



In situ determination of K–Ar ages from minerals and rocks using simultaneous laser-induced plasma spectroscopy and noble gas mass spectrometry



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ABSTRACT

Geochronology is one of the foundations of Earth Sciences and is evolving constantly towards higher reliability and usefulness. Currently, Ar–Ar and U–Pb dating are the geochronological techniques most used. However, the classical K–Ar technique can be modified to measure the age of single minerals or rock sections in situ. This new technique combines the use of laser-induced plasma spectroscopy for the determination of potassium, with noble gas mass spectrometry for the determination of argon, both extracted simultaneously by laser ablation. This work constitutes both a proof-of-concept and a test of this method on 13 samples (53 analyses), with ages in the range 950–70 Ma. Deviations from the conventional K–Ar age are lower than 5% for most samples. The method is characterized by easy analytical procedures and relatively low uncertainty with the equipment used. This method is excellent for exploratory chronology of the earth and extraterrestrial bodies owing to the simple sample preparation and low turnaround time for the analysis.

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1. Introduction

The K–Ar method—including the ^{39}Ar – ^{40}Ar technique—has been the most performed form of geochronology since its inception in the middle of the twentieth century. The success of the K–Ar method must be attributed to several reasons, among them: a) the ideal half-life of ^{40}K decay (about one quarter of the age of the earth); b) a simple procedure for extracting a noble gas from a solid (by heating); c) a relatively easy separation of noble gases from a gas mixture; and d) development of static vacuum mass spectrometry capable of providing very high sensitivity (Reynolds, 1956).

The practical realization of the K–Ar technique turned sixty in 2010 (Smits and Gentner, 1950). Its companion method, Ar–Ar, is more recent (Sigurgeirsson, 1962; Merrihue and Turner, 1966), but has been utilized extensively during the last two decades. The advantages of Ar–Ar over K–Ar are noteworthy: no measurement of K; age is calculated from isotopic ratios; very small sample size; single crystal dating, in situ dating on single crystals and rock sections; detection of geochronological sample disturbances; and derivation of cooling histories. Despite the power of the method it is not perfect, as it has four main drawbacks: generation of radioactive samples; redistribution of argon by recoil; limitations on the maximum sample size owing to the amount of permitted

radioactivities; and very long turnaround times. Radioactivity is unavoidable and forces users to make studies of the sample before sending it to the neutron reactor. Recoil artifacts are only significant for small grain sizes (e.g., clays), or in dating minerals with exsolutions. Maximum sample size is determined by a reactor's technical limitations, and the amount of radioactive material that can be safely handled. Turnaround times are inevitable owing to the need for careful sample preparation, delivery to the reactor, the irradiation schedule, storage for safe handling, and the return of samples to the laboratory. After all this delay, samples can be mounted on the extraction line. There are only a few Ar–Ar laboratories in the world which have a reactor to hand, and are able to deliver Ar–Ar results within a few months. In general, it is common to wait between six months and more than one year for results.

Technical progress in dating techniques from the last decade seems to have been dominated by two opposing trends: a) the dating of high precision and accuracy at the expense of a large analytical work and b) in situ dating using laser ablation for higher spatial resolution and analytical throughput. Although both trends are not mutually exclusive, they tend to diverge by analytical reasons. The information obtained by both trends is somewhat complementary; well-calibrated, high-precision dating can give the most accurate data for a problem, whereas in situ dating can give fast analysis and precise spatial information at the expense of poorer precision. Examples of the first trend are: the high precision and accuracy U–Pb ages of meteorites, to date the early history of the Solar System (e.g. Amelin et al., 2010; Bouvier et al., 2011); high-

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precision U–Pb ages of magmatic zircons (e.g., Mattinson, 2005; Schaltegger et al., 2008); Ar–Ar ages of micas and feldspars from volcanic rocks for the refinement of the stratigraphic scale (e.g. Singer et al., 2004; Rivera et al., 2011); and high-precision ages from the Cretaceous–Paleogene boundary (Renne et al., 2013). Examples of the second trend are U–Pb ages by laser ablation, coupled with ICP–MS instruments (e.g., Horn et al., 2000; Solari et al., 2009), and in situ Ar–Ar ages from single crystals (e.g., Hodges and Bowring, 1995; Cosca et al., 2011; Beltrando et al., 2013), for deciphering diffusion profiles (i.e., thermal histories). Both trends have room for creativity and improvement owing to the large demand of geochronological data in Earth Science (e.g., Solar System evolution, continental tectonic reconstruction, volcanic hazards, and climate change from past to present).

The purpose of this work is to introduce a new technique that must be included in the “in situ” group. The method can measure K–Ar ages on discrete parts of a K-bearing mineral under an ultra-high vacuum using laser ablation, such as the laser microprobe used for Ar–Ar dating. The main difference with respect to the Ar–Ar method is that samples are not irradiated at all, and K is measured by means of the light emitted by the plasma generated during laser ablation of the sample, using the methods of laser-induced breakdown spectroscopy (LIBS). This new technique was first proposed by the author (Solé, 2008, 2009), and developed in the following years, and is described here in detail. Comparable methods have been proposed recently for remote Mars exploration by four independent groups (Cho et al., 2012; Cohen et al., 2012; Devismes et al., 2012; Stipe et al., 2012; Cho et al., 2013; Cohen et al., 2013a,b; Devismes et al., 2013; Cohen et al., 2014). These methods differ from the method proposed here in the fact that concentrations of potassium, argon and ablated volume are needed. Our methodology obviates the knowledge of these absolute quantities, since only Ar and K in arbitrary units must be known for reference and from unknown samples, in order to compute the K–Ar age.

2. Theoretical background

The main idea behind this new method derives from the combination of two facts: a) the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio is the only quantity necessary to calculate a K–Ar age; and b) the laser ablation of a solid sample will preserve its $^{40}\text{Ar}^*/^{40}\text{K}$ ratio in the plasma if stoichiometric ablation is assured. The logical conclusion based on these two facts is that a K–Ar age can be obtained from a solid sample after the laser ablation of an unknown volume (i.e. mass), if we can measure the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio of the plasma. Moreover, absolute K and Ar amounts are not required; only the ratio is needed, so arranging the equations to eliminate concentrations can give a solution to the problem.

The new method is thus based on a simultaneous measurement of both K and Ar on a single small area of a sample, but using different techniques for the measurement of K and Ar. Potassium is measured using optical spectroscopy on the plasma itself, and argon is measured by means of noble gas mass spectrometry, after the released argon has been expanded and cleaned in the vacuum line. Therefore, the two quantities must be linked together using the same physical units (atoms, moles, etc.), or by using a conversion factor. The latter method is used here, as in the Ar–Ar geochronology. An added advantage of the method is the simultaneous detection of many elements of the sample in the plasma, by means of the same optical spectroscopy used to measure potassium (ideally the argon amount can be measured also by optical spectroscopy, but the amount of argon is very low, it maybe a future development).

2.1. K–Ar and Ar–Ar equations

The K–Ar age of a sample is calculated from the following equation:

$$t = \frac{1}{\lambda} \ln \left[\frac{^{40}\text{Ar}^*}{^{40}\text{K}} \left(\frac{\lambda}{\lambda_e} \right) + 1 \right] \quad (1)$$

where $^{40}\text{Ar}^*$ is the radiogenic argon [atoms], ^{40}K is the radioactive K [atoms], and λ and λ_e [a^{-1}] are the total decay and electron capture constants of ^{40}K , respectively (Schaeffer and Zahringer, 1966; Dalrymple and Lanphere, 1969).

Since λ and λ_e are constants, the age is directly related to the ratio $^{40}\text{Ar}^*/^{40}\text{K}$. The Ar–Ar method substitutes the last equation with the following:

$$t = \frac{1}{\lambda} \ln \left[J \frac{^{40}\text{Ar}^*}{^{39}\text{Ar}_K} + 1 \right] \quad (2)$$

The age is also related to the ratio $^{40}\text{Ar}^*/^{40}\text{K}$ (^{40}K is substituted by $^{39}\text{Ar}_K$; i.e. the ^{39}Ar generated from ^{39}K during irradiation in the nuclear reactor), but multiplied by the J parameter, which is calculated after the measurement of reference samples interspersed with the unknowns. The J for each irradiation (or parts therein) is given by:

$$J = \frac{e^{\lambda t_{\text{ref}}} - 1}{^{40}\text{Ar}^*/^{39}\text{Ar}_K} \quad (3)$$

where t_{ref} is the age of a reference sample (see McDougall and Harrison, 1999).

2.2. Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is a well-established method that has been known for a long time (Brecht and Cross, 1962), but it has received great attention in the last decade owing to the availability of high power lasers and spectroscopic instruments manufactured by reliable companies (Cremers and Radziemski, 2006; Miziolek et al., 2006; Singh and Thakur, 2007; Noll, 2012).

A laser incident on a solid sample can heat, melt, vaporize, atomize, excite or ionize the atoms on the surface. When laser irradiation is high enough, atomization, excitation and ionization is produced, and atomic (and molecular) emission lines can be observed in the plasma by using appropriate instruments. If the assumption is made that the plasma is under local thermodynamic equilibrium (this will be discussed later), then the intensity of the emission line of an atomic species is given by (modified from Tognoni et al., 2006):

$$I_{x,ij} = F(\Omega, n_s, M_{\text{ablat}}) C_x \frac{g_i A_{ij}}{U(T)} e^{-E_i/k_B T} \quad (4)$$

where $I_{x,ij}$ is the integrated intensity of the emission line from element x corresponding to the transition $i \rightarrow j$ [counts $\cdot \text{s}^{-1}$]; F is a function of the optical arrangement, light transmission, and wavelength sensitivity of spectrometer (i.e. a dimensionless instrumental correction factor, named Ω), electron number density (n_s) [cm^{-3}], and ablated mass (M_{ablat}) [g]; C_x is the concentration of the element x in the plasma (i.e., in the target, if stoichiometric ablation is assumed) [$\text{g} \cdot \text{g}^{-1}$]; g_i is the statistical weight of the quantum state i [dimensionless]; A_{ij} is the Einstein transition probability for $i \rightarrow j$ transition [s^{-1}]; $U(T)$ is the partition function, which is equal to the summation over all states $\sum g_n \exp(-E_n / k_B T)$ [dimensionless]; E_i is the energy of upper state i [J]; k_B is the Boltzmann constant [$\text{J} \cdot \text{K}^{-1}$]; and T is the temperature [K].

For a specific transition of a given element (i.e., a spectral line) g_i , A_{ij} and E_i are constants. If certain instrumental parameters, such as the optical arrangement (fiber, lens, spectrometer), laser type, laser energy, laser repetition rate, and focusing size are optimized and fixed, it can be assumed that, for a given mineral, similar plasma evolution will be obtained at each ablation. Thus, $F(\Omega, n_s)$ and T are approximately constants and the above Eq. (4) can be simplified to:

$$S_1 = F(\Omega, n_s) \frac{g_i A_{ij}}{U(T)} e^{-E_i/k_B T} \quad (5)$$

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