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$^{40}Ar/^{39}Ar$ analyses on Quaternary K–Ar standard BB-24: Evaluations

Fei Wang [a,*], Ri-Xiang Zhu [a], Lie-Kun Yang [a], Huai-Yu He [a], Ching-Hua Lo [b]

[a] *PGL, State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China*
[b] *Department of Geosciences, National Taiwan University, Taipei, Taiwan*

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Abstract

Quaternary K–Ar standard BB-24 is evaluated by $^{40}Ar/^{39}Ar$ analyses. Total-fusion results show that BB-24 is poorly reproducible either as $^{40}Ar^{*}$ (radiogenic ^{40}Ar) or as $^{39}Ar_k$, at a sample size of 15–40 mg. Much lower ages produced by the purified aliquots of BB-24 show the excess $^{40}Ar^{*}$ sited in the olivine component within the standard. The step-heating experiment produces a different total gas age of 440 ± 21.2 ka and a plateau age of 424.4 ± 15.0 ka, indicating different components degassing at different temperatures. The first and last steps have elevated ages and distort the age spectrum. This is vital when total-fusion experiments are performed. Age spectra of purified aliquots produce concordant age spectra, implying mineral impurities or excess ^{40}Ar within the sample. As a conclusion, BB-24 is not a suitable neutron monitor in $^{40}Ar/^{39}Ar$ dating.

Keywords: BB-24; $^{40}Ar/^{39}Ar$ analyses; Evaluations

1. Introduction

The age standards in isotopic dating work, especially for $^{40}Ar/^{39}Ar$ measurements are crucial. Though the $^{40}Ar/^{39}Ar$ dating technique yields high-precision results, all ages are reported relative to that of the standard (monitor) irradiated along with the unknown samples. Most such standards were originally calibrated and timed using the K–Ar method, when the splits analysed were on the order of tens to hundreds of milligrams and the instrumental sensibility was by far lower then present. Some of these standards proved to be unsuitable when small amounts were used for $^{40}Ar/^{39}Ar$ dating.

BB-24 was recollected from the same outcrop as BB-6 at Datong, northern China. As a basaltic whole rock standard, BB-6 was prepared by the Abteilung für Isotoppengeologie of the Berne University, Switzerland, and was recommended by CCOP [1] and IGCP [2]. According to the first study [3], BB-6 is very reproducible at a sample size of ~1 g for ^{40}Ar and at 0.3 g for K. The examination of BB-6 was done by Fuhrmann et al. [4] employing the $^{40}Ar/^{39}Ar$ dating method, and the results clearly showed the presence of excess ^{40}Ar within the sample (probably within olivine). The $^{40}Ar/^{39}Ar$ analyses on BB-6 [4] also showed that the integrated $^{40}Ar/^{39}Ar$ age was older than the conventional K–Ar age given by Jäger et al. [3]. Fuhrmann et al. [4] hypothesized that there could be ^{39}Ar loss during the irradiation due to recoil, and recommended avoiding the use of BB-6 in $^{40}Ar/^{39}Ar$ dating.

BB-24 was derived from a new sampling at the same site as BB-6 [2,5], and prepared by Chen et al. [2,5]. The basaltic lavas contain phenocrysts of fresh, unaltered olivine and augitic-pyroxene set in a crystalline groundmass of plagioclase laths, augitic-pyroxene, magnetite and ilmenite [3]. Olivine phenocrysts 0.75 mm in diameter constitute about 8% of the total volume [3]. A flow texture is suggested by the slight preferred orientation of the plagioclase laths. The olivine crystals may capture excess argon when they formed in the magmatic chamber. The large size rock was crushed to 60–90 mesh, and then most phenocrysts of olivine and pyroxene were removed by conventional magnetic and heavy liquid techniques [2]. As a result, the groundmass was the main component of BB-24. The preliminary K–Ar studies [2,5] showed that this recollected material yielded corresponding Ar and K concentrations for all aliquots of ~1 g.

Herein, we report on the examination and evaluation of BB-24 by using $^{40}Ar/^{39}Ar$ total-fusion and step-heating techniques to check Ar and K distribution in as far as they may be detected by this techniques as a monitor in $^{40}Ar/^{39}Ar$ dating. Furthermore, it is of interest to evaluate whether they yield undisturbed or

* Corresponding author.
E-mail address: wangfei@mail.iggcas.ac.cn (F. Wang).

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accordant age spectra, and compare any plateau ages with the total-fusion values. Finally, we comment on the utility of BB-24 as a suitable Quaternary standard for $^{40}Ar/^{39}Ar$ dating.

2. Analytical techniques

Samples were prepared using the following procedure. First the BB-24 container was homogenized by shaking. Then two splits were made. From one split, olivine granules were removed by hand-picking to produce a purified BB-24 sample and a sample of olivine granules. Both the purified and olivine samples were ultrasonically cleaned in acetone three times, 20 min for each. The purified and unpurified splits of BB-24 were then weighed into several aliquots, respectively, with weights ranging from ∼15 to 40 mg.

All aliquots (including olivine granules) were wrapped in aluminium foil to form wafers, and stacked in quartz vials with the international standards ACs sanidine (Alder Creek rhyolite). The vial is ∼40 mm in length and has an inner diameter of 6.5 mm, and the position for every sample was recorded as the distance from the bottom of the vial. The first vial was loaded with unpurified BB-24 and ACs (Table 1), whilst the second vial contained aliquots of purified BB-24 and ACs (Table 2). Then the vials were sealed and put in a quartz canister. The canister was wrapped with cadmium foil (0.5 mm in thickness) for shielding slow neutrons in order to prevent interface reactions during the irradiation.

Neutron irradiation was carried out in position H8 of 49-2 Nuclear Reactor (49-2 NR), Beijing (China), with a flux of $\sim 6.5 \times 10^{12}$ n $(cm^2\ s)^{-1}$ for 3.2 h, yielding *J*-values of ∼0.00065 and 0.00068 for vials #1 and #2, respectively. The H8 position lies in the core of the reactor and receives flux from all directions. Specimens were not rotated during the fast neutron irradiation.

The irradiated samples were transferred into a high-vacuumed "Christmas tree". Following a 72 h bakeout at 250 °C, the sample wafer was dropped into a Ta tube resting in the Ta crucible of an automated double-vacuum resistance furnace and heated at 600 °C for 30 min. Total fusion and step heating were carried out. Temperature of 1500 °C was held for a duration of 10 min for total fusion; the step heating was schemed from 700 or 800 to 1500 °C at a pace of 50 or 100 °C; each step took 10 min. The heating scheme is controlled by a programmed thyristor and the temperature is measured and feedbacked through a thermocouple which is about 1 mm under the tantalum crucial of the furnace. The extracted gas was purified by two SAES getters (NP10) for 8–20 min according to the volume of the release; one Zr–Al getter was operated at 80 °C in order to eliminate H_2 whereas the other getter was set at 400 °C to remove the active gases such as N_2, O_2, CO_2.

Isotopic measurements were made on the MM5400 mass spectrometer at Institute of Geology and Geophysics of Chinese Science Academy (IGGCAS), Beijing, China. The procedure for $^{40}Ar/^{39}Ar$ analyses follows Wang et al. [6]. System blanks at 1500 °C determined several times each day prior to degassing the samples were typically 3×10^{-16} mol ^{40}Ar and 9×10^{-19} mol ^{36}Ar in nearly atmospheric ratios, ∼1/50 of magnitude of sam-

Table 1
$^{40}Ar/^{39}Ar$ data of total fusions of BB-24

Position (mm)	Mass (mg)	$^{36}Ar_a/^{39}Ar_k$	$^{37}Ar_{Ca}/^{39}Ar_k$	$^{40}Ar/^{39}Ar_k$	$^{36}Ar_a$ (10^{-10} cm^3 STP/g)	$^{39}Ar_k$ (10^{-8} cm^3 STP/g)	$^{40}Ar^*$ (10^{-8} cm^3 STP/g)	$^{40}Ar^*$ (%)	K/Ca	$^{40}Ar^*/^{39}Ar_k$	Apparent age (ka)	*J*-value
Unpurified BB-24, vial 1												
2.5	15.92	0.01211	1.93277	3.95437	5.55414	5.96085	2.23519	9.47	0.291	0.37498	439.0 ± 98.8	0.000651 ± 0.000004
3.5	15.76	0.00998	1.45851	3.36444	6.9469	6.9640	2.9020	12.37	0.385	0.41671	487.8 ± 72.3	0.000649 ± 0.000003
4.5	19.69	0.01006	1.57262	3.37537	6.35074	6.31506	2.54923	11.95	0.357	0.40367	472.6 ± 71.9	0.000649 ± 0.000003
5.5	19.88	0.00796	1.64536	2.70437	5.05802	6.35780	2.24741	13.05	0.341	0.35349	413.8 ± 57.3	0.000648 ± 0.000004
9.0	30.48	0.00560	1.57974	2.02887	3.23559	5.78106	2.16788	18.45	0.356	0.37500	439.0 ± 45.5	0.000646 ± 0.000003
10.0	30.08	0.00924	1.62629	3.10816	5.9499	6.4392	2.4319	12.14	0.345	0.37768	442.2 ± 72.1	0.000645 ± 0.000003
11.5	39.9	0.00533	1.56316	1.95257	3.46651	6.49967	2.44758	19.25	0.359	0.37657	440.9 ± 43.5	0.000644 ± 0.000005
13.0	39.54	0.00709	1.56232	2.47531	4.28756	6.04932	2.30422	15.36	0.360	0.38091	445.9 ± 56.0	0.000643 ± 0.000003
16.5	40.04	0.00837	1.55484	2.83976	5.23204	6.25005	2.28795	12.87	0.361	0.36607	428.6 ± 57.3	0.000640 ± 0.000005
Purified BB-24, vial 2												
10.5	15.07	0.00767	1.59449	2.60760	5.68319	5.92577	2.00996	13.10	0.352	0.34208	421.5 ± 61.3	0.000684 ± 0.000004
12.0	15.40	0.00150	1.55429	0.77864	8.1952	6.70725	2.25279	42.90	0.361	0.33565	413.5 ± 51.0	0.000684 ± 0.000003
13.0	21.14	0.00959	1.55310	3.17322	5.91792	6.56791	2.24573	10.68	0.362	0.33919	417.9 ± 74.0	0.000684 ± 0.000004
18.0	29.9	0.00901	1.62640	3.00449	4.69688	6.98556	2.31987	11.37	0.345	0.34192	421.3 ± 71.3	0.000683 ± 0.000004
19.5	30.57	0.01222	1.63157	3.94642	4.89078	6.37920	2.18217	8.50	0.344	0.33587	413.8 ± 87.3	0.000683 ± 0.000005
21.0	40.64	0.00672	1.62756	2.31895	8.78234	5.85836	1.96636	14.30	0.345	0.33210	409.2 ± 53.3	0.000683 ± 0.000003
24.0	40.33	0.00424	1.64843	1.59277	2.58458	6.10028	2.07893	21.35	0.341	0.34079	419.9 ± 41.1	0.000683 ± 0.000004
27.5	39.99	0.00521	1.53028	1.89802	8.3563	6.4133	2.2954	18.82	0.367	0.35791	419.0 ± 44.7	0.000683 ± 0.000004

$^{40}Ar^*$ denotes the radiogenic ^{40}Ar.

Table 2
$^{40}Ar/^{39}Ar$ data of step heating of unpurified BB-24, purified BB-24 and olivine

T (°C)	$^{36}Ar_a/^{39}Ar_k$	$^{37}Ar_{Ca}/^{39}Ar_k$	$^{40}Ar/^{39}Ar_k$	$^{40}Ar^*$ (%)	Cumulative $^{39}Ar_k$ (%)	K/Ca	$^{40}Ar^*/^{39}Ar_k$	Apparent age (ka)
Unpurified BB-24, 40.24 mg, $J = 0.000638 \pm 0.000005$								
700	0.00466	0.62659	1.82974	24.70	6.29	0.897	0.45284	521.1 ± 47.8
770	0.00173	0.47743	0.87981	41.66	22.12	1.177	0.36808	423.6 ± 18.1
840	0.00961	0.45434	3.20581	11.36	40.07	1.237	0.36463	419.6 ± 64.6
900	0.00486	0.47584	1.81608	20.83	48.60	1.181	0.37904	436.2 ± 61.2
980	0.00679	0.73463	2.37257	15.37	56.60	0.765	0.36527	420.4 ± 76.7
1060	0.00721	0.80126	2.49474	14.62	66.01	0.701	0.36527	420.4 ± 70.1
1120	0.00521	1.06999	1.91177	19.46	80.61	0.525	0.37277	429.0 ± 54.2
1190	0.00459	4.62021	1.71212	20.67	96.25	0.122	0.35467	408.2 ± 58.2
1280	0.01112	7.66585	3.76632	12.72	99.13	0.073	0.47945	551.8 ± 154.8
1400	0.04398	6.75947	14.19567	8.45	100.00	0.083	1.19998	1380.6 ± 472.2
Purified BB-24, 40.13 mg, $J = 0.000683 \pm 0.000004$								
800	0.00210	0.48877	0.95858	35.01	28.94	1.149	0.33693	415.1 ± 16.8
900	0.01270	0.44484	4.13112	9.13	45.28	1.263	0.37756	465.2 ± 45.0
980	0.00886	0.66895	2.96966	11.82	53.53	0.840	0.35147	433.0 ± 37.1
1060	0.00824	0.77576	2.77062	12.15	63.27	0.724	0.33696	415.1 ± 44.3
1160	0.00595	1.96637	2.08637	15.65	90.95	0.286	0.32709	403.0 ± 27.3
1250	0.00554	7.47811	1.99461	17.94	98.81	0.075	0.35847	441.6 ± 53.1
1350	0.04970	6.70866	15.05763	2.46	99.57	0.084	0.36985	455.7 ± 245.6
1500	0.04946	5.68785	15.20114	3.85	100.00	0.099	0.58564	721.5 ± 287.0
Purified BB-24, 20.59 mg, $J = 0.000683 \pm 0.000005$								
800	0.00269	0.47629	1.11918	28.99	28.32	1.180	0.32554	401.1 ± 53.4
910	0.01949	0.43997	6.10083	5.61	43.97	1.277	0.34240	421.9 ± 158.0
1010	0.00802	0.65919	2.71726	12.71	56.16	0.852	0.34588	426.1 ± 83.5
1100	0.00694	0.97111	2.36945	13.49	75.19	0.579	0.32016	394.4 ± 57.9
1210	0.00428	3.96808	1.61712	21.73	96.38	0.142	0.35220	433.9 ± 58.7
1350	0.06170	6.63826	18.51059	1.51	98.27	0.085	0.27899	343.7 ± 499.7
1500	0.13309	6.01479	40.10723	1.94	100.00	0.093	0.77881	959.4 ± 943.4
T (°C)	$^{36}Ar_a/^{39}Ar_k$	$^{37}Ar_{Ca}/^{39}Ar_k$	$^{40}Ar/^{39}Ar_k$	$^{40}Ar^*$ (%)	Cumulative $^{39}Ar_k$ (%)	K/Ca	$^{40}Ar^*/^{39}Ar_k$	Apparent age (Ma)
Olivine, 45.77 mg, $J = 0.000635 \pm 0.000004$								
800	0.01942	0.17258	12.60428	54.46	21.71	3.255	6.86647	7.9 ± 0.4
880	0.28631	0.37738	86.51415	2.21	38.84	1.489	1.90880	2.2 ± 1.9
940	0.10477	0.43789	34.46405	10.17	53.31	1.283	3.50469	4.0 ± 0.8
1000	0.09495	0.55314	31.51393	10.97	60.36	1.016	3.45762	4.0 ± 0.7
1080	0.13966	0.70861	43.48997	5.10	70.95	0.793	2.21977	2.5 ± 1.0
1180	0.07378	1.65164	25.05175	12.97	86.69	0.340	3.24932	3.7 ± 0.8
1280	0.10301	7.55057	34.56064	11.92	96.77	0.074	4.12092	4.7 ± 0.9
1380	0.52303	15.80379	201.11045	23.15	98.91	0.036	46.55530	52.6 ± 4.1
1500	1.71779	37.75085	550.67243	7.82	100.00	0.015	43.06420	48.7 ± 15.3

ple signals. Although the mean blank errors were generally ~2% for ^{40}Ar and ~5% for ^{36}Ar, the large size of the samples relative to the blank minimized the impact of propagating these errors into the final age calculations. For step heating, the blanks were subtracted from sample measurements at various temperatures by interpolating the curve which was determined by a series of measured blanks.

The ion currents were measured in the order ^{40}Ar, ^{39}Ar, ^{38}Ar, ^{37}Ar and ^{36}Ar, and involved eight cycles. For each peak and baseline measurement, the ion beam of ^{40}Ar, ^{39}Ar, ^{38}Ar, ^{37}Ar was integrated for 10 s, ^{36}Ar for 30 and 4 s for baselines. Baseline measurements were basically taken at a half mass unit away from the peaks, except that between ^{39}Ar and ^{40}Ar; the baseline between masses 40 and 39 was set at 39.3. Isotope ratios were extrapolated to zero time by the least-square regression from eight cycle measurements. Usually the "memory effect" of the instrument was negligible; the variety of $^{40}Ar/^{39}Ar$ was less than 1% in one run and the analytic error was less than 0.1%. K_2SO_4 and CaF_2 crystals were fused to calculate Ca, K correction factors: $[^{36}Ar/^{37}Ar]_{Ca} = 0.000278 \pm 0.0000142$, $[^{39}Ar/^{37}Ar]_{Ca} = 0.000852 \pm 0.0000281$ and $[^{40}Ar/^{39}Ar]_K = 0.003804 \pm 0.000225$. Ages were calculated using the decay constant listed by Steiger and Jäger [7], and all errors were quoted at the 2σ level. Mass discrimination was monitored using an on-line air pipette from which multiple measurements were made before and after each experiment, the mean over this period was $0.99978 \pm 0.00024\ amu^{-1}$ and the uncertainty of this value was propagated into all age calculations.

Plateau ages were determined from three or more contiguous steps, comprising >50% of the ^{39}Ar released, revealing concordant ages at the 95% confidence level. The uncertainties in plateau ages reflect multiplication by the MSWD and were obtained by standard weighting of errors for individual steps according the variance [8]. Thus, more precise determinations

were given greater weight than those of lower precision and the overall uncertainty about the mean value may be greatly reduced. Because no assumption is made regarding the trapped component, the preferred ages are isochrones, calculated from the results of plateau steps using the *York* regression algorithm [9].

Uncertainties on all data reported herein are at the 95% confidence level. Where data from the literature are discussed that were originally reported at the 68% confidence level, the uncertainties are doubled for consistency. The data herein were processed using ArArCALC [10].

3. $^{40}Ar/^{39}Ar$ analysis results

3.1. Total-fusion experiments

Results of total-fusion analyses on ~15 to ~40 mg aliquots of unpurified BB-24 and purified BB-24 are summarized in Table 1.

Relative to the 1.194 ± 0.014 Ma Alder Creek sanidine (ACs) monitor [11], nine replicated measurements on BB-24 yield ages in a range from 413.8 ± 57.3 to 487.8 ± 72.3 ka (Table 1), giving a weighted average age of 438.5 ± 21.4 ka, whilst the five splits of larger size (~30–40 mg) give ages in a smaller range from 428.6 ± 57.3 to 445.9 ± 56.0 ka with a weighted average value of 439.3 ± 23.5 ka. Eight measurements on purified BB-24 yield ages from 409.2.6 ± 53.3 to 421.5 ± 61.3 ka with a weighted average value of 416.7 ± 22.0 ka. Complete external errors, including those arising from the decay constants were propagated.

Resulting $^{40}Ar^{*}$ and $^{39}Ar_k$ contents, K/Ca ratios and atmospheric argon contents ($^{36}Ar_a$) are also listed in Table 2. $^{40}Ar^{*}$ and $^{39}Ar_k$ contents for each split of a standard were evaluated in a semi-quantitative manner, because of the fluctuating sensibility or manometric stability exhibited by the mass spectrometer on a given day, and the errors in the volume correction limited the accuracy of such measurements to about ±3–5%.

K/Ca ratios were calculated from the measurements of $^{39}Ar_k/^{37}Ar_{Ca}$ ratios by multiplying by 1/1.78 [6]. Using $K = 1.76\%$ [2], the calculated Ca content (~5.1%) is in good agreement with that (5.4%) reported by Fan et al. [12]. K/Ca values of BB-24 are in the range of 0.341–0.361 except one of 0.291, with an average value of 0.356. Using $K = 1.76\%$ [2], the calculated Ca content (~4.9%) is in agreement with the result (5.4%) reported by Fan et al. [12].

3.2. Step-heating experiments

3.2.1. BB-24

In order to assess the distribution of $^{40}Ar^{*}$ and $^{39}Ar_k$ within the sample, conventional step-heating experiments on unpurified BB-24 were performed, because the observation of an age spectrum could reveal homogeneity or any distortion within the sample [13]. To evaluate the influence of excess argon on age spectra, a step-heating experiment was also performed on both aliquots of purified BB-24.

The step-heating age spectrum for the split of BB-24 is discordant, exhibiting an age of 521 ka for the first ~7% of gas released, followed by a flat plateau with an age of 424.4 ± 15.0 ka for more than 80% of gas release (Fig. 1). The last two highest temperature steps which gave anomalous higher ages, 552 and 1381 ka, accounted for ~4% of gas released. The integrated (total gas) age is 440.0 ± 21.2 ka (Table 2) and is similar to the average age obtained for total fusions (Table 1) on nine splits of BB-24. Data from those steps forming the plateau determine a statistically valid inverse isochron with an age of 420.5 ± 24.7 ka, and initial $(^{40}Ar/^{36}Ar)_i$ value of 296.7 ± 5.1 indistinguishable from atmospheric value at 95% confidence level plausibly. The mean squared weighted deviation (MSWD) value of 0.51 ($N = 7$) for the isochron indicates that observed scatter is less than would be expected from the errors in the individual step analyses, therefore, the errors on individual step analyses are likely to have been slightly overestimated, or some error correlations are unaccounted for in the regression used [14]. K/Ca ratios decrease with temperature increase (Fig. 1), suggesting a Ca-rich, K-poor phase (pyroxene) degassing at high temperature; the weighted average K/Ca ratio of 0.36 ± 0.02 is similar to those of total fusions (Table 1).

Replicated step-heating experiments on two aliquots of purified BB-24 give both flat age spectra with a total of 11 plateau steps and show a more concordant age spectrum than the unpurified aliquot (Fig. 1). A plateau was defined with age of 417.0 ± 18.8 ka and an isochron age of 411.1 ± 29.1 ka (Fig. 1). The anomalous higher age values are also present at the last two high temperature steps consisting of ~1% of gas released (Fig. 1). The total-gas age is 423.9 ± 22.6 ka which is similar to the average value of total-fusion experiments. The initial $(^{40}Ar/^{36}Ar)_i$ value defined by the isochron is 296.3 ± 3.5 indicating no excess argon distinguished at a 95% confidence level. The MSWD value of 0.32 ($N = 11$) also suggests that the observed scatter about the isochron is less than would be expected. K/Ca spectrum patterns for the replicated experiments are rather similar (Fig. 1) with that of the split of BB-24, also indicating the refractory Ca-rich and K-poor phase degassing at high temperature steps.

3.2.2. Olivine separates

It is recognized that the BB-24 standard contains excess argon, which mainly concentrates in the olivine crystals [2,3,5,15]. In order to evaluate the excess argon source and degassing pattern, the olivine mineral separates collected from the BB-24 were analysed using a step-heating method with ACs sanidine as the fluence monitor (Table 2 and Fig. 2).

Most steps of the age spectrum of olivine give ages in the range of 2.2–4.7 Ma, except the first one and last two steps exhibiting much higher ages (7.8–53 Ma) which raise the total gas age up to 6.0 Ma. The age spectrum pattern shows a relatively even degassing from low to high temperatures. The total gas data show that the $^{40}Ar^{*}$ and $^{39}Ar_k$ contents are much lower that those of BB-24. Compared with BB-24 the K/Ca ratio spectrum of the olivine separates exhibits a lower total gas value (0.091) but a similar pattern, implying a slight contamination from the host materials.

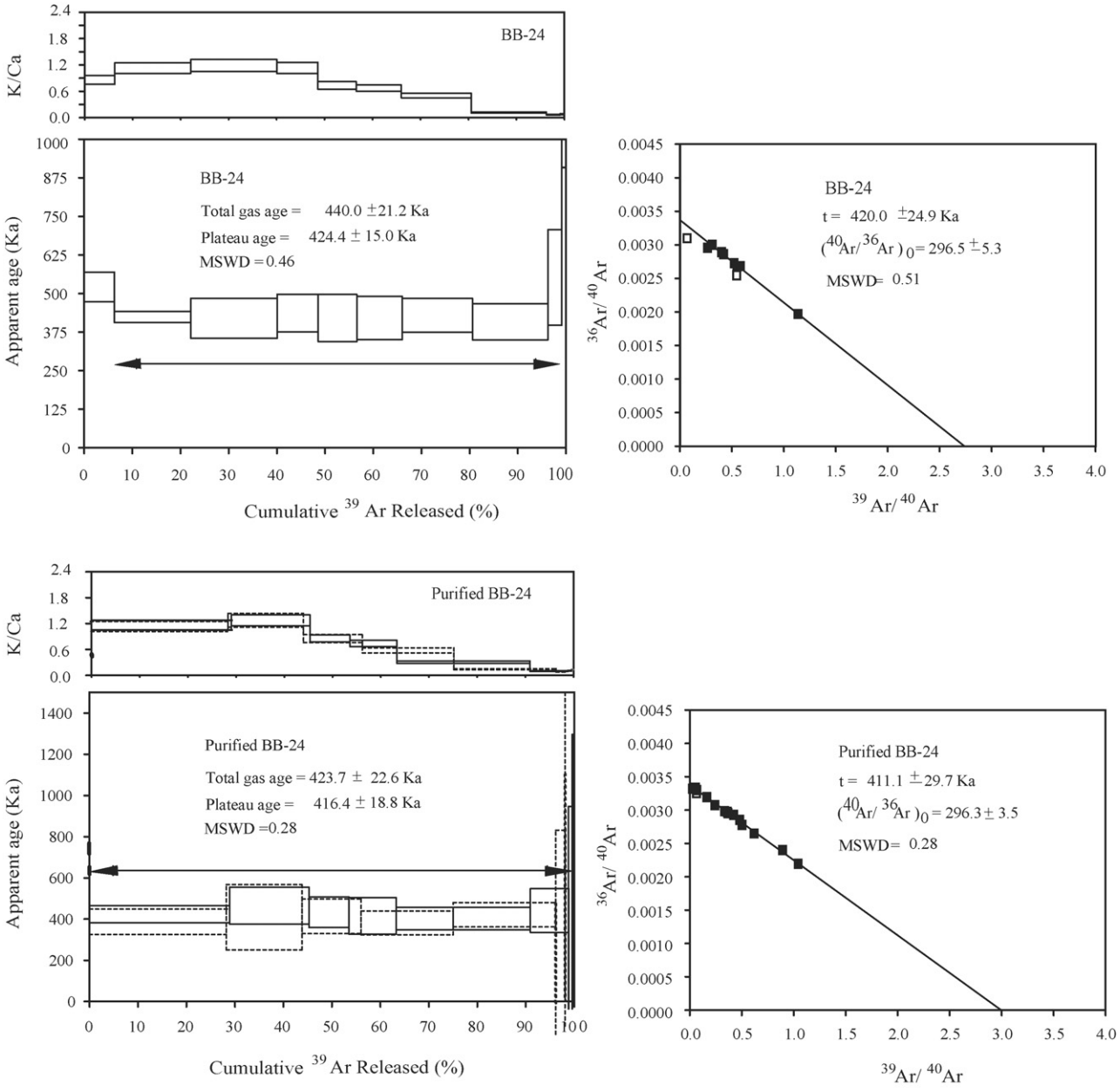

Fig. 1. Age, K/Ca spectra, and inverse isochrones of BB-24 and purified BB-24. All errors are $\pm 2\sigma$.

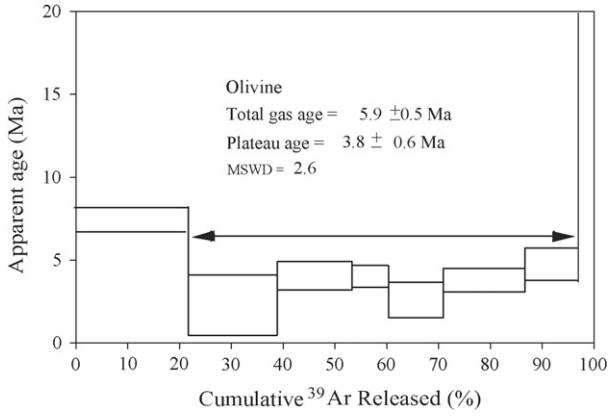

Fig. 2. Age spectra of olivine.

4. Discussion and conclusions

4.1. Excess argon in BB-24

Olivine crystals are the carriers of excess argon in basaltic rocks. This has been recognized since the 1980s. Excess argon has a strong influence on the dating of young volcanic rocks, and it has been found that the excess argon is widespread in Datong Quaternary basalts. The influence of excess argon on the age of BB-24 has been previously discussed [2,3,5,15]. Although BB-24 is a collection following the conventional magnetic and heavy liquid procedure, the fine grains of phenocrystic olivine cannot be eliminated completely when the rock is crushed to a grain size of 0.25–0.16 mm (60–90 mesh). Phenocrystic olivine is very likely to be the source of excess argon, whereas groundmass

olivine, crystallized in equilibrium with the atmosphere, is less likely to contain excess argon. The much higher ages (total gas age of 5.9 Ma, Fig. 2) produced by olivine separates implies that they are from phenocrysts, not groundmass.

The relative even degassing pattern of the olivine in the step-heating experiment (Fig. 2) suggests that the contribution (if any) of the olivine to the whole rock sample should be similar at low and high temperature steps. Therefore, the influence of excess argon may be exerted at all temperatures. The purified BB-24 gives a much lower age (average 416.7 ± 22.0 Ma) than those of BB-24 (average 44.6 ± 23.5 Ma), and may be due to the removal of olivine crystals, although this deduction is obscured by the large errors. The plateau ages of unpurified BB-24 (424.4 ± 15.0 Ma) and purified BB-24 (416.4 ± 18.8 Ma) also show the contribution of excess ^{40}Ar from olivine. However, the initial values of ^{40}Ar/^{36}Ar for both unpurified BB-24 (296.7 ± 5.1) and purified BB-24 (296.3 ± 3.5) do not exhibit excess argon at a 95% confidence level. Although in some cases the isochron cannot indicate the excess argon [16,17], the excess argon in BB-24 may be blurred by a high content of atmospheric argon and large uncertainties in the measurements. This is very characteristic of dating young volcanic rocks using the step-heating method.

4.2. Is BB-24 an appropriate Quaternary ^{40}Ar/^{39}Ar dating standard?

The total-fusion results of nine unpurified BB-24 splits show a considerable scatter in the concentrations of ^{40}Ar* from 2.16788×10^{-8} to 2.902×10^{-8} cm^3 STP/g and of ^{39}Ar$_k$ from 5.96085×10^{-8} to 6.964×10^{-8} cm^3 STP/g (Table 1 and Fig. 3). Splits of unpurified BB-24 also yield unstable ^{40}Ar*/^{39}Ar$_k$ values: from 0.35349 to 0.41671 (Table 1 and Fig. 3). The final apparent ages scatter in a range from 413.8 to 487.8, and a difference is up to 17.8%. In this study, the average age is 44.6 ± 23.5 ka, 4.8% older than that of the K–Ar ages reported by Chen at al. [2,5] (425 ± 42 ka). The five splits with a larger size of ~30–40 mg yielded relatively reproducible ages in a range from 428.6 to 445.9 ka (Table 2), varying within 3.8%. The above clearly indicate that BB-24 is inhomogeneous in Ar and K.

The purified aliquots of BB-24 show less dispersedness in the content of ^{40}Ar* (from 1.96636×10^{-8} to 2.31987×10^{-8} cm^3 STP/g) and ^{39}Ar$_k$ (from 5.85836×10^{-8} to 6.98556×10^{-8} cm^3 STP/g), and in apparent ages (413.5–421.5 ka with 1.9% difference) (Table 1 and Fig. 3), indicating mineral impurities in the sample and that results can be improved by removing olivine phenocrysts.

Stepwise heating of a split of ~40 mg of unpurified BB-24 yielded a flat age spectrum in the midcourse temperatures (Fig. 1). The plateau age (424.4 ± 15.0 ka) agrees well with the conventional K–Ar result given by Chen et al. [2,5], and the total gas age (440.0 ± 21.2 ka) is older than that reported by Chen et al. [2,5] and consistent with the result of total fusion in this study. The same phenomena was also observed by Fuhrmann et al. [4] when they examined BB-6 and were ascribed to the excess ^{40}Ar or to ^{39}Ar loss during neutron irradiation. However, the plateau of aliquot of BB-24 in this study consisting of more than 80% of gas released at intermediate temperature steps suggests that the effects of ^{39}Ar$_k$ recoil to the plateau portion of the age spectrum are negligible. The higher temperature steps of the degassing are dominated by increasing ages, indicating excess ^{40}Ar in the high temperature melting K-poor phase. This

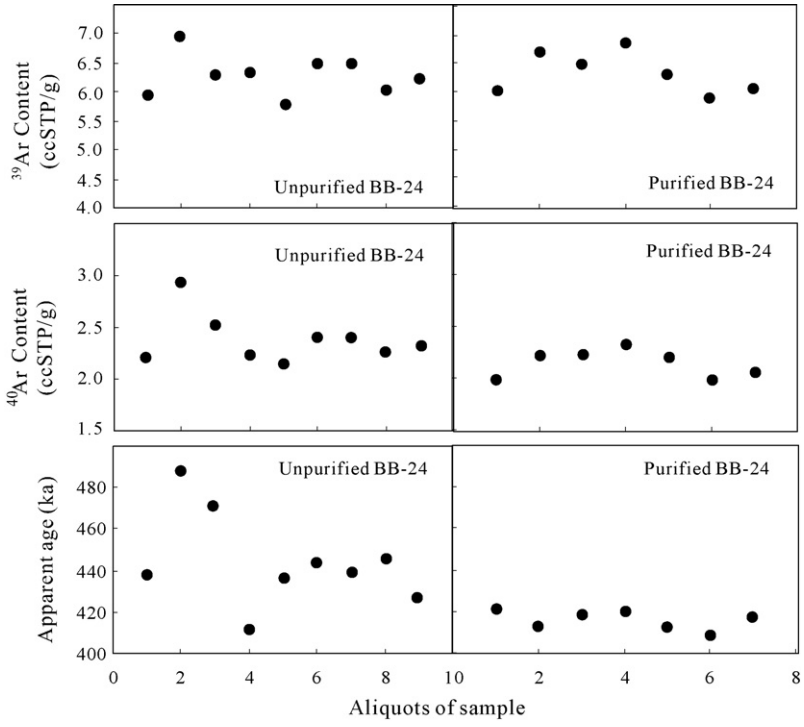

Fig. 3. Scatters in ^{39}Ar$_k$, ^{40}Ar* contents and apparent ages.

is proved by the K/Ca spectrum that the K/Ca ratios decrease at high temperature steps (Fig. 1). The high age value at the first (lowest temperature) step, accounting for ∼7% of the total degassing, may be due to the excess ^{40}Ar gained from alteration or to ^{39}Ar loss during irradiation. It is worthy to note that the shape of the olivine age spectrum (Fig. 2) is similar to the unpurified BB-24 (Fig. 1), implying the contribution of the olivine to the BB-24 in degassing. This is indicated by the spectra of two purified aliquots of BB-24 (Fig. 1) which give very concordant age spectra and a lower plateau age (416.4 ± 18.8 ka) compared with the unpurified one. We note that the age spectrum of purified BB-24 does not appear to exhibit these older ages with the first and last few percent gas released as BB-24 does. The excess ^{40}Ar of the components degassing at high temperatures could be troublesome when the samples are not degassed under the same conditions [4]. This could be problematic when a total-fusion experiment is performed. Based on the discussion above, we conclude that BB-24 is not a good irradiation monitor for ^{40}Ar/^{39}Ar dating.

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