrasting chemical behaviors of Potassium and Argon. During geological processes such as re-heating, the transformation of minerals is generally accompagned by a separation of phases causing the release of fluids, including Ar, towards the Earth surface and atmosphere, while Potassium will be integrated into a secondary solid mineral. Radiogenic argon (^{40}Ar*) will then be produced by the decay of ^{40}K in the new mineral. If the rock is not subjected to further transformation, the measurement of ^{40}K and ^{40}Ar* will allow to date the last thermic event.

The general equation age for radiometric dating is:

$$t = \left(\frac{1}{\lambda}\right)\ln\left(1 + \frac{D}{N}\right) \qquad (1)$$

where D is in the case of K/Ar the sum of radiogenic ^{40}Ca and ^{40}Ar, *i.e.* (^{40}Ca*+^{40}Ar*).

Calcium 40 is not directly measured, but it is deduced from the measurement of ^{40}Ar, provided that:

$$\frac{^{40}Ca^{*}}{\lambda\beta} = \frac{^{40}Ar^{*}}{\lambda\varepsilon}, \text{ which can be expressed as:}$$

$$^{40}Ca^{\star} = \frac{^{40}Ar^{\star}.\lambda\beta}{\lambda\varepsilon}$$

Equation (1) thus can be developed and simplified into:

$$t = \frac{1}{\lambda\beta+\lambda\varepsilon}\ln\left[\left(\frac{\lambda\beta+\lambda\varepsilon}{\lambda\varepsilon}\right).\frac{^{40}Ar^{*}}{^{40}K}+1\right]$$

The age of the mineral can thus be determined by measuring ^{40}Ar* and ^{40}K in laboratory.

2. 2. *Conventional K/Ar*

It is based on the independent measurement of potassium and argon from a homogeneous mineral preparation.

Potassium is generally measured through a chemical way. The radioactive isotope ^{40}K, indeed, presently accounts for 0.01167% of total Potassium in nature (TABLE

1). Measuring the K elementary composition of the rock or the mineral thus allows the present ^{40}K composition to be deduced per gram of sample. This value is reported in equation (1). The analytical precision in the determination of K in laboratory is thus crucial to get an accurate age, especially in the case of old samples (> 1 Ma) for which the radiogenic ^{40}Ar accumulated is sufficiently high to be measured accurately. Flamme spectrophotometry is the most commonly used technique to determine the K composition of natural samples. An aliquote of the mineral sample is attacked and dissolved by a mixture of acids, including fluorhydric acid (HF), to destruct the silicated structure of the mineral and release the various cations from the assemblage. The solution thus obtained is injected in the flamme of the spectrophotometer. The temperature of the flame is adjusted by an appropriate combination of carburant and comburant, so as to excite specifically the potassium element. The excitation is followed by a photonic emission, which is selected by a monochromator and amplified by a photo-multiplicator. The intensity measured is proportional to the K content of the solution, which is determined by comparison with standards of known composition. This technique is suitable to measure the whole range of K compositions in rocks and minerals, from less than 0.1% to up to 15%, with a relative uncertainty of 1% in all cases. The K elementary composition of natural samples can also be determined with other techniques such as X-ray fluorescence or solid-phase mass spectrometry using ^{41}K isotopic dilution. In the latter case, the analytical precision is better than 1%. Such a precision is, however, meaningfull if the mineral preparation is homogeneous enough at this order of magnitude.

Radiogenic ^{40}Ar produced by *in situ* decay of ^{40}K in the mineral is extracted by fusing the sample under high-vaccuum conditions. The fusion is generally achieved with a high-frequency inductive furnace. With such system, temperatures of about 2000 °C can be reached. Most of natural minerals fuse between 800 °C and 1200 °C, releasing several types of gas, mainly H_2O, CO_2, hydrocarbures, and relatively small amounts of Argon, which will be measured for dating. The gases extracted from the sample are purified by interacting with titane foams heated at about 800 °C. Active gases react with the Ti metal, while Argon, which is chemically inactive, remains free. Argon is then condensated on active charcoal cooled with liquid nitrogen. Other noble gas such as Helium, Neon and Krypton may also be present, but He is not condensated at the temperature of liquid nitrogen in such low-pressure conditions. Neon and Krypton, if present, have a very low concentration and they do not, anyway, influence the measurement within the mass-spectrometer due to their low mass.

Purified argon is then introduced in the mass spectrometer. The most widespread technique of measurement uses the isotopic dilution of Argon by adding pure ^{38}Ar as a tracer. The quantity of ^{38}Ar added to the sample is known from standards, the K content and the age

of which have been determined by inter-calibration between various laboratories. In the mass spectrometer, the ratio between the different Ar isotopes is determined. Since the amount of ^{38}Ar is known, the concentration of the other isotopes can be calculated.

This technique is suitable for old samples which have accumulated a significant amount of radiogenic Argon. Most of the Argon measured is radiogenic while the amount of contamination by atmospheric Argon is negligible. The first developments of K/Ar using this technique measured the total amount of Argon with a pressure gauge (McLeod type). For very old samples with high-K content, *e.g.*, biotites and muscovites from granitic rocks, the approximation was valid with a relative accuracy of a few percents.

2.2.1. Correction of the atmospheric Contamination

For younger samples, however, the amount of radiogenic Argon accumulated is significantly lower, especially if the mineral has a low-K concentration. In such a case, atmospheric contamination becomes preponderant. Atmospheric contamination corresponds to 1. atmospheric Argon trapped within the mineral during sub-aerial cristallization, 2. atmospheric argon eventually incorporated in the mineral during alteration processes, and 3. atmospheric Argon adsorbed either at the surface of the mineral during the preparation of the sample or on the different surfaces used in the analytical procedure (quartz and pyrex from the heating sector, titane sponge used for purification, …). Improvements in the determination of very young ages thus partly depend on our capacity to lower the base level of atmospheric contamination during the analytical procedure, which is a permanent preoccupation of the analyst. On the other hand, it is crucial to make the measurement on a fresh, carefully separated, mineral phase. Altered grains including golfes of corrosion are particularly unsuitable, since their high specific surface favors air adsorption and thus increase the amount of atmospheric contamination. Present relative abundances in the Earth atmosphere are ^{40}Ar/^{36}Ar= 296 and ^{40}Ar/
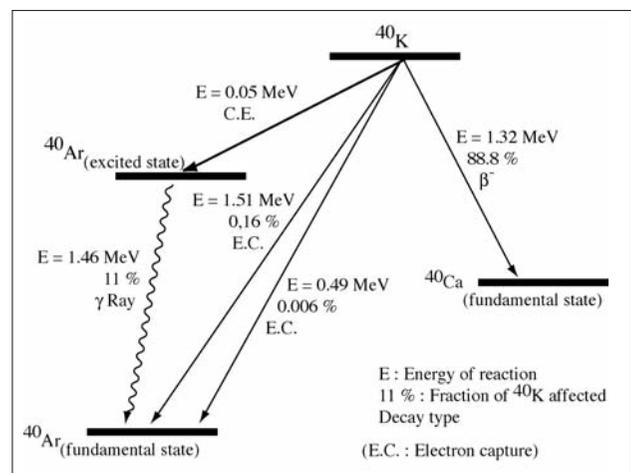

FIG. 2. Decay scheme of Potassium 40.

^{38}Ar = 1535 (Table 2). The measurement of ^{36}Ar and ^{38}Ar in laboratory thus can be used to estimate the level of ^{40}Ar corresponding to atmospheric contamination. Hence, the amount of radiogenic Argon (^{40}Ar*) can be determined by substracting the atmospheric contribution of ^{40}Ar from the total quantity of ^{40}Ar measured, since:

$$^{40}\text{Ar total} = {}^{40}\text{Ar radiogenic} +$$
$$^{40}\text{Ar from atmospheric contamination.}$$

Practically, this correction is based on the measurement of ^{36}Ar which is five times more abundant than ^{38}Ar, and hence is easier to determine accurately. Note that, during this procedure of correction, the analytical uncertainty on the measurement of ^{36}Ar is amplified by a factor 296, which we report on the determination of the amount of ^{40}Ar*.

2.2.2. Range of Applications and Limitations

The younger the sample is, the lower ^{40}Ar* accumulated is. Hence, the higher the uncertainty on the correction of atmospheric contamination will be. In contrast, older samples will be characterized by a higher content of radiogenic argon, and the uncertainty associated with the correction of atmospheric contamination will rapidly vanish and become negligible.

Taking into account the half-life period of decay of ^{40}K (T = 1.25 Ga), the K/Ar method is *a priori* more appropriate to date old geological systems. Old rocks, however, cannot be dated in all cases, since the chronometer is particularly sensitive, due to 1. the chemical reactivity of Potassium alkaline element and 2. the diffusive behavior of Argon during geological transformations such as compression (a few kbars) and re-heating (from 200 °C to 500 °C depending on the mineral).

The sensitive character of the geochronometer, however, explains why it has recorded geological events during most of the Earth history, up to historical periods. This is why the K/Ar dating method has been used to calibrate most of the geological timescale, especially for the phanerozoic (Fig. 1). Nevertheless, mineral transformations can in some cases affect the reliability of the K/Ar conventional technique.

2.2.2.1. Argon Loss

If the transformation occurs at high temperature and/or high pressure (re-heating, metamorphism), these conditions will favor Argon diffusion. In such cases, Argon will be partially removed from the mineral system, and the apparent age measured will be younger than the true cristallization age. We will see later that Argon potentially remaining in the system (if Argon from the heated rock has not been completely diffused) can also pose severe problems to get a meaningfull age of formation.

2.2.2.2. Potassium Lixiviation

If the transformation occurs at the surface, under ambient temperature, potassium will be removed by lixivi-

ation, while radiogenic argon already accumulated will stay in the dominent part of secondary phase of neoformation: this is the case of argilitization, low-temperature chloritization, and all other phenomenas associated with weathering. The K/Ar age measured will be apparently too old.

2.2.2.3. Excess Argon

While the two uppermost cases of remobilization of potassium and argon always can be identified from carefull petrographical and mineralogical analyses, the case of Argon inheritance is harder to characterize. Such an inheritance corresponds to either:

- the integration in the rock of mineral phases cristallized earlier. These include co-genetic phenocrysts or cumulates formed in the magma chamber at relatively high equilibrium pressures. In such cristallizing conditions, radiogenic ^{40}Ar previously produced by the decay of ^{40}K in the deep Earth is incorporated in the mineral phase, which will disturb the chronometer. Xenoliths from the surrounding host rocks may also be mechanically incorporated in the arising magma toward the surface and bring inherited Argon. Such xenoliths, however, will be recognizable from carefull petrographic examination and removed from carefull sample preparation. The better way to avoid excess Argon in volcanic rocks thus requires the selection and the extraction of a pure mineral phase representative of magma cooling at the surface, *i.e.*, typically groundmass or feldspar microlites in basalts, glass, alkali feldspars or biotites in differentiated rocks;

- imperfect resetting of the chronometer during the latest transformation at high temperature (re-heating, metamorphism), which corresponds to an incomplete extraction of ^{40}Ar from the system. Conventionnal K/Ar dating will yield an age intermediate between the age of formation of the rock and the age of the crisis. In this case, ^{40}Ar/^{39}Ar dating with a step-heating procedure will be the only way to determine the age of the crisis and the age of formation of the rock.

2.3. *The technique of Analysis ^{40}Ar/^{39}Ar*

With this technique, a part of the potassium from the sample is transformed into argon by neutron activation in a nuclear reactor. The dominant isotope ^{39}K is essentially transformed into ^{39}Ar, which will be analyzed along with the other argon isotopes, including radiogenic ^{40}Ar, from the same aliquote. The technique of measurement ^{40}Ar/^{39}Ar, which is now extensively used in geochronology, has been described in the early sixties by Sigugeirsson 1962, Naughton 1963, Merrihue 1965 and Mitchell 1968. These autors precised the effects of neutronic irradiation and optimized the conditions of the analytical procedure. Harisson and McDougall 1989 reviewed the conditions and the domains of application of the technique.

The transformation of ^{39}K into ^{39}Ar involves a neutron-proton reaction:

$$^{39}\text{K}_{19} + \text{neutron} \longrightarrow {}^{39}\text{Ar}_{18} + \text{proton.}$$
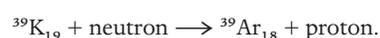
The energy of the neutron flux and the period of irradiation are adapted to form, according to the age and the mineralogical properties of the sample, a quantity of ^{39}Ar which will be as close as possible to the quantity of radiogenic ^{40}Ar, in order to optimize the conditions of measurement over the mass spectrum. Artificial ^{39}Ar produced by sample irradiation is radioactive with a half-life period of 265 years. Variations in its concentration at the timescale of the measurement are thus negligible.

To determine the efficiency of the neutron activation, dependent of the flux in the reactor, geological standards are used as fluence monitors. The age and the K-concentration of these standards have been previously determined by conventionnal techniques, mainly K/Ar. Before irradiation, the reference standards are distributed at different heights in the tube to be irradiated, along with the geological samples to date.

After irradiation, the standards are analyzed, allowing the efficiency of the neutron activation at successive points of the tube to be deduced. With this procedure, the vertical heterogeneity of the neutron flux is taken into account. A law of interpolation is then applied, which allows to constrain precisely the effects of irradation for each of the samples to date. The ratio ^{40}Ar/^{39}Ar measured on the sample is directly compared with the ratio measured on the standard, which directly provides the age:

$t_i = 1/\lambda \ln (1 + \{(^{40}Ar^\star/^{39}Ar)_i / (^{40}Ar^\star/^{39}Ar)_s\}(e^{\lambda ts} - 1)$
where λ is the sum of the decay constants of ^{40}K,
it is the age of the sample to date and ts the age of the standard, $(^{40}Ar^\star/^{39}Ar)_i$ is the ratio between radiogenic ^{40}Ar and ^{39}Ar determined for the sample to date, and $(^{40}Ar^\star/^{39}Ar)_s$ the ratio measured for the standard.

In this technical approach of the K/Ar dating method, the principle remains the same than for conventional K/Ar, which means that ^{36}Ar must be measured to make a correction of atmospheric contamination and thus determine the amount of radiogenic argon (^{40}Ar*).

2.3.1. Advantages of the ^{40}Ar/^{39}Ar technique

The ^{40}Ar/^{39}Ar technique offers several advantages compared to the conventional K/Ar dating technique, which result from the facts that:
- the totality of the analytical procedure is based on the measurement of isotopic ratios. It is thus no more necessary to know the weight of sample from which Argon is extracted;
- the respective abundances between the father (^{40}K deduced from ^{39}K, *i.e.* from measured ^{39}Ar) and the daughter (^{40}Ar*) are determined on the same aliquote of sample.
This allows:
1. to date samples, even in very low quantity, independently from problems of heterogeneity. For instance, an age can be determined on isolated grains from a rock or on a single mineral mono-grain. ^{40}Ar/

^{39}Ar analyses can even be realized on single spots of a mineral using laser ablation (*e.g.* Kelley *et alii* 1994);
2. to determine ages without need to extract the totality of Argon from the mineral, which allows to perform incremental degassing with a step-heating procedure.

2.3.1.1. ANALYSES ON SEPARATED GRAINS

While the K-Ar conventionnal technique requires a large and homogeneous mineral preparation to make independent determinations of K and Ar on distinct aliquotes, ^{40}Ar/^{39}Ar technique is applicable to single grains, each of which can be analyzed independently. Such a possibility is particularly appropriate to date heterogeneous deposits including minerals of various provenance, *e.g.* volcanic tephras. For such systems, a statistical analysis can be applied to distinguish xenolitic inherited grains from juvenile magmatic grains. It is even possible to use a laser to volatilize a micro quantity in a spot of a mineral ($< 30\ \mu$m in size), provided that Argon released is abundant enough to be analyzed. Such a peculiar procedure is thus essentially applicable to old samples.

2.3.1.2. DEGASING WITH A STEP-HEATING PROCEDURE

Since the age of the mineral is deduced directly from the ratio 40/39, it is not needed to achieve total fusion of a known quantity of sample. It is possible to extract argon by diffusion and to measure the ratio 40/39, *i.e.*, to determine an apparent age, at successive steps of heating. The apparent ages thus obtained can be drawn in a diagram as a function of the quantity of ^{39}Argon released, which depends directly from the temperature applied to the sample and the duration of the heating step. Once the sample is fused, all Argon has been released, which correspond to 100 percent of ^{39}Ar formed in the potassic site. Of course, the age obtained subsequent to total fusion of the sample is similar to the age determined by conventional K/Ar. The spectrum obtained by ^{40}Ar/^{39}Ar with a the step-heating procedure, however, is suitable to analyze the distribution of the different potassium sites in the mineral, to test its heterogeneity, and to establish if it was subjected to a complex geological history.

In the case of a pure mineral phase, the spectrum will be generally regular, indicating that the ratio ^{40}Ar/^{39}Ar is conserved during the successive heating increments. The successive steps will form a plateau (FIG. 3a), and a «plateau age» will thus be determined. However, as shown in Figure 3b, it is possible to observe two distinct plateaux, at low and high temperature, respectively. Such a kind of diagram indicates a re-opening of the chronometer associated with Argon released during a thermic or tectonic crisis. With the K/Ar conventional technique, dating such a rock would have yielded an apparent age comprised between the true age of formation of the rock, and the age of the thermic event. With a differential thermic analysis such as ^{40}Ar/^{39}Ar with a step-heating procedure, also termed «thermochronology», the thermic history of the sam-
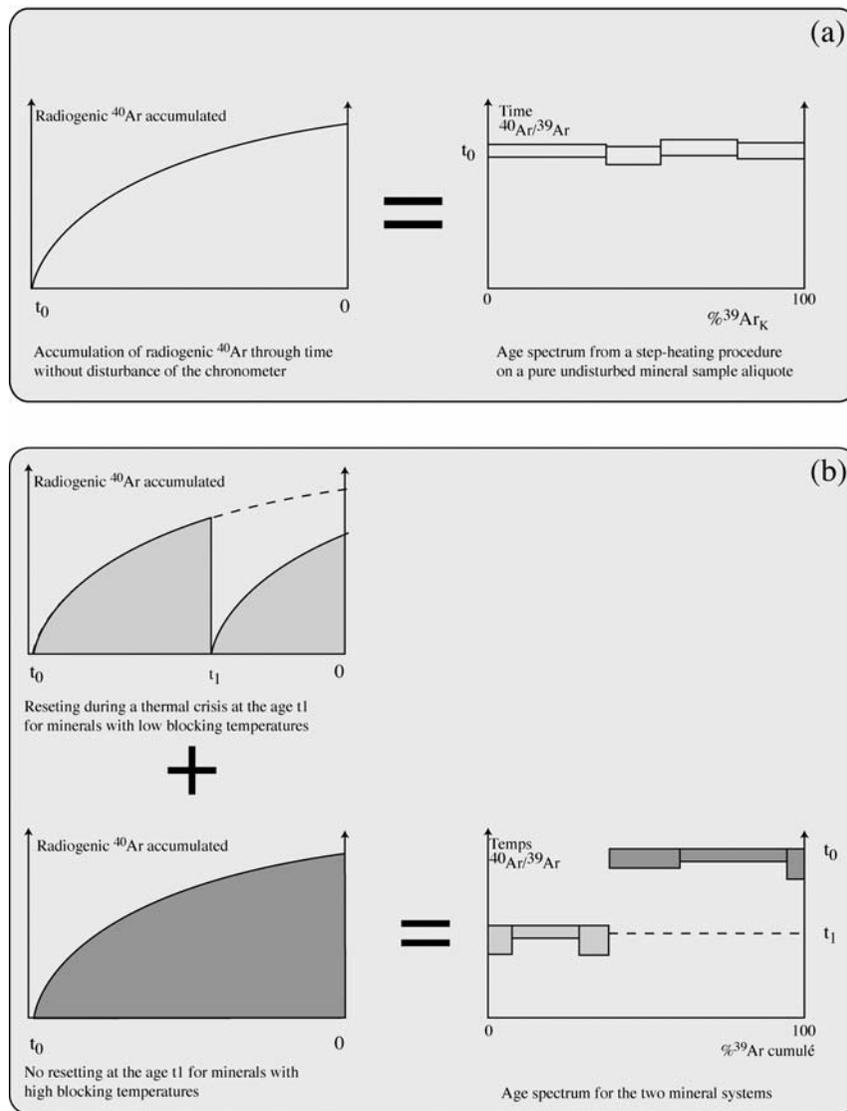
Fɪɢ. 3. a) Degasing spectrum for a pure mineral phase.
b) Degasing spectrum subsequent to partial re-opening of the chronometer.

ple can be deduced. The apparent ages obtained at high temperatures will constrain the age of mineral formation. If a plateau exists at low temperatures, the age of the thermic crisis will be possible to determine, especially if analyses are made on different mineral phases with various characteristics of Argon retentivity with respect to temperature.

This approach is powerfull if applied to geological samples sufficiently old to have been subjected to such thermic or tectonic crises. In the case of young rocks concerning historical or pre-historical periods, ^{40}Ar/^{39}Ar with a step-heating procedure is, however, also suitable, since partial degasing can be realized without affecting the age deduced from the following steps, despite a possible release of radiogenic Argon during the first steps of heating. The advantage is to eliminate the dominant part of atmospheric contamination at low temperatures, and hence to increase the amount of radiogenic argon released at higher temperatures. Argon signals released at high temperatures will be, however, very low, requiring high-sensitivity collector systems such as electron multipliers, which are now currently used in modern mass-spectrometry.

2.3.2. Limitations

Irradiation of the samples in a fast neutron nuclear reactor involves several nuclear reactions which produce a number of radioactive elements other than ^{39}Ar. For instance, ^{40}Ar is produced from ^{40}K at a rate which is not a simple function of the initial proportion between ^{40}K and ^{39}K in the sample, since the two elements do not have exactly the same physical properties. A factor of correction is thus determined by measuring the ratio ^{40}Ar/^{39}Ar from a pure potassic salt, generally K_2SO_4 or KF, irradiated in the same conditions as the samples to date. Similarly, the artificial production of ^{36}Ar, ^{37}Ar, ^{38}Ar, and ^{39}Ar, mainly from Calcium and Chlorine, need to be accounted for. Figure 4 shows the mass spectrum of Argon isotopes extracted from an irradiated miner-
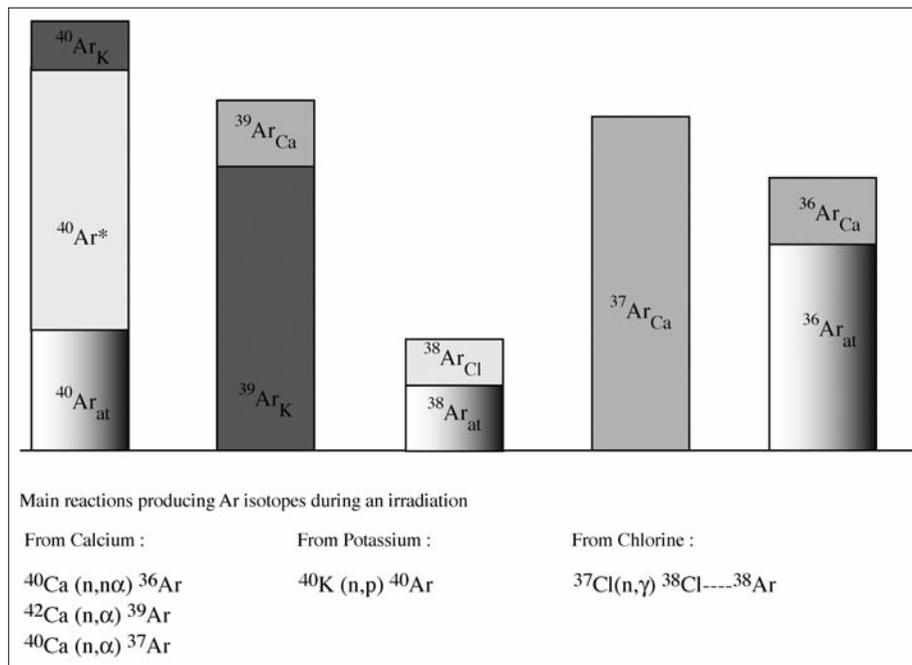
Fig. 4. Different reactions and argon isotopes produced during fast neutron irradiation of a sample.

al, precising the origin of the different components: radiogenic, atmospheric, or resulting from the activation of Potassium, Calcium, and Chlorine. The amounts of ^{36}Ar and ^{39}Ar produced by the neutron activation of Calcium are deduced from the measurement of ^{37}Ar, which also results from a neutron alpha nuclear reaction but is exclusively produced from Calcium. Again, the factors of corrections are deduced from the measurement of ^{37}Ar extracted from a pure salt of Calcum (CaF2) irradiated in the same conditions as the samples. The term of uncertainty associated with this correction becomes preponderant for young Ca-rich and K-poor minerals. Such samples, indeed, have a very low $^{40}Ar^{\star}$ yield, and the ^{36}Ar measurement, used for estimate and correction of atmospheric contamination must be corrected itself of the ^{36}Ar produced from calcium by neutron activation. The later amount is deduced from the ^{37}Ar measurement, but it is critic for calcic rocks and minerals, when ^{36}Ar produced by irradiation is some orders of magnitude larger than atmospheric ^{36}Ar from atmospheric contamination. Dating of low-K young volcanic rocks (< 1 Ma) such as tholeiitic basalts from the oceanic sea-floor or rift zones with the $^{40}Ar/^{39}Ar$ technique is thus delicate and in most cases inaccurate.

The $^{40}Ar/^{39}Ar$ technique requires the use of geological standards, the ^{40}K and ^{40}Ar composition of which have been generally calibrated with the conventional K/Ar technique. Their age is known with a relative uncertainty of 2% from inter-laboratories comparisons. Though modern mass spectrometers allow to reach analytical uncertainties as low as a few permill, the total uncertainty on the age thus should rigorously integrate the uncertainty on the age of the standards used as fluence monitors, and hence shoud not be lower than 1-2% at the 1σ level (Coulié *et alii* 2003).

3. The K/Ar Dating Method applied to Holocene volcanic Eruptions in Southern Italy

Despite the rather long radioactive period of ^{40}K, and the presence of ^{40}Ar in the atmosphere making necessary an accurate correction of atmospheric contamination, the K/Ar dating method has been extended to late Quaternary volcanic eruptions (Gillot *et alii* 1982, Cassignol and Gillot 1982, Gillot and Cornette 1986). More recently, the range of application of $^{40}Ar/^{39}Ar$ has been extended to the historical period (Renne *et alii* 1997, Lanphere *et alii* 2006).

3.1. *K-Ar dating up to kyrs with the Cassignol technique*

We developed in the eighties a new analytical approach of conventional K/Ar to detect minute amounts of radiogenic argon and thus to date very recent events down to the historical times (Gillot *et alii* 1982, Cassignol and Gillot 1982, Gillot and Cornette 1986, Quidelleur *et alii* 2001). Dalrymple 1969 already checked the inferior limit of K-Ar method by analyzing historical lava flows, showing evidence for the absence of radiogenic argon inheritance. Dalrymple 1969 also dated alkali feldspars from lava flows erupted during the ultimate 30,000 years, and obtained ages in fairly good agreement with available radiocarbon ages.

The detection of the smallest proportion of radiogenic ^{40}Ar requires the most accurate correction of atmospheric contamination, which is possible by reducing the sources of analytical errors and especially the factors induced by spiking (in the conventional technique) or isotopic contagion linked to neutron activation (in the case of argon-argon technique).
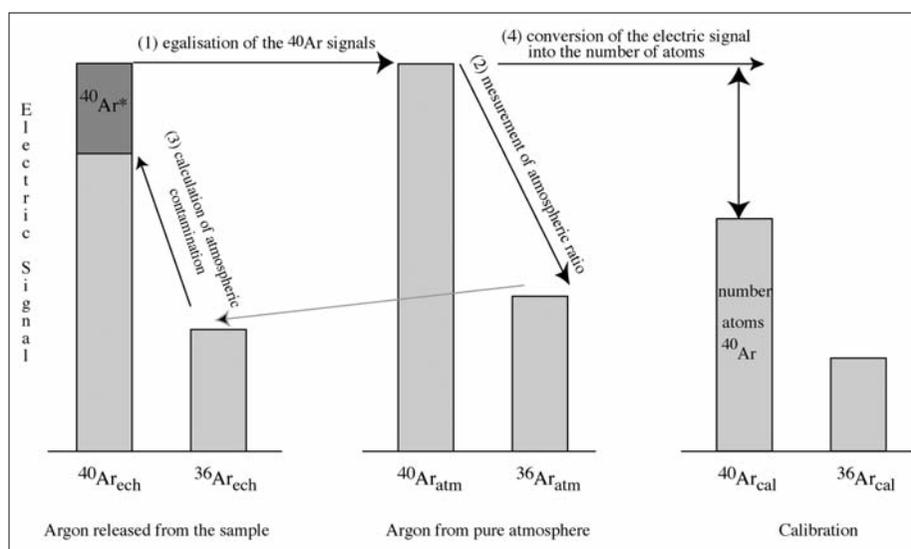
FIG. 5. Principle of atmospheric correction and signal calibration.

In a mineral sample of near-zero age, the amount of atmospheric argon, even if very small, corresponds to almost 100% of the total argon measured. Thus, K-Ar dating very young lavas implies to detect a tiny quantity of radiogenic ^{40}Ar diluted by the ^{40}Ar of the atmospheric contamination. Up to some tens of ka, the proportion of radiogenic argon in the total argon from the sample is lower than 10%, and it is lower than 1% for the last thousands of years. A peculiar analytical procedure is thus necessary to detect radiogenic ^{40}Ar accumulated in the sample within some centuries (Cassignol and Gillot 1982, Gillot and Cornette 1986, Gillot and Lefèvre 1994).

This is achieved by comparing the signal of argon extracted from an aliquote of the mineral sample to a signal of the same level measured from pure atmosphere under rigorously identical analytical conditions (FIG. 5). For an identical quantity of ^{40}Ar, the difference between the ^{36}Ar signals measured from the sample and from pure atmosphere respectively determines the proportion or radiogenic argon in the sample.

In the Cassignol technique for potassium-argon dating, the mass spectrometer is used to achieved absolute measurements of argon signals instead of the relative measurement of isotopic ratios as performed in the conventional K-Ar or in the argon-argon techniques.

With the unspiked 'Cassignol technique', the quantification of the ^{40}Ar and ^{36}Ar is obtained by comparing the signals from the sample to the one obtained from an accurately defined air volume sampled in the atmosphere of the laboratory. The whole argon measurement procedure thus corresponds to a double comparison with atmospheric argon:

1. The first one by introducing in the mass spectrometer atmospheric argon with a ^{40}Ar signal identical to the one of the sample. This allows to determine the amount of radiogenic ^{40}Ar (^{40}Ar*), reducing as far as possible the uncertainties linked to the mass spectrometer according to the 'double weighting' process;

2. The second one by using a known quantity of atmospheric argon, which allows the volumetric determination of the number of atoms of radiogenic ^{40}Ar extracted during fusion of the sample, independently from any mineral sample reference.

To achieve such a double comparison, the response of the mass spectrometer must be constant during the

Sample	K/Ar ages (a)	^{14}C / historic ages	References
Ischia, Arso flow	600 ± 500	1302.	Gillot *et alii* 1992
Ischia, Fondo d'Oglio	1300 ± 300	IIIe-VIe SC. AD	Gillot *et alii* 1982
Lipari Obsidian	1100 ± 700	V^e SC. AD	Gillot and Cornette 1986
Vulcano, Palizzi 1	2200 ± 600	IIIe-IVe SC. BC	Frazzetta *et alii* 1984
Vulcano, Palizzi 2	1600 ± 500	IIe SC. AD	Frazzetta *et alii* 1984
Astroni Crater	3700 ± 800	3700 ± 200	Cassignol and Gillot 1982
Tuffo Gialo Napolitano	14800 ± 800	11700 ± 250	Cassignol and Gillot 1982
Mt. Etna Biancavilla	15900 ± 900	14200 ± 300	Gillot *et alii* 1994
Vesuvius, Mt. Somma	20000 ± 1200	17000 ± 400	Gillot and Cornette 1986
Campanian Ignimbrite	35000 ± 1000	35000 ± 1000	Cassignol and Gillot 1982

TABLE 3. Comparison of published conventional K/Ar and radiocarbon ages on Holocene volcanic eruptions in Southern Italy.
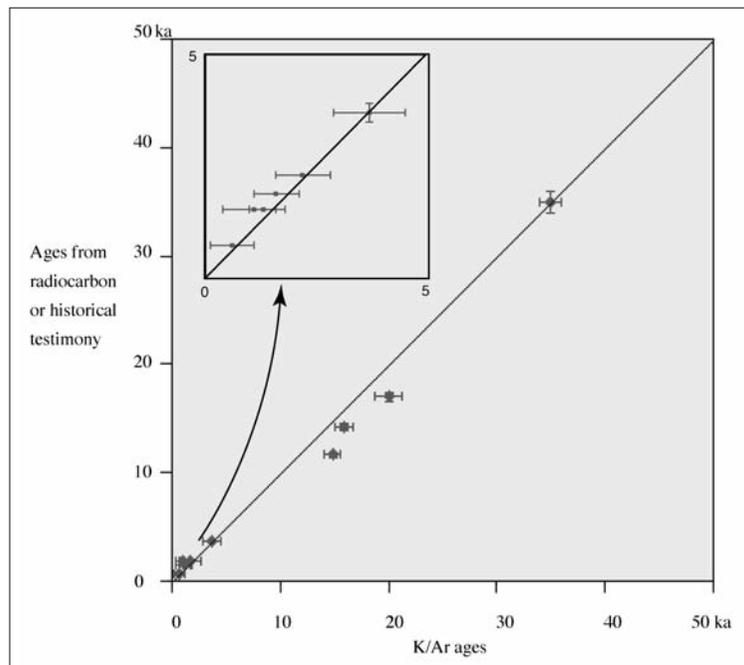
Fɪɢ. 6. Comparaison between K/Ar ages and available radiocarbon ages or historical reports (see Table 3).

whole analytical procedure. The total and permanent purification of argon during the whole measuring process, the simultaneous collection of argon ion beams, the isotopic measurement focused on the natural argon isotopes, without any artificial isotope added, and the steadiness of the ion source makes it possible. The stability of the analytical conditions is demonstrated by the high reproducibility of the signal measured for atmospheric argon from the calibrated volume, with a relative discrepancy of only a few permill over one week running.

The Cassignol-Gillot technique allows the detection of amounts of radiogenic argon as low as of 0.1%, which corresponds to some thousands of years for alkali basalts, and some centuries in the case of K-rich minerals such a sanidines.

Direct comparisons between K-Ar dating achieved with this technique and available radiocarbon ages or historical testimony are presented in Table 3 and reported in Figure 6. The deviation to the 45°-line evidences an under-estimation of radiocarbon ages up to 20% around 20,000 years. This likely corresponds to a significant excess of ^{14}C in atmosphere around the last glacial maximum. Re-calibration of the radiocarbon ages with dendro-chronology is now available for the period covering the last 11,900 years (Bard *et alii* 1998). As proposed by Gillot and Cornette 1986, the K/Ar ages presented in Figure 6 provide additional constraints beyond 12 ka, but they do not, however, constitute a continuous record. Direct comparison between K/Ar and radiocarbon, indeed, require for the same eruptive event volcanic products with mineral phases suitable for K/Ar dating in association with fossil carbon, which is scarce. The systematic comparison was realized by comparing radiocarbon and U-Th mass spectrometric measurements (Bard *et alii* 1990). Since coral growth involves CO_2 consumption and Ca and Th concretion from marine water, a given coral sample can be dated with both radiocarbon and U-Th methods. The comparison was completed between 30,000 years and present (Bard *et alii* 1998). It confirms an under-estimation of radiocarbon dating with a maximum departure around 20,000 years (> 10%) and a relative convergence over 35,000 years. All the points of our study lies on the curve of Bard *et alii* 1998 within the range of analytical errors.

3. 2. *Dating the Avellino Eruption with the unspiked K/Ar Cassignol-Gillot technique*

We here present new age determinations obtained with the conventional K/Ar unspiked Cassignol-Gillot technique on volcanic tephras from the Monte Somma-Vesuvius eruptive complex (Tᴀʙʟᴇ 4). Despite several radiocarbon studies Mt. Vesuvius successive tephra remain, indeed, poorly dated (for further references, see Albore-Livadie *et alii* 1998). Albore-Livadie *et alii* 1998 proposed new AMS ^{14}C dating of the Avelino eruption, the products of which recovered human sites from the Brass age several tens of kilometers ɴᴇ of the eruptive center. The calibrated ages obtained by these authors on charcoal fragments range between 1880 ʙᴄ and 1680 ʙᴄ, and thus have a mean value higher than previous radiocarbon determinations measured on paleosoils (*e.g.* Vogel *et alii* 1990). We here present new K/Ar ages on pumice samples from the Avelino eruption. The tephra were sampled in two distinct outcrops: one at the croce del Papa cross-road (Nola), which lies on the prehistoric village from the Brass age destructed by the eruption; the second in the Cava No-

Sample	Facies	Location	Phase	K%	$^{40}Ar^\star$ (%)	Age (a)	Unc. (a)
89AA	Grey pumice	Nola	sanidine	10.373	2.15	3900	190
					2.74	3800	150
					1.85	3720	210
89AC	Grey pumice	C. Novasche	sanidine	10.173	2.39	3810	170
					2.23	3970	190
					Mean	**3840**	**180**

TABLE 4. New age determinations with the unspiked K/Ar Cassignol-Gillot technique on sanidines from tephra related to the Avellino volcanic eruption at Somma-Vesuvius.

vasche quarry. These two sites are separated one from each other by several kilometers. The new K/Ar ages achieved on each of the two samples are fully compatible in the range of the analytical uncertainties (TABLE 4). They yield a mean value of 3840 ± 180 yr, which is in complete agreement with the value determined independently from AMS radiocarbon dating analyses (Albore-Livadie *et alii* 1998). It confirms the reliability of the K/Ar dating method down to the historical period, especially for potassic minerals, with a typical accuracy on the order of one century. That is, at the same level of atmospheric contamination, on the order of one thousand of years for a basaltic lava with a K-content of 1%, and on the order of 10,000 years for a 0.1% one. However, the pure selected mineral phases are generally less contaminated by atmosphere than the glassy groundmass of the lava flows.

4. CONCLUSIONS

We present here the improvements of potassium-argon dating over a 30 years period, for both K-Ar and Ar-Ar techniques. The limit of the method towards recent times reaches now an order of magnitude of about thousand years, the century in the most favourable cases. The range of application of the method extends largely over the one of radiocarbon and thermoluminescence dating, *i.e.*, from the last 40,000 years up to historical times: *e.g.* the dating of volcanic event in the last millenium (Quidelleur *et alii* 2001) or the one of the 79 AD eruption of Mount Vesuvius (Renne *et alii* 1997). We report here results obtained on potassic feldspars from the Pumices of the Avellino plinian eruption of Vesuvius. They are in good agreement with radiocarbon dating by Albore-Livadie *et alii* 1998 and show that K-Ar dating is now a usefull tool for archeometry and volcanic hazards estimate.

Only volcanic products are suitable for K-Ar dating within the last millenium: they are the only rocks with a rather instantaneous reseting, due to the eruptive process and rapid solidification of the lava, after degasing. These dating are hence particularly relevant for volcanological and archeological studies. We have shown how technical development including more and more sensitive detectors make it possible to progress towards historical times. This progress is not yet achieved: the detectability of radiogenic argon measurement in the minerals from historical lavas remains limited by the techniques and machine sensitivity: the limit of the potassium-argon chronometer has not yet been reached.

REFERENCES

Albore-Livadie C., Campajola L., D'Onofrio A., Monito R. K., Roca V., Romano M., Russo F. and Terrasi F. (1998). Evidence of the adverse impact of the «Avellino pumices» eruption of Somma-Vesuvius on old Bronze age sites in the Campanian region (Southern Italy). «Quaternaire», 9, 37-43.

Aldrich L. T., Nier A. O. (1948). Argon 40 in potassium minerals. «Phys. Rev.», 74, 876-877.

Bard E., Hamelin B., Fairbanks R. G., Zindler A., Mathieu G. and Arnold M. (1990). U/Th and C14 ages of corals from Barbados and their use for calibrating the C14 time scale beyond 9,000 years BP. «Nuclear Instruments and Methods in Physics», 52, 3-4, 461-468.

Bard E., Arnold M., Hamelin B., Tinera-Laborde N. and Cabioch G. (1998). Radiocarbon calibration by means of mass spectrometric Th230/U234 and C14 ages of corals: an updated data base including samples from Barbados, Mururoa and Tahiti. «Radiocarbon», 40, 3, 1085-1092.

Cassignol C., Gillot P.-Y. (1982). Range and effectiveness of unspiked potassium-argon dating: experimental groundwork and applications. In: G. S. Odin (ed.), Numerical Dating in Stratigraphy, Chichester, Willey, 159-179.

Coulié E., Quidelleur X., Gillot P.-Y., Courtillot V., Lefèvre J.-C. and Chiesa S. (2003). Comparative K-Ar and $^{40}Ar/^{39}Ar$ dating of Ethiopian and Yemenite Oligocene volcanism: implications for timing and duration of the Ethiopian traps. «Earth Planet. Sci. Lett.», 206, 477-492.

Dalrymple G. B. (1967). Potassium-argon ages of recent rhyolites of the Mono and Inyo craters, California. «Earth Planet. Sci. Lett.», 3, 289-298.

Dalrymple G. B., Lanphere M. A. (1969). Potassium-argon dating, principles, techniques and applications to geochronology, San Francisco, W. H. Freeman and C° ed., 258 pp.

Frazzetta G., Gillot P.-Y., La Volpe L., Sheridan M. F. (1984). Volcanic hazards at Fossa of Vulcano: data from the last 6,000 years. «Bull. Volcanol.», 47, 1, 105-124.

Garner E. L., Murphy T. J., Gramlich J. W., Paulsen P. J. and Barnes I. L. (1975). Absolute isotopic abundance ratios and the atomic weight of a reference sample of potassium. «J. Res. Natl. Bureau Stand.», 79A, 713-725.

Gillot P.-Y., Chiesa S., Pasquarè G., Vezzoli L. (1982). < 33,000 years K.Ar dating of the volcano-tectonic horst of the Isle of Ischia, Gulf of Naples. «Nature», 299, 242-244.

Gillot P.-Y., Cornette Y. (1986). The "Cassignol technique" for potassium-argon dating, precision and accuracy: examples from the Late Pleistocene to recent volcanics from Southern Italy. «Chem. Geol. (Isot. Geos. Sect.)», 59, 205-222.

Gillot P.-Y., Cornette Y., Max N. and Floris B. (1992). Presentation of two reference materials for argon dating (K.Ar and 40Ar/39Ar) of Pleistocene and Holocene rocks. «Geostandards Newletter», XVI, 1, 55-60.

Gillot P.-Y., Kieffer G. and Romano R. (1994). The evolution of mount Etna in the light of potassium-argon dating. «Acta Volcanologica», 5, 81-87.

Gillot P.-Y., Lefèvre J.-C. (1994). Datation potassium-argon de roches volcaniques du Pléistocène Supérieur et de l'Holocène: exemple de l'Ita-

lie du Sud; application à l'archéologie. «Bull. Soc. Préhist. Fr.», 91, 2, 145-148.

Harrisson T. M., McDougall I. (1988). Geochronology and thermochronology by the 40Ar/39Ar method, New York-Oxford, Oxford University Press-Clarendon Press, 212 pp.

Kelley S. P., Arnaud N. O. and Turner S. P. (1994). High spatial resolution Ar40/Ar39 investigations using an ultra-violet laser probe extraction technique. «Geochim. Cosmochim. Acta», 58, 16, 3519-3525.

Lanphere M., Champion D., Melluso L., Morra V., Perrotta A., Scarpati C., Tedesco D. and Calvert A. (2007). Ar-40-Ar-39 ages of the AD 79 eruption of Vesuvius, Italy. «Bull. Volcanol.», 63, 3, 259-263.

Merrihue C. and Turner G. (1966). Potassium argon dating by activation by fast neutrons. «J. Geophys. Res.», 71, 11, 2852-2857.

Mitchell J. G. (1968). The Ar40/Ar39 method for potassium-argon age determinations. «Geochim. Cosmochim. Acta», 32, 781-790.

Naughton J. J. (1963). Possible use of argon 39 in the potassium-argon method of age determination. «Nature», 197, 661-663.

Nier A. O. (1950). A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. «Phys. Rev.», 77, 6, 789-793.

Odin G. S. (1990). Echelle numérique des temps géologiques. «Geochronique, Soc. Geol. Fr.», 35, 12-21.

Odin G. S. (1994). Geological time scale. «C. R. Acad. Sci. Paris», s. II, 318, 1, part 2, 59-71.

Quidelleur X., Gillot P.-Y., Soler V. and Lefèvre J.-C. (2001). K/Ar dating extended into the last millennium: Application to the youngest effusive episode of the Teide volcano (Canary Islands, Spain). «Geophys. Res. Lett.», 28, 3067-3070.

Renne P. R., Sharp W. D., Deino A. L., Orsi G., Civetta L. (1997). 40Ar/39Ar dating into the historical realm: calibration against Pliny the Younger. «Science», 277, 1279-1280.

Roth E., Poty B. (1985). Méthodes de datation par les phénomènes nucléaires naturels, Masson («Application», coll. CEA), 631 pp.

Schaeffer A. O., Zähringer J. (1966). Potassium-argon dating, Berlin-Heidelberg-New York, Springer Verlag, 187 pp.

Sigurgeirson T. (1962). Dating recent basalt by the potassium-argon method, Rep. Phys. Lab. Univ. Iceland, 9 pp.

Steiger R. H., Jaeger E. (1977). Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. «Earth Planet. Sci. Lett.», 36, 359-362.

Vogel J. S., Cornell W., Nelson D. E. and Southon J. R. (1990). Vesuvius Avellino, one possible source of 17th century BC climatic disturbance. «Nature», 344, 534-537.

Von Weizsäcker C. F. (1937). Über die Muglochkeiteines dua Len ß-Zerfalls von Kalium. «Phys. Zeitschr.», 38, 623-624.

⋆

Manuscripts may be submitted to one of the Editors.

⋆

⋆

Front of cover: The fumarolic fields in the Western Crater of Turrialba Volcano (Costa Rica).
Photo taken in February 2008, by courtesy of Eliecer Duarte (ovsicori, Heredia, Costa Rica).

VOLCANOLOGY AND SURROUNDINGS: TECHNICAL AND SCIENTIFIC INTER-CHANGES BETWEEN VOLCANOLOGY AND OTHER DISCIPLINES

★

CONTENTS