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Exploring the multicollection approach for the ⁴⁰Ar/³⁹Ar dating technique

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[1] We present an original analytical system for 40 Ar/ 39 Ar dating. It makes use of a 180° sector multicollection mass spectrometer equipped with five Faraday cups, which renders peak switching unnecessary during argon isotopic analyses. Compared to the single-collector approach commonly used for argon isotopic analyses, our system presents greater stability during data acquisition. Faraday cup efficiencies, which can be a limiting factor for the multicollection mass spectrometer, were highly reproducible. The analytical validity of the 40 Ar/ 39 Ar ages obtained using this new mass spectrometer has been preliminarily tested using geological standard minerals (MMhb-1, FCT-San, and HD-B1) commonly used as neutron fluence monitors. Independent plateau age determinations of Ethiopian samples duplicated over a 1-year interval demonstrated the reproducibility of the analyses. The results of these measurements highlight the good behavior of this new instrument for 40 Ar/ 39 Ar step heating dating. The age reproducibility of successive steps leads to analytical errors lower than 0.1% for well-behaved samples. This system, still in its initial stage of development, represents an alternative solution that is worth exploring in order to improve absolute dating by the 40 Ar/ 39 Ar technique.

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1. Introduction

[2] During the last decade, the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ technique has demonstrated its versatility and high precision for dating geological material, from the earliest continental formation to the historic period. Most of the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating laboratories rely on rather similar approaches using commercial grade high resolution mass spectrometer, with a sector magnet of 60° or 90°. In order to propose an alternative solution to make sure that no systematic errors, resulting from similar analytical procedures performed worldwide, limit the accuracy of the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ technique, we have developed a new instrument at the UPS-IPGP

Geochronology Laboratory of Orsay [Coulié, 2001; Lefèvre, 1992].

[3] Argon analyses for ⁴⁰Ar/³⁹Ar dating technique are usually performed using a single-collector mass spectrometer. With such instrument, the five isotopes of argon, from ⁴⁰Ar to ³⁶Ar, are measured successively by peak switching. This cycle is then repeated several times in order to monitor signal changes over time. During a single Ar analysis, which takes about 15 minutes, the isotopic composition of the analyzed gas is continuously evolving. This is attributed to both instrument surface desorption, usually referred to as the "memory effect", which influences small Ar signals, and





Figure 1. Schematic view of mass spectrometer cell, including the Nier-type source and the multicollector. Schematic argon beam trajectories are shown for Ar peaks from ⁴⁰Ar to ³⁶Ar.

signal implantation onto the surfaces of the source and collector, which influences large Ar signals. A zero-time extrapolation is needed to account for signal drift subsequent to gas admittance. In order to limit this effect, Stacey et al. [*Stacey et al.*, 1981] described a 60° sector multicollection system. It was equipped with five Faraday cups and used a relatively high accelerating potential of 2000 V. Although stable analytical conditions were obtained, short-term variations in the interchannel calibration factors prevented its use for 40 Ar/ 39 Ar dating.

[4] The new system for ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating, which we have developed, relies on an original 180° sector multiple collection instrument with five Faraday cups placed in the focal plane (Figure 1).

2. Description of the Instrument

[5] Efforts have been concentrated toward reaching very stable conditions. Memory effects and desorption have been limited by the mass spectrometer small volume, the use of carbon-free material (Monel, a Ni-Cu alloy), and the use of low acceleration potential in the ion source helped to reduce implantation. The 180° magnetic sector geometry mass spectrometer has a radius of 78 mm for ⁴⁰Ar beam and a cell width of 16 mm. The total volume of the mass spectrometer is only 200 ml, approximately one order of magnitude lower than mass spectrometers actually marketed.

[6] A magnetic field of 2930 Gauss (maximum value of 3610 Gauss), monitored by a Hall probe, was provided by a Drush electromagnet. Peaks were precisely positioned by field increments of 0.16 Gauss. A field stabilization better than 10^{-4} Gauss was obtained during a time length of several hours.

[7] A Nier-type source, similar to the one described by *Gillot and Cornette* [1986], was chosen for its simplicity and its volume of only 4 ml (Figure 2a). Moreover, a low emission filament current (with a total energy level of 0.1500 mA and 48 eV) limited the mass discrimination variations as a function of argon pressure and provided a great stability, and filament longevity (>10 years). Emission linearity was demonstrated for high signal values [*Gillot and Cornette*, 1986], and was further investigated for low signals in the present study. In order to limit the implantation of argon ions, an acceleration voltage of only 700 V was applied.

[8] The collector design consists of an assembly of five independent Faraday cups mounted in a silica block (Figure 2b). Due to a compact geometry design, theoretical cup emplacements within the focal plane are close to each other. The 10×16 mm block ensured an accurate cup positioning centered on each ion beam trajectory, as well as electrical isolation between cups. In order to limit secondary electron capture, the block was inclined at an angle



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Figure 2. (a) Source and (b) collector designs.

of 6.5°, which allowed a staircase cup arrangement (Figure 2b). Positioned 1 mm apart, cup dimensions were $1.1 \times 1 \times 8$ mm. They were each equipped with guard-rings and grounded shields. A grounded double-stage collector slit was used to strongly limit electrical charges due to collisions between the ion beam and the silica block.

[9] The argon ion beam was focused using two half-plates. The 180° flight tube geometry limits the angular divergence. For magnetic field and accelerating potential set at routine measurements values, the calculated ratio of the radius of masses 40 and 39, and of masses 40 and 36, was 1.0121 and 1.0542, respectively, which compare well with the respective theoretical values of 1.0127 and 1.0541. The beam width was calculated to be

 $0.45\,$ mm, and hence fully collected with collector slits of 0.8 mm.

[10] Multiple collection is performed using five Faraday cups fitted with their own pre-amplifiers and electrometers. Low cost JFA Electronique products specially designed for this system, with pre-amplifier resistances value of $10^9 \Omega$, were used for masses 38 and 37, and Keithley 642 electrometers, with a one order of magnitude lower detection level of 10^{-17} A, were used for masses 40, 39 and 36. For each channel, the analog signal was digitized using a National Instruments 32 bits A/N converter.

3. Performance of the Instrument

[11] Magnetic field scanning performed from m/e =35.5 to 40.5 shows that peak separation is satisfactory. The 2 mm of physical separation between peak centers in the collector corresponds to 10 Gauss. Figure 3 shows that, within uncertainty, each peak top is relatively flat, with intensity variations as low as 0.03 and 0.16% observed over the 1 Gauss field range for the respective ⁴⁰Ar and ³⁹Ar peak. Using 0.16 Gauss increments of magnetic field control, the simultaneous collection of the five peaks was rather straightforward (thick line in Figure 3). A mass spectrometer resolution of approximately 80 and 110 was estimated using the 5% and 50% peak amplitude convention respectively [Roboz, 1968]. This resolution is much lower than the 90° or 60° geometry mass spectrometer generally used. Because isobaric hydrocarbon interferences have been avoided by using C-free material for the entire MS (source, cell and collector), it was sufficient for the Ar isotopic analyses which require 1 a.m.u. difference [McDougall and Harrison, 1999]. Tailing effects were easily determined by the simultaneous collection of adjacent masses. The mass spectrometer was routinely quantified by measurements of air aliquots with 40 signals ranging from 10 to 0.1×10^{-11} A. In the present configuration, a mean abundance sensitivity of -4×10^{-4} was measured for each channel. This value was probably due to the collection of secondary electrons extracted from the collector exit slit. It can be noted that the relatively large effect of the ³⁷Ar beam on the ³⁶Ar Faraday cup, which would be due to an irradiated Ca-rich sample, represents the major limitation of this instrument in the present configuration.

[12] Good linearity of each channel was mandatory for obtaining constant ratios within the dynamic





Magnetic field voltage command (mV)

Figure 3. Masses 40 to 36 peak profiles from a gas mixture of several irradiated samples acquired simultaneously over an 8.3 Gauss range. The inset shows the ⁴⁰Ar/³⁹Ar ratio standard deviation (1 σ) calculated within the 1 Gauss magnetic field interval where peaks were simultaneously collected (delimited by gray areas). Thick line: selected operating field.

range of signals to be measured. Multiple tests showed that linearity was improved when the source current was kept at a relatively low value (i.e., 2.15 A [*Coulié*, 2001]). Although this approach limits sensitivity, it was the preferred setup for the operation of the mass spectrometer.

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[13] The signal stability during measurement (Figure 4) shows the 500 data acquisitions for 40 Ar and 39 Ar, and the ratio stability during the 300 seconds, twice the time of a typical run. After equilibrium was achieved following gas introduction (which takes approximately 20 seconds), signal drift as low as 0.018% and 0.011% were observed for the 40 Ar and 39 Ar peaks, respectively. Therefore the 40 Ar/ 39 Ar ratio stability was approximately 0.015%. The consequence of such stability is to obviate long extrapolation to inlet time.

[14] On the basis of the interlaboratory geological standard GL-O, with the ${}^{40}\text{Ar}^*$ concentration of

 6.679×10^{14} at/g of ${}^{40}\text{Ar}^*$ (i.e., 1.109×10^{-9} moles ${}^{40}\text{Ar}^*/\text{g}$ [*Odin et al.*, 1982]), the sensitivity of the ${}^{40}\text{Ar}$ cup gave a transfer function of 1.6 A/mol. The sensitivity of other detectors was derived by intercalibration, performed by field scanning the ${}^{40}\text{Ar}$ ion beam onto each cup. Response ratios, from ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ to ${}^{36}\text{Ar}/{}^{39}\text{Ar}$, have been found to be highly reproducible, with a 1σ standard deviation, calculated from ten successive independent determinations, lower than 0.08% for each ratio. Such very good behavior can be attributed to the stability of the analytical conditions.

[15] From ten independent measurements of air aliquots with typical signals of 40 Ar (i.e., 1.5 × 10^{-11} A), mass discrimination ranged from 0.9985 ± 0.0013 to 0.9989 ± 0.0017 (1 a.m.u.). A 1σ standard deviation better than 0.05% was obtained for this population. This spectrometer was especially tuned to reduce the pressure depen-





Figure 4. Simultaneous ⁴⁰Ar and ³⁹Ar signal evolution within one typical run of 500 data points. The inset shows the evolution of the ⁴⁰Ar/³⁹Ar ratio calculated from these measurements. Also given is the relative 1σ standard deviation, which highlights the stability of the measuring conditions.

dency of mass discrimination to as low as possible by using a suitable half-plate voltage, source magnets positions, and filament current values [*Coulié*, 2001].

4. Testing the Mass Spectrometer Linearity

[16] The linearity of response was tested in operating conditions, i.e., with a constant magnetic field, using successive decrements of total-fusion gas aliquots (S_o). Backgrounds levels were measured first prior to the admission of each sample, and successive decrements of 31.03% of the remaining total gas fraction were retained in the extraction line, pumping away the gas within the mass spectrometer. As shown in Figure 5, which represents the expected signal S_i, calculated for the *i*th decrement using S_i = S_o × 0.6897ⁱ, as a function of the measured signal S_m, the linearity is very good over the whole range of intensity of interest for our machine.

[17] In a second experiment, in order to test that duplicate ages could be obtained from the same sample measured at different pressures, we applied the same approach using the total gas released from a 30 Ma Ethiopian Traps K-feldspar sample [Coulié et al., 2003]. The apparent age spectrum calculated from each of the successive decrements is shown in Figure 6. It should be noted that, following the criteria commonly used [e.g., Lanphere and Dalrymple, 1978], a "plateau age" of 30.00 ± 0.02 Ma, i.e., with an uncertainty (weighted mean) lower than 0.07%, could be determined using all the different sized decrements. Note that the 1σ standard deviation calculated using all "steps" was only 0.81%. If the last two data were excluded, this was reduced to less than 0.15%. These tests demonstrated that measured apparent ages did not vary as a function of the argon pressure within the mass spectrometer. In other words, that mass discrimination, signal response and interchannel calibration changes are properly monitored over a large range of signal intensity.

[18] Thus, from the above experiments, a threshold value of about 0.2×10^{-11} A was applied for either ⁴⁰Ar or ³⁹Ar signal in order to prevent any departure from linearity affecting our measured isotopic signals. Lower sample signals are kept aside on a



Figure 5. Successive decrements of an initial gas sample for ⁴⁰Ar, ³⁹Ar, ³⁷Ar, and ³⁶Ar (see text for details). S_m , measured value (in 10^{-11} A); S_i , calculated value for the *i*th decrement (in 10^{-11} A). Black line is the best linear fit. R, Pearson's correlation coefficient.



Figure 6. Age spectrum obtained from nine decrements of a midtemperature step extracted from an Ethiopian Traps ignimbrite K-feldspar sample.

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chilled charcoal and mixed with the following step heating increment.

5. Blank Level

[19] Gas was extracted using either a 3000 W Radio-Frequency (RF) furnace for step-heating analyses, or using a 100 W Nd-YAG 1064 nm infrared laser for total fusion experiments. After heating gas was first purified by Ti foam heated to 700°C, followed by 15 minutes using an AP10GP SAES getter heated to 400°C. After extraction and purification of the gas, each section of the line, including the mass spectrometer, was equipped with one SAES Al-Zr getter in order to maintain the lowest possible blank and constant cleaning of the desorbed gas. Prior to gas admittance, baseline values are measured while MS remains under pumping using a charcoal trap. At full laser power laser fusion blanks were undetectable. As is generally recognized, the highest blank signals come from the RF furnace. A total ⁴⁰Ar line blank, including heating up to 1100° C, of 18×10^{-13} A (7.0 × 10¹¹ atoms of ⁴⁰Ar) was obtained. The ⁴⁰Ar/³⁶Ar and ⁴⁰Ar/³⁸Ar isotopic composition of blanks was routinely checked, and within uncertainties, did not deviate from atmospheric values. The ³⁹Ar and ³⁷Ar blanks were undetectable; hence no corrections for line blanks were applied.

6. ⁴⁰Ar/³⁹Ar Analyses of Dating Standards

[20] The analytical validity of the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages obtained using the new mass spectrometer presented here was tested with minerals commonly used as neutron fluence monitors. We selected samples MMhb-1 hornblende, FCT sanidine and HD-B1 biotite, which displayed a wide range of composition and ages. MMhb-1 hornblende was separated from a syenite from McClure Mountains of Colorado, USA [Alexander et al., 1978] with a recommended K/Ar age of 520.4 ± 1.7 Ma [Samson and Alexander, 1987]. FCT sanidine, a widely used neutron fluence monitor [e.g., Hurford and Hammerschmidt, 1985], was extracted from the Fish Canyon Tuff, San Juan Mountains, Colorado, USA. Because the age of this standard is still debated [e.g., Lanphere and Baadsgaard, 2000; Renne et al., 1998; Spell and McDougall, 2003], we have elected to use the earlier value of 27.8 Ma [Cebula et al., 1986] for this present study. HD-B1 is an Oligocene biotite separated from a granodiorite of the Bergell Massif, Southern Alps.

K/Ar and 40 Ar/ 39 Ar analyses attest to the homogeneity of this sample at the 40 mg level [*Fuhrmann et al.*, 1987]. By interlaboratory comparison, an age of 24.21 ± 0.32 Ma has been proposed for this standard [*Hess and Lippolt*, 1994].

[21] Approximately 187 and 125 mg of MMhb-1 and FCT-San were irradiated for 50 hours in the CLICIT position at the University of Oregon facility, while 128 mg of HD-B1 was irradiated for 25 hours. The canister was rotated halfway through the irradiation in order to limit the neutron flux heterogeneity within the canister. Four 10–15 mg aliquots of MMhb-1, FCT-San and HD-B1, bracketing the unknowns in order to measure the J factor, were distributed within a 6 cm high vacuum-sealed quartz tube. Interfering reactions from Ca and K were monitored using CaF₂ and K₂SO₄ pure salts.

[22] In the experiments described below, each age standard was used both as an unknown sample, and as a fluence monitor. The fluence monitors were fused in one single temperature step, while the unknown was step-heated.

[23] Using the K/Ar ages of, 520.4, 28.7 and 24.2 Ma, for MM-hb1, FCT-San and HD-B1, respectively, J factors of 1.218, 1.216 and 0.638×10^{-2} , respectively, were determined by second-order polynomial regressions of the data. Step-heating age spectra and associated isochrons are shown in Figure 7, and isotopic data are reported in Table 1.

[24] A well defined plateau age of 517.1 ± 1.0 Ma was obtained over 88% of the ³⁹Ar released for MMhb-1 hornblende (Figure 7). The 0.6% difference between the obtained total gas age (517.3 \pm 4.7 Ma) and the 520.4 Ma K/Ar reference age used to calculate the J factor of this sample, can be accounted for by the uncertainties of the polynomial interpolation between fluence monitors. In addition, the previously recognized heterogeneity of small aliquots of MMhb-1 could also be a determining factor [Baksi et al., 1996; Renne et al., 1998]. Ca/K ratios ranged from 3.98-4.32 for the 4 main steps (Table 1), slightly lower than the average value of 4.45 reported by Baksi et al. [Baksi et al., 1996]. As also noted by Harrison [1981], a lower Ca/K was observed for the first 40% of ³⁹Ar gas released. Such features could be caused by the inhomogeneity of this age standard.

[25] Seventeen heating steps were performed on FCT-San, ten of which gave a plateau age of 27.88 \pm 0.07 Ma for >85% of the ³⁹Ar released (Figure 7). This value is in perfect agreement with





Figure 7. Age spectra and inverse isochron plots of analyzed fluence monitor age standards. The arrows indicate the plateau age contribution. The calculations of ${}^{40}\text{Ar}*{}^{39}\text{Ar}_k$, ages, and uncertainties were performed following *McDougall and Harrison* [1999]. Note that J factor uncertainty (Table 1) has been propagated into the age uncertainty. The statistical method of *Mahon* [1996], derived from *York* [1969], was used for the isochron regression and mean squared weighted deviation (MSWD) goodness-of-fit parameter calculations. Corrections for interfering reactions were based on analyses of CaF₂ and K₂SO₄ pure salts, and those reported by *Renne et al.* [1998] for the CLICIT facility of the Oregon State University TRIGA reactor. Ages were calculated using the decay constants quoted by *Steiger and Jäger* [1977]. All errors were reported at the 1 σ level.

	Error	0.1791	0.0404	0.0424	0.0427	0.0452			0.1330	0.0096	0.0349	0.0130	0.0054	0.0025	0.0033	0.0040	0.0028	0.0024	0.0027	0.0038	0.0027	0.0054	0.0093	0.0098	0.1658		0.0012	0.0051	0.0024	0.0031	0.0056	0.0009	0.0007	0100.0	
	Ca/K	1.0290	3.9805	4.2352	4.2859	4.5215			-0.147	0.0450	0.0105	0.0359	0.0171	0.0094	0.0078	0.0024	0.0103	0.0106	0.0067	0.0153	0.0040	0.0115	0.0115	-0.020	-0.050		0.0000	0.0018	0.0068	0.0091	0.0168	0.0122	0.0146	00/10.0	
	Error	0.0051	0.0004	0.0002	0.0002	0.0519			0.0105	0.0006	0.0005	0.0006	0.0002	0.0002	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0013	0.0024		0.0001	0.0006	0.0001	0.0004	0.0003	0.0001	0.0002	0.0002	
	CI/K	-0.0029	0.0008	0.0008	0.0004	-0.1454		-0.0026	-0.0019	0.0001	-0.0010	-0.0003	0.0001	-0.0004	0.0002	-0.0001	0.0000	-0.0001	0.0000	0.0002	-0.0001	-0.0003	-0.0004	-0.0041		0.0001	-0.0003	0.0001	-0.0003	-0.0002	0.0000	0.0002	-0.000		
Total	Error, Ma	22.3	4.6	4.5	4.5 2.7	4.0 677.1			16.46	1.01	1.23	0.53	0.34	0.31	0.39	0.32	0.35	0.31	0.30	0.50	0.32	0.30	0.56	1.00	1.93		0.25	0.46	0.29	0.28	0.31	0.26	0.27	0.47	
	Anal. Error, Ma	21.8	0.7	0.6	0.6	0.9 677.1			16.46	0.97	1.20	0.46	0.19	0.14	0.27	0.16	0.22	0.13	0.13	0.41	0.16	0.10	0.49	0.96	1.91		0.05	0.39	0.16	0.14	0.19	0.09	0.13	0.12	
	Age, Ma	521.5	516.7	517.3	517.3	233.0 233.0			28.76	28.07	27.13	27.01	27.90	27.92	28.07	27.84	27.60	28.08	27.60	27.75	27.83	27.99	26.85	29.12	21.46		24.19	23.91	24.27	24.03	24.13	24.29	24.30	24.29	
	Error	± 0.00002 1.3274	0.0450	0.0389	0.0360	0.0540 35.063		± 0.00002	0.7625	0.0448	0.0554	0.0211	0.0090	0.0064	0.0125	0.0075	0.0101	0.0061	0.0060	0.0191	0.0074	0.0048	0.0227	0.0444	0.0883	± 0.00003	0.0048	0.0344	0.0138	0.0121	0.0166	0.0078	0.0110	CU10.0	
	${}^{40}\mathrm{Ar}^{*/39}\mathrm{Ar}$	J = 0.01218 27.516	27.226	27.264	27.264	27.401 11.318		J = 0.01216 1.3216	3 - 0.01210 1.3216 1.2895	1.2895	1.2459	1.2405	1.2818	1.2826	1.2897	1.2787	1.2679	1.2900	1.2680	1.2745	1.2785	1.2859	1.2331	1.3383	0.9839	I = 0.00638	2.1159	2.0913	2.1230	2.1017	2.1101	2.1245	2.1255	2.1242	
è	$^{40}_{ m Ar}$ *	<i>MMhb-1</i> , 72.8	98.8	98.9	99.5 200.7	98./ 9.8		FCT-San,	14.2	99.3	92.5	97.8	97.6	97.9	99.3	97.6	97.5	99.3	98.3	100.0	99.1	100.4	83.9	81.1	50.2	HD-B1.	89.0	91.9	94.2	90.2	87.4	95.3	95.3 07.6	92.0	
39 .	(10^{10} atoms)	0.0892	4.2625	2.6324	2.5393	0.0090			0.0666	0.8232	0.8287	1.1875	3.5302	3.7069	3.4230	4.2613	3.3575	4.8630	5.9789	5.2122	4.9621	4.4442	2.0589	0.5866	0.1576		9.0644	1.5696	2.5089	1.8566	2.3661	6.1112	3.8977	0177.0	
	$^{36}\mathrm{Ar}/^{39}\mathrm{Ar}$	0.03494	0.00182	0.00180	0.00120	0.35354			0.02689	0.00004	0.00034	0.00010	0.00011	0.00009	0.00003	0.00010	0.00011	0.00003	0.00007	0.00000	0.00004	-0.00002	0.00080	0.00105	0.00329		0.00088	0.00062	0.00044	0.00077	0.00103	0.00036	0.00036	60000.0	
	$^{37}\mathrm{Ar}/^{39}\mathrm{Ar}$	0.5092	1.9670	2.0927	2.1176	2.1351 1.2473			-0.0728	0.0223	0.0052	0.0178	0.0085	0.0047	0.0038	0.0012	0.0051	0.0052	0.0033	0.0076	0.0020	0.0057	0.0057	-0.0098	-0.0250		0.0000	0.0009	0.0034	0.0045	0.0083	0.0060	0.0072	cocn.n	
	$^{38}\mathrm{Ar}/^{39}\mathrm{Ar}$	0.0082	0.0149	0.0152	0.0137	-0.4462			0.0078	0.0052	0.0124	0.0083	0.0109	0.0125	0.0106	0.0128	0.0118	0.0121	0.0118	0.0121	0.0128	0.0118	0.0110	0.0108	-0.0023		0.0124	0.0110	0.0125	0.0112	0.0116	0.0120	0.0128	0.0112	at 1 a
	$^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$	37.776	27.511	27.527	27.348	27.712 115.65			9.2757	1.2989	1.3467	1.2680	1.3139	1.3102	1.2987	1.3096	1.3003	1.2993	1.2898	1.2745	1.2903	1.2805	1.4705	1.6499	1.9583		2.3778	2.2760	2.2528	2.3307	2.4137	2.2304	2.2311	1067.7	errors anoted
	Step	-	0	ς.	4 4	0 V	,	,	- 1	7	ς,	4	5	9	7	8	6	10	11	12	13	14	15	16	17		1	2	m	4	5	9	└ °	0	^a All







Figure 8. Duplicated age spectra of Ethiopian samples (see [*Coulié et al.*, 2003] for details). An: analytical uncertainty, including J factor uncertainty, calculated following *McDougall and Harrison* [1999]; Tot., total uncertainty. Same as An. with a 1% relative uncertainty on the age of the HD-B1 fluence monitor.

the total gas age of 27.8 ± 0.4 Ma, the latter being identical to the K/Ar reference value of 27.8 Ma [*Cebula et al.*, 1986] used for the J factor calculation. The inverse isochron plot displayed data points clustered near the radiogenic component, thereby poorly defining the 40 Ar/ 36 Ar ratio (Figure 7). The Ca/K ratio remains below 0.05 for all steps.

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[26] HD-B1 display well defined age plateau over the whole gas interval (Figure 7), with an age of 24.21 ± 0.13 Ma. The inverse isochron ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratio is atmospheric at the 2σ level.

[27] Finally, it is important to emphasize that in the three cases described above, all the total gas ages (Figure 7) are consistent, within uncertainty, with the reference age standard used for the J factor calculation. Similarly the inverse isochron, plateau and total gas ages were all in agreement.

7. Analyses of Ethiopian Samples

[28] Four replicated age spectra from Ethiopian K-feldspars are shown in Figure 8. Three of them, with ages clustering around 29.5 Ma, are from the main stage of volcanism of the Ethiopian traps

[Coulié et al., 2003]. One is from a rhyolitic episode, probably related to the initiation of opening of the Red Sea and Gulf of Aden. Replicates have been obtained using the same mineral preparation from independent irradiation runs performed at more than one-year interval. Hence they represent a test for the reproducibility of our measurements. As previously highlighted by *Coulié et al.* [2003], most ⁴⁰Ar/³⁹Ar plateau ages, calculated relative to HD-B1 standard at 24.2 Ma, are here in agreement at 1 sigma-level with K/Ar ages obtained from the same mineral preparations. All four duplicates shown in Figure 8 are internally consistent and agree within their analytical uncertainty level. The reproducibility between replicates, between 0.3 and 0.0%, demonstrated that steady results are obtained using our multicollection instrument.

8. Conclusions

^[29] The experiments performed here on standard minerals and Ethiopian samples highlighted the good behavior of this new multicollector mass spectrometer for step heating ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating.



The age reproducibility of successive steps was satisfactory and can lead to analytical errors lower than 0.1%. The total error of approximately 1% is dominated by errors in the J value determination and in the fluence monitors ages [*Renne et al.*, 1998].

[30] Future improvements of the mass spectrometer system presented here are already envisioned. A modification of the collectors will be performed in order to limit abundance sensitivity by placing grounded surfaces between each Faraday cup. In addition, if ongoing tests regarding the stability of the 2 mm large Sjuts channeltron electron multiplier are successful, five of these multipliers will be positioned together. With an expected gain improvement of 10^2-10^3 , this configuration will allow single grains to be measured.

[31] In its present configuration, the new multicollector mass spectrometer has enabled us to perform highly reproducible 40 Ar/ 39 Ar analyses. Compared to a single-collector mass spectrometer commonly used for argon isotopic analyses, our system presents much greater stability during data acquisition, which obviates long extrapolation to inlet time. This system, still in its initial stage of development, represents an alternative solution that is worth exploring in order to improve absolute dating by the 40 Ar/ 39 Ar technique.

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