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

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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

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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.