Intercalibration of the Hb3gr $^{40}Ar/^{39}Ar$ dating standard

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Abstract

The $^{40}Ar/^{39}Ar$ dating technique is based on the knowledge of the age of neutron fluence monitors (standards). Recent investigations have improved the accuracy and precision of the ages of most of the Phanerozoic-aged standards (e.g. Fish Canyon Tuff sanidine (FCs), Alder Creek sanidine, GA1550 biotite and LP-6 biotite); however, no specific study has been undertaken on the older standards (i.e. Hb3gr hornblende and NL-25 hornblende) generally used to date Precambrian, high Ca/K, and/or meteoritic rocks.

In this study, we show that Hb3gr hornblende is relatively homogenous in age, composition (Ca/K) and atmospheric contamination at the single grain level. The mean standard deviation of the $^{40}Ar^{*}/^{39}Ar_K$ (F-value) derived from this study is 0.49%, comparable to the most homogeneous standards. The intercalibration factor (which allows direct comparison between standards) between Hb3gr and FCs is $R_{FCs}^{Hb3gr} = 51.945 \pm 0.167$. Using an age of 28.02 Ma for FCs, the age of Hb3gr derived from the R-value is 1073.6 ± 5.3 Ma (1σ; internal error only) and ± 8.8 Ma (including all sources of error). This age is indistinguishable within uncertainty from the K/Ar age previously reported at 1072 ± 11 Ma (Turner et al., 1971; [Turner G., Huneke, J.C., Podosek, F.A., Wasserburg, G.J., 1971. ^{40}Ar-^{39}Ar ages and cosmic ray exposure ages of Apollo 14 samples. *Earth Planet. Sci. Lett.* 12, 19-350]).

The R-value determined in this study can also be used to intercalibrate FCs if we consider the K/Ar date of 1072 Ma as a reference age for Hb3gr. We derive an age of 27.95 ± 0.19 Ma (1σ; internal error only) for FCs which is in agreement with the previous determinations. Altogether, this shows that Hb3gr is a suitable standard for $^{40}Ar/^{39}Ar$ geochronology.

1. Introduction

The $^{40}Ar/^{39}Ar$ technique is one of the most powerful methods, supplanting the conventional K/Ar method because it is possible to better evaluate the accuracy of an age (i.e. using age spectrum).

In return, $^{40}Ar/^{39}Ar$ dating is based on the knowledge of the ages of standards (neutron fluence monitors) because of the irradiation of samples and is thus directly dependent on how accurately and precisely their ages are known. The age of a standard can be determined either directly by conventional K/Ar dating (primary standards such as GA1550 biotite, McDougall and Roksandic (1974) and NL-25 hornblende, Schaeffer and Schaeffer (1977)) or through $^{40}Ar/^{39}Ar$ intercalibration with a primary standard (secondary standards such as Fish Canyon sanidine (FCs); Cebula et al. (1986)). Secondary standards may be used, in turn, to calibrate "higher order" standards (e.g. Alder Creek sanidine (ACs) calibrated against FCs; Nomade et al., 2005). In this case, the age and error of the intermediate standard(s) should be propagated in the final result (Renne et al., 1998; Nomade et al., 2005). Currently, analytical precision on isotopic ratios measured with high-resolution, low-background mass spectrometers may reach ± 0.1-0.2 %, whereas the ages of fluence monitors are generally considered to be known to ± 0.5 % (1σ) if we neglect the error on the decay constant (e.g. FCs, ACs, GA1550; Renne et al., 1998). Therefore, the overall uncertainty on the age of an unknown is partially limited by the uncertainty on the age of the fluence monitor. Additionally, recent studies (Renne et al., 1998; Min et al., 2000) have focused on systematic errors including the ^{40}K decay constant uncertainties (and possibly accuracy) which is the most significant error contributor to the global error on the age. The value of the decay constant is currently in question (e.g. Min et al., 2000; Kwon et al., 2002) but will not be discussed here.

The uncertainty on the age of a $^{40}Ar/^{39}Ar$ standard is also dependent of the chemical homogeneity of the mineral at the single grain level. This is crucial for $^{40}Ar/^{39}Ar$ dating because standards are generally measured on single grains using a laser device. K/Ar measurement of a primary standard requires much larger amounts of material compared to $^{40}Ar/^{39}Ar$ dating and thus, homogenizes the $^{40}Ar^{*}/^{40}K$ ratio of the standard. Studies concerning the homogeneity of standards have recently been conducted on some of the most widely used standards (e.g. Baksi et al, 1996; Renne et al., 1998; Spell & McDougall, 2003). Ideally, a standard should be chosen to approximate the age and/or composition of the unknown sample to minimize the range of isotopic ratios measured (c.f. Renne et al., 1997, 1998; Nomade et al., 2005). In addition, a standard must be homogeneous in composition (i.e. without secondary inclusions) at single-grains scale (Roddick, 1983).

The dating of Precambrian and/or high Ca/K rocks mostly relies on two available standards - NL-25 hornblende (2660 Ma; Schaeffer and Schaeffer, 1977; particularly used for meteorite study) and Hb3gr hornblende (1072 Ma; Turner et al., 1971). Nevertheless, the homogeneity of these standards at the single grain level has never been properly documented. Here, we investigate the age and composition of the Hb3gr standard.

The apparent age of the Hb3gr hornblende standard was determined to be 1072 ± 11[1] Ma more than three decades ago using the K/Ar method (Turner et al.; 1971). The age of Hb3gr is therefore known to ± 1 % and can be compared to other widely-used standards such as GA1550 and FCs, which are known to 1% (including error on the decay constant; Renne et al., 1998). The Hb3gr standard is currently in use in several laboratories and has been used in many studies for which a precision of the $^{40}Ar/^{39}Ar$ ages better than 1% is desirable. (e.g. Turner et al. 1971; Roddick et al. 1983, Hall et al., 1984; McConville et al., 1988; Courtillot et al., 2000, Renne, 2000; Nomade et al., 2001; LeGall et al., 2002; Whitby et al., 2002, Yibas et al., 2002, Roberts et al., 2002 Lenoir et al., 2003, Jourdan et al., 2004; Burgess et al., 2004; Verati et al., 2005). Therefore, to take full advantage of the Hb3gr standard, it is crucial that (1) the age of Hb3gr currently adopted is re-assessed, (2) the precision on the age should be improved and (3) the homogeneity of the hornblende at the single grains level should be evaluated. In order to do so, we conducted 72 single grain $^{40}Ar/^{39}Ar$ total fusion analyses on the Hb3gr hornblende monitor irradiated along with 87 grains of the FCs standards (28.02 Ma; Renne et al., 1998). Additionally, we determined the intercalibration factor (R-value) which, in this case, is the $^{40}Ar^{*}/^{39}Ar$ ratio of Hb3gr to that of FCs (see Renne et al., 1998). The intercalibration factor makes it possible to compare different standards. Finally, we propose a new age and uncertainty for Hb3gr hornblende using the full propagation error calculation of Renne et al. (1998).

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[1] All uncertainties concerning the ages of standards in this paper are given at the 1σ level unless otherwise indicated.

2. Description and ages of the studied standards

2.1. Fish Canyon sanidine (FCs)

The Fish Canyon sanidine comes from the large Fish Canyon ash-flow tuff (~5000 km^3; Lipman, 1997) located in San Juan Volcanic field, south-western Colorado. The tuff contains abundant phenocrysts (35-50%) of plagioclase, sanidine, biotite, hornblende, quartz, zircon, titanite and apatite (Lipman et al., 1997).

The Fish Canyon tuff has a relatively simple history, and therefore, the FCs was introduced as a potential ^{40}Ar/^{39}Ar standard by Cebula et al. (1986). Since then, the FCs has become one of the most widely used neutron fluence monitors. Numerous studies attempted to determine its age either as (1) a primary standard (i.e. by K-Ar measurement; Steven et al., 1967; Hurford and Hammerschmidt, 1985); however, it is difficult to extract all the ^{40}Ar* from viscous sanidine melts (Webb and McDougall, 1967), or (2) a secondary standard (i.e. relative to a primary standard used as a fluence monitor; Renne et al., 1994; Hilgen et al., 1997; Renne et al., 1998; Villeneuve et al., 2000; Lanphere & Baadsgaard, 2001; Spell & McDougall, 2003; Dazé et al., 2003).

The precision and accuracy required for the ^{40}Ar/^{39}Ar dating standard imply that the age used for a standard should be the same in every laboratory. If we discard the younger age of 27.57 ± 0.18 Ma published by Lamphere & Badsgaard, (2001) based on the poorly constrained SB-3 biotite monitor (see Spell & McDougall, 2003 and Schmitz et al., 2003), the various ages obtained from more recent measurements using the ^{40}Ar/^{39}Ar technique are in good agreement within uncertainties. Using the decay constant of Steiger and Jager (1977) but without taking uncertainties on the decay constant into account, the ages are 28.15 ± 0.19 Ma (Hilgren et al., 1997), 27.98 ± 0.08 Ma (Villeneuve et al.; 2000), 28.10 ± 0.04 (Spell and McDougall; 2003) and 28.02 ± 0.16 Ma (Renne et al.; 1998). Published ^{40}Ar/^{39}Ar age spectra are flat (Lanphere & Baadsgaard, 2001, and Spell and McDougall, 2003) highlighting the superior homogeneity of this standard.

In this study, we adopted the age published in Renne et al. (1998) for FCs as 28.02 ± 0.16 Ma based in turn on an age of 98.79 ±0.5 Ma (K/Ar age) for the primary standard GA1550 (both age errors exclude uncertainties on the decay constant). We use this age because the K and ^{40}Ar* concentrations of GA1550 have been determined recently (Renne et al., 1998) by the 'first principles' and can be assumed to be more reliable than the K and Ar* concentration of

Hb3gr determined more than 34 years ago. The corresponding $R_{GA-1550}^{FCs}$ value is 0.27811 ± 0.000295.

2.2. Hb3gr hornblende

The Hb3gr hornblende was originally analyzed by Zartman (1964) and re-analyzed after purification by Turner et al. (1971). It was extracted from the Lone Grove Pluton (LGP) located in Texas (USA) (Zartman, 1964; Turner et al., 1971; Rougvie et al., 1999). The LGP has a simple cooling history with a titanite U/Pb age of 1093 ± 6 Ma and hornblende and biotite $^{40}Ar/^{39}Ar$ weighted-mean ages (from a different location than Hb3gr) of 1076 ± 8 and 1079 ± 8 Ma, respectively (Rougvie et al., 1999). From these ages, Rougvie et al (1999) estimated a cooling rate of ~14°C/Myr for the LGP.

The hornblende was originally chosen by Turner et al. (1971) as a neutron fluence monitor because of its relatively simple history with no subsequent metamorphism. Hornblende was preferred to biotite mostly because of its higher closure temperature (~600°C; Villa et al., 1996) than biotite (~300°C; Harrison et al., 1985). Subsequently, Roddick (1983) demonstrated that the Hb3gr hornblende bulk sample appeared homogenous in age at the 0.1% level.

Zartman (1964) first provided a K-Ar age for the Hb3gr hornblende of 1060 ± 20 Ma. Turner et al. (1971) refined this age, and Roddick (1983) recalculated it using the decay constant of Steiger and Jager (1977) to get an age of 1072 ± 11 Ma. The age of 1072 ± 11 Ma became the "official age" for the Hb3gr monitor in 1983. A more recent investigation of Hb3gr concerned the measurement of two sets of hornblende grains (a re-preparation of the Hb3gr standard referred to as PP-20). These hornblende crystals were co-irradiated with FCs with the purpose of dating the Acapulco meteorite (Renne, 2000). Both samples consisted of 38 grains each and yielded two ages of 1074 ± 4 and 1073 ± 4 Ma (analytical errors only; based on the FCs monitor with an age of 28.02 Ma; Renne et al., 1998). However, no detailed interpretation of these ages was provided.

3. Analytical techniques

We investigated pre-existing mineral separates of Hb3gr hornblende (n = 72; 125-200 μm fraction) and FC sanidine (n = 87; 200-315 μm fraction). All standards were carefully handpicked under a binocular microscope to avoid impurities or inclusions such as quartz or microcline (Turner et al., 1971; Roddick et al., 1983). This intercalibration was performed by using three distinct irradiations with two different durations, so as to address any issues related to irradiation conditions. For each irradiation, the Hb3gr and FCs standards were loaded separately in three square-shaped, flat packages (7-10 mm wide) made of aluminum foil. To ensure a minimum neutron flux variation during the irradiation, the packages were assembled as follows: one package including 30 grains of Hb3gr was framed by two packages including 15 grains of FCs each (irradiation MC36) and 30 grains of FCs framed by two packages of 15 grains of Hb3gr each (irradiations MC34 and MC37). For each irradiation, the three packages were placed side-by-side along with other unrelated samples in a 15 cm-long package made of aluminum foil. The standards were irradiated for 150h (MC34) and 70h (MC36 and MC37) in the Hamilton McMaster University nuclear reactor (Canada) in position 5C (i.e. in the high flux area and receiving flux from all directions). The total neutron flux density during irradiation was $1.9\text{x}10^{19}$ neutron/cm² (MC34) and $8.8\text{x}10^{18}$ neutron/cm² (MC36 and MC37). The flux gradient ranges from 0 to 0.1% per mm in length of the final package and is laterally negligible. Each grain of standard was analyzed separately in a single fusion experiment using a CO_2 Synrad 48-5 laser beam. The gas was purified in a stainless and glass extraction line using two Al-Zr getters (working at 400°C and ambient temperature, respectively) and a liquid nitrogen cold trap. Isotopic measurements were performed with a VG3600 mass spectrometer and a Daly-photomultiplier system. $^{40}\text{Ar}^{*}/^{39}\text{Ar}_{K}$ values (Table 1) were corrected for blank, mass discrimination, radioactive decay and interference isotopes. Mass discrimination was monitored weekly using an online air pipette providing $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ranging from 282.2 to 289.9 with error of ± 0.5%. This corresponds to corrections ranging from 1.01178 to 1.00483 per atomic mass unit. The correction factors for interfering isotopes were measured using Ca and K pure silicates and were $(^{39}\text{Ar}/^{37}\text{Ar})_{Ca} = 7.06\text{x}10^{-4}$ (± 4%), $(^{36}\text{Ar}/^{37}\text{Ar})_{Ca} = 2.79\text{x}10^{-4}$ (± 3%) and $(^{40}\text{Ar}/^{39}\text{Ar})_{K} = 2.97\text{x}10^{-2}$ (± 3%). The $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained for the Hb3gr monitor are based on the reference age of 28.02 ± 0.16 Ma (Renne et al., 1998; neglecting the error on the decay constant). For each irradiation, the neutron fluence value (J) was determined using the $^{40}\text{Ar}^{*}/^{39}\text{Ar}_{K}$ (F-value) weighted-mean ratio obtained for the FCs grains. The J-values are (3.5381 ±0.0033) $\text{x}10^{-2}$; (1.6162 ± 0.0019) $\text{x}10^{-2}$ and (1.7268 ± 0.0018) $\text{x}10^{-2}$ for MC34, MC36 and MC37 suite respectively. Individual errors in Table 1 are given at the 1σ level. The decay constants are those recommended by Steiger & Jager (1977).

4. Results / discussion

4.1. Fish Canyon monitor

The three F-value suites obtained for FCs from the three irradiations have been plotted as probability density distribution diagrams (Sircombe et al., 2004) in Fig. 1. The three probability curves show simple and symmetric Gaussian distributions. Their weighted-mean F-values (Table 2) are 0.4424 ± 0.0002 (MSWD=1.19; n= 27), 0.9686 ± 0.0006 (MSWD=0.96; n=28), and 0.9064 ± 0.0005 (MSWD=1.98; n=31) for irradiation MC34, MC36 and MC37, respectively. These values exclude discordant data deviating more than 3σ from the weighted-mean values. These values are not directly comparable as they depend of the irradiation duration and neutron flux; they can be converted in age after mathematical treatment using their associated J-values. The three mean F-value standard deviations (1σ) describe the overall dispersion of the data and range from 0.26% to 0.48%.

The standard deviation values must be compared with analytical errors alone because the errors from interference factors and mass discrimination corrections represent constant values for each irradiation. For each irradiation suite, the average analytical error values vary from 0.26% to 0.38% and are similar to the F-value standard deviations. Altogether, close-to-1 MSWD values and relatively low standard deviations obtained on the FCs standard are similar to the results of previous studies (e.g. Renne et al., 1998). These results confirm that the analyzed FCs crystals have strong between-analysis reproducibility and are homogenous at the single crystal level.

4.2. Hb3gr hornblende

4.2.1. Hornblende reproducibility

The three different irradiation batches yield mean F-values standard deviations for Hb3gr hornblende of 0.33% (MC34; n=14), 0.62% (MC36; n=28) and 0.51% (MC37; n=28) (Table 2) excluding two outlying data points (MC34-3 and MC36-i30) which lie greater than 3σ outside the weighted-mean value of a given irradiation. These values are roughly similar to those obtained from the FCs although the MC36 suite shows a higher standard deviation. MSWD values are varying alike the standard deviations, with relatively low MSWD for MC34 and MC37 batches (1.07 and 2.4 respectively) and a substantially higher MSWD-value of 4.1 for the MC36 suite. The high MSWD of MC36 clearly shows that error cannot be attributed to analytical error alone because the three values obtained by averaging the analytical errors for the three irradiations vary from 0.30% to 0.34%. This discrepancy is mirrored by the probability curves of F-value of MC34 and MC37 suites which show well-defined Gaussian curves whereas MC36 exhibits an asymmetrical curve with 2 peaks and a relative difference between the two peaks equal to 0.6%. No correlation is apparent between the age (F-value) of the data and their respective $^{37}Ar_{Ca}/^{39}Ar_K$ ratios (proxy for Ca/K) and atmospheric ^{40}Ar content. The reason for the skewed distribution of the MC36 suite is not understood.

The estimated Ca/K composition derived from the $^{37}Ar/^{39}Ar$ ratios (Ca/K = 1.79 x $^{37}Ar_{ca}/^{39}Ar_K$) shows minor variation mostly from 5.0 to 6.5 and is in agreement with the chemical composition of the hornblende (P.R. Renne, unpublished data). Moreover, $^{40}Ar/^{39}Ar$ measurements show that the Hb3gr hornblende grains have a relatively low and constant atmospheric contamination (0.2-1.2%; Table 1), showing no correlation with the F-value. Therefore, the interference correction of $^{36}Ar_{Ca}$ is almost negligible (despite a high CaO concentration) and the propagation of the uncertainties linked to this interference correction factor is minimized. Altogether, this suggests that the small, 7.5% younger, inclusions of microcline (K≈ 13%) reported in some Hb3gr hornblende (Zartman, 1964) have been successfully eliminated during grain selection, thus, these inclusions are probably not the factor responsible for the MC36 F-value variation. The two age populations from MC36 could reflect heterogeneity of the neutron flux from side to side of the 1 cm-wide package, but previous experiments done on McMaster irradiated samples have failed to demonstrate this effect (G.F. unpublished data). In addition, it would be hard to explain why this effect is not observed in the MC34 and MC37 suites.

The average standard deviation of the Hb3gr F-values at the single grain level calculated for the three suites is 0.49 % and is inversely proportional to the reproducibility. If we exclude younger additional outliers (MC34-1, MC34-2, MC36-I22, and MC37-X6; Table 1) which are inside the 3σ confidence limit but "visually discordant" (i.e. ranging from 1.7 to 2σ) in F-value vs. analysis (not shown) and age vs. analysis plots (Fig. 2A), the global standard deviation becomes 0.38%. These values are on the same order than those derived from other commonly used standards such as: GA1550 (0.17-0.36%), TCs (0.30-0.51%) and MMhb-1 (0.15-0.61%) determined by Renne et al. (1998), or GA1550 (0.39%), MMhb-1 (0.82%), 92-176 sanidine (0.60%), and LP-6 (1.45%) determined by Spell & McDougall (2003). This comparison therefore suggests that the Hb3gr hornblende is relatively homogenous at the single crystal level and shows a good reproducibility although lower than FCs (s.d. = 0.34%; this study).

4.2.2. Intercalibration value (R_{FCs}^{Hb3gr})

The intercalibration (R) value allows a direct comparison between standards of different ages. It is defined as the ratio of the F-value ($^{40}Ar^*/^{39}Ar_K$) between two standards after their co-irradiation (Renne et al., 1998). This value is particularly useful for the recalculation of previously published ages using a different age for the fluence monitor. It also allows a full propagation of the errors when only analytical errors plus error on J-value are quoted (i.e. excluding uncertainties of the decay constant and the age of the monitor; e.g. Min et al., 2000).

The R-values for the three suites of irradiation (Table 3) are deduced from weighted-means of the F-values (Table 2). The overall R-value (Table 4) may be obtained by different statistical approaches using: (1) the weighted-mean (and weighted-mean error) of each R-value (e.g. Spell & McDougall, 2003), (2) the arithmetic mean with either the standard error of the mean (i.e. the standard deviation divided by the roots-squared of the number of analyses (e.g. Renne et al., 1998), or the standard deviation (Nomade et al., 2005) as uncertainties. Although the arithmetic and weighted-mean calculation provides similar values; the error values are substantially different (Table 4).

The overall mean R_{FCs}^{Hb3gr} values derived from R_{MC34}, R_{MC36} and R_{MC37} calculated using the arithmetic mean and weighted-mean are 51.945 and 51.965, respectively, and are concordant within uncertainties. The weighted-mean error, the standard error of the mean and the standard deviation values are 0.025 [relative error (r.e.).= 0.05%], 0.167 [r.e.= 0.33%] and 0.292 [r.e.= 0.56%], respectively.

The weighted-mean may not be the best calculation when using a small dataset (i.e. 3 R-values), but the choice between arithmetic and weighted-mean does not sensibly affect the final value. However, the error on the weighted-mean tends to minimize the uncertainties on the final results. The calculation of the weighted-mean error includes only the error associated with each measurement (here, R-values) and does not take into account the natural dispersion of the dataset due to compositional heterogeneities, crystal defects, etc… For instance, the calculated weighted-mean error (0.05%) on R_{FCs}^{Hb3gr} is lower than for $R_{GA-1550}^{FCs}$ (0.11%; Renne et al., 1998) although we previously showed that Hb3gr has a grain to grain reproducibility noticeably lower than FCs and GA1550. Similarly, the standard deviation provides good information on the dispersion of the data relative to the mean, but is not relevant to estimate the uncertainty on a mean value. It is more appropriate when one tries to describe the error associated with a mean calculated from a gradient. The standard error of the mean better describes our datasets as it combines information about the dispersion of the data relative to the mean and takes into account the number of analyses (i.e. increasing the number of measurements leads to better precision, e.g. Mandel, 1984).

For these reasons, we report hereafter the age calculated with the arithmetic mean and the standard error of the mean where R^{Hb3gr}_{FCs} = 51.945 ± 0.167 [0.33%]

4.2.3. Age of Hb3gr

Apparent individual ages obtained for Hb3gr mostly range from 1063 ± 3 to 1085 ± 3 Ma (Fig. 2A, Table 1) based on an age of 28.02 Ma for FCs (Renne et al., 1998). Two analyses displaying much younger ages (1055 and 1043 Ma), clearly discordant from the range mentioned above, have been rejected. However, the ages are not equally distributed depending on the irradiation batch. The MC34 irradiation includes generally younger ages varying from 1063 ± 3 to 1071 ± 2 Ma (n=14), whereas MC36 and MC37 show a broader age spectrum varying from 1064 ± 3 to 1085 ± 3 Ma (n=29) and 1064 ± 2 to 1081 ± 4 Ma (n=28), respectively (Fig. 2).

The weighted-mean ages of the three suites are concordant, with values of 1069 ± 5, 1078 ± 10 and 1074± 8 Ma for MC34, MC36 and MC37, respectively. However, the Hb3gr global age is calculated by using the previously calculated overall R^{Hb3gr}_{FCs} value of 51.945 ± 0.167 instead of the average of all individual age measurements. As previously mentioned, this allows calculating and propagating all external sources of errors (Renne et al., 1998). The total uncertainty on the age of Hb3gr therefore includes errors on: (1) the GA-1550 primary standard $^{40}Ar^{*}/^{40}K$ ratio (0.0059 ± 0.0000332), (2) the $R^{FCs}_{GA-1550}$ intercalibration factor (0.27811 ± 0.000295), and (3) the calculated R^{Hb3gr}_{FCs} value (51.945 ± 0.167), in addition to the internal, J-value, and mass discrimination errors and the interference corrections. Depending on the purpose of the study, the total uncertainty may also include error on the decay constant.

Excluding the uncertainties on the decay constant, we obtain an age at 1073.6 ± 5.3 Ma (Table 4). This age is similar to the age of 1073.9 ± 4.6 Ma obtained by using the R-value calculated with the weighted-mean. On the other hand, using the weighted-mean error, the standard error of the mean or the standard deviation for the calculation of R-value, yields substantially different uncertainties in the final results (respectively 4.6 Ma [r.e.=0.43%]; 5.3 Ma [r.e.=0.50%] and 6.50 Ma [r.e.=0.60%]). Including the uncertainties on the decay constant into the calculation (Min et al., 2000) almost doubles the global uncertainties (+45%), yielding a mean age of 1073.6 ± 8.8 Ma [0.82%].

A global (n=70) age-data probability diagram (Fig. 2B) shows a nearly Gaussian curve with the peak age at 1073 Ma, slightly lower by 0.15% than the weighted-mean age (although largely in agreement within uncertainties). This age discrepancy likely results from the slight departure of the probability curve from a perfect Gaussian plot (visible on the right side of the curve).

From a geological point of view, we can establish how the age and the precision of an unknown sample (measured using the Hb3gr monitor) will be affected by the results presented here. For instance, a sample measured with Hb3gr monitor and using an age of 1072.0 ± 6.6 Ma (Turner et al., 1971; analytical uncertainties only) yields an (arbitrary) age of 100.0 ± 1.4 Ma (including all uncertainties). Application of equations (1), (3), (4) and (7) of Renne et al. (1998) for age calculation and error propagation and using an age of 1073.6 ± 5.3 Ma for Hb3gr, yield a slightly older age of 100.2 ± 1.4 Ma. The precision of the age is not significantly modified mainly because the contributions of the decay constant and analytical errors may represent a dominant source of errors relatively to the improvement of the age of Hb3gr standard.

In summary, the global age and internal error of 1073.6 ± 5.3 Ma obtained in this study is in agreement within uncertainties with the previously reported K/Ar (1072 ± 7 Ma; analytical error only; Turner et al., 1971) and $^{40}Ar/^{39}Ar$ (1074 ± 4 and 1073 ± 4 Ma; Renne, 2000) ages. The age variation shown in the double-peak probability curve displayed for the MC36 suite results (Fig. 1) suggests that the Hb3gr hornblende monitor exhibits a slight departure from homogeneity. These variations contribute to decrease the precision on the age of the Hb3gr standard. Therefore, the total reproducibility (standard deviation) calculated over 70 single grains (0.49 %, and possibly 0.38% by removing ~2σ outliers) is similar to the most reliable standards (e.g. GA-1550; ACs; FCs) and suggests that the Hb3gr hornblende is relatively homogeneous at the single crystal level.

5. Circular statement: the age of the FCs

Hb3gr could also be considered as a primary standard for which the K-Ar age was determined by Turner et al. (1971). These authors measured K and $^{40}Ar^*$ concentrations of 1.247 ± 0.008 % and 7.09×10^{-7} cc/gm standard temperature and pressure (STP), respectively using 'first principles' (i.e. the $^{40}Ar^*$ has been calibrated relatively to a known volume of air) and isotopes dilution techniques. Using the decay constants suggested by Steiger & Jäger (1977), this composition yielded the widely used age of 1072 ± 11 Ma (including errors on the decay constant). As mentioned above, the new $^{40}Ar/^{39}Ar$ ages obtained for Hb3gr hornblende grains (1073.6 ± 8.8 Ma) is in agreement within uncertainties with the K/Ar age determined by Turner et al. (1971). If we assume that the K/Ar age determined on the Hb3gr standard has the same accuracy as the one obtained for GA-1550, we can use the Hb3gr hornblende as a fluence monitor to directly intercalibrate FCs (using a R^{FCs}_{Hb3gr} value of 0.01925 ± 0.00006 (=1/ R^{Hb3gr}_{FCs})). We obtained an age of 27.95 ± 0.19 Ma ([0.68%;] for FCs, excluding uncertainties on the decay constant; Table 4B). This age is in agreement with the most recent age determinations of 28.15 ± 0.19 Ma (Hilgren et al., 1997), 28.02 ± 0.16 Ma (Renne et al., 1998), 27.98 ± 0.08 Ma (Villeneuve et al., 2000) and 28.10 ± 0.04 (Spell and McDougall, 2003) although it should be noted that the reported errors are (unfortunately) calculated using different statistical approaches.

A re-evaluation of the FCs age is out of the topic of this paper because it would require further detailed intercalibration using the most reproducible and well known primary standards. If the age of the FCs is modified by future investigations, the R^{Hb3gr}_{FCs} value provided in this study should allow a rapid recalculation of the age of the Hb3gr without further measurement.

6. Conclusions

We studied the age and suitability of the widely-used Hb3gr hornblende fluence monitor using 70 individual grains distributed over three irradiations and co-irradiated with the Fish Canyon sanidine standard. The major conclusions include:

1. The relatively low mean standard deviation (0.49% and possibly 0.38% if we exclude outliers) of the three F-values (= $^{40}Ar^*/^{39}Ar_K$) of Hb3gr, the low atmospheric contamination and the relatively invariant Ca/K composition from grain to grain

altogether suggest that Hb3gr is age-homogeneous and is therefore suitable as a single-grain $^{40}Ar/^{39}Ar$ dating standard.

2. The intercalibration factor (R_{FCs}^{Hb3gr} value) calculated from the arithmetic mean and standard error of the mean of three R-values obtained from three irradiations is 51.947 ± 0.169 (n=70). Considering an age of 28.02 Ma for FCs (Renne et al., 1998), the age calculated for Hb3gr is 1073.6 ± 5.4 Ma (internal error only) and ± 8.8 Ma (including all sources of error). This age is indistinguishable (though more precise) from the K/Ar age of 1072 ± 11 Ma determined by Turner et al. (1971) more than 3 decades ago.
3. Assuming that the K/Ar age determined by Turner et al. (1971) on Hb3gr is correct, and using the Hb3gr as a fluence monitor to intercalibrate FCs, we obtained a FCs age of 27.95 ± 0.19 (internal error only) and ± 0.30 (full error propagation) in agreement with previous determinations. Nevertheless, more data from various primary standards are required to improve the age of FCs.

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References

Baksi A.K., Archibald, D.A., Farrar, E., 1996. Intercalibration of $^{40}Ar/^{39}Ar$ dating standard. Chem. Geol. 129, 307-324.

Burgess R., Kiviets, G.B., Harris, J.W., 2004. Ar–Ar age determinations of eclogitic clinopyroxene and garnet inclusions in diamonds from the Venetia and Orapa kimberlites. Lithos 77, 113-124.

Cebula G.T., Kunk, M.J., Mehnert, H.H., Naeser, C.W., Obredovich, J.D., Sutter, J.F., 1986. The Fish Canyon tuff, a potential standard for the $^{40}Ar/^{39}Ar$ and fission-track methods. Terra Cognita 6, 139-140.

Courtillot V., Gallet, Y, Rocchia, R, Feraud, G, Robin, E, Hofmann, C, Bhandari, N, Ghevariya, Z.G., 2000. Cosmic markers, ^{40}Ar/^{39}Ar dating and paleomagnetism of the KT sections in the Anjar area of the Deccan large igneous province. Earth Planet. Sci. Lett. 182, 137-156.

Féraud G., Alric, V., Fornari, M., Bertrand, H., Haller, M., 1999. ^{40}Ar/^{39}Ar dating of the Jurassic volcanic province of Patagonia: migrating magmatism related to Gondwana break-up and subduction. Earth Planet. Sci. Lett. 172, 83-96.

Hall C.M., Walter, R.C., Westage, J.A., York, D., 1984. Geochronolgy, stratigraphy and geochemistry of Cindery Tuff in Pliocene hominid-bearing sediments of the Middle Awash, Ethiopia. Nature 308, 1984.

Harrison T.M., Duncan, I., McDougall, I., 1985. Diffusion of ^{40}Ar in biotite; temperature, pressure and compositional effects. Geochim. Cosmochim. Acta 49, 2461-2468.

Hurford A.J., Hammerschmidt, K., 1985. ^{40}Ar/^{39}Ar and K/Ar dating of the Bishop and Fish Canyon Tuffs: calibration of ages for fission-track dating standards. Chem. Geol. 58, 23-32.

Jourdan F., Féraud, G., Bertrand, H., Kampunzu, A.B., Tshoso, G., Le Gall, B., Tiercelin, J.J. & Capiez P., 2004. The Karoo triple junction questioned : evidence from ^{40}Ar/^{39}Ar Jurassic and Proterozoïc ages and geochemistry of the Okavango dyke swarm (Botswana). Earth Planet. Sci. Lett. 222, 989-1006.

Kwon J., Min, K., Bickel, P., Renne, P.R., 2002. Statistical methods for jointly estimating decay constant of ^{40}K and age of a dating standard. Mathematical Geology 175, 457-474.

Lanphere M.A., Baadsgaard, H., 2001. Precise K-Ar, ^{40}Ar-^{39}Ar, Rb-Sr and U/Pb mineral ages from the 27.5 Ma Fish Canyon Tuff reference standard. Chem. Geol. 175, 653-671.

Le Gall B., G. Tshoso, F. Jourdan, G. Féraud, H. Bertrand, J.J. Tiercelin, A.B. Kampunzu, M.P. Modisi, J. Dyment, M. Maia., 2002. ^{40}Ar/^{39}Ar geochronology and structural data from the giant Okavango and related mafic dyke swarms, Karoo igneous province, Botswana. Earth Planet. Sci. Lett. 202, 595-606.

LeNoir X., Feraud, G., Geoffroy, L., 2003. High-rate flexure of the East Greenland volcanic margin; constraints from ^{40}Ar/^{39}Ar dating of basaltic dykes. Earth Planet. Sci. Lett. 214, 515-528.

Lipman P., Dungan, M., Bachmann, O., 1997. Comagmatic granophyric granite in the Fish Canyon Tuff, Colorado: implications for magma-chamber processes during a large ash-flow eruption. Geology 25, 915-918.

Mandel, J. (1984) The statistical analysis of experimental data, Dover publication, Mineolta, N.Y.

Mc Dougall I., Roksandic, Z., 1974. Total fusion ^{40}Ar/^{39}Ar ages using HIFAR reactor. J. Geol. Soc. Aust. 21, 81-89.

McConville P., Kelley, S., Turner, G., 1988. Laser probe ^{40}Ar-^{39}Ar studies of the Peace River shcocked L6 chondrite. Geochim. Cosmochim. Acta 52, 2487-2499.

Min K., Mundil, R., Renne, P.R., Ludwig, K., 2000. A test for systematic errors in ^{40}Ar/^{39}Ar geochronology through comparison with U/Pb analysis of a 1.1 Ga rhyolite. Geochim. Cosmochim. Acta 64, 78-98.

Nomade S., Chen, Y., Féraud, G., Pouclet, A., Théveniau, H., 2001. First paleomagnetic and ^{40}Ar/^{39}Ar study of Paleoproterozoic rocks from the French Guyana (Camopi and Oyapok rivers), northeastern Guyana Shield. Precambrian Research 109, 239-256.

Nomade S., Renne, P., Vogel, N., Deino, A.L., Sharp, W.D., Beker, T.A., Jaouni, A.B., Mundil, R., 2005. Alder Creek sanidine (ACs-2): A Quaternary ^{40}Ar/^{39}Ar dating standard tied to the Cobb Mountain geomagnetic event. Chem. Geol. 218, 315-338.

Renne P.R., A.L. Deino, R.C. Walter, B.D. Turrin, C.C. Swisher, T.A. Becker, G.H. Curthis, W.D. Sharp., 1994. Intercalibration of astronomical and radioisotopic time. Geology 22, 783-786.

Renne P.R., Sharp, W.D., Deino, A.L., Orsi, G., Civetta, L., 1997. ^{40}Ar/^{39}Ar dating into the historic realm: calibration against pliny the younger. Science 277, 1279-1280.

Renne P.R., C.C. Swisher, A.L. Deino, D.B. Karner, T. Owens, D.J. Depaolo., 1998. Intercalibration of Standards, absolute ages and uncertainties in ^{40}Ar/^{39}Ar dating. Chem. Geol. 145, 117-152.

Renne P.R., 2000. ^{40}Ar/^{39}Ar age of plagioclase from Acapulco meteorite and the problem of systematic errors in geochronology. Earth Planet. Sci. Lett. 175, 13-26.

Roberts H.J., Kelley, S.P., Dahl, P.S., 2001. Obtaining geologically meaningful ^{40}Ar-^{39}Ar ages from altered biotite. Chem. Geol. 172, 277-290.

Roddick J.C., 1983. High precision intercalibration of ^{40}Ar-^{39}Ar standards. Geochim. Cosmochim. Acta 47, 887-898.

Rougvie J.R., Carlson, W.D., Copeland, P., Connelly, J.N., 1999. Late thermal evolution of Proterozoic rocks in the northeastern Llano Uplift, central Texas. Precambrian Research 94, 49-72.

Schaeffer G.A., Schaeffer, O.A., 1977. ^{39}Ar-^{40}Ar ages of lunar rocks. Proc. Lun. Plan. Sci. Conf. 8, 2253-2300.

Schmitz, M.D., Bowring, S.A., Ludwig, K.R., Renne, P.R., 2003. Comment on "Precise K-Ar and ^{40}Ar-^{39}Ar, Rb-Sr and U-Pb mineral ages from the 27.5 Ma Fish Canyon Tuff reference standards" by M.A. Lanphere and H. Baadsgaard (2003) Chem. Geol. 199, 277-280.

Sircombe K.N., 2004. AgeDisplay: an EXCEL workbook to evaluate and display univariate geochronological data using binned frequency histograms and probability density distributions. Computers & Geosciences 30, 21-31.

Spell T.L., McDougall, I.; 2003. Characterization and calibration of ^{40}Ar/^{39}Ar dating standards. Chem. Geol. 198, 189-211.

Steiger R.H., E. Jager., 1977. Subcommission on geochronology: convention of the use of decay constants in geo- and cosmochronology. Earth Planet. Sci. Lett. 36, 359-362.

Steven T.A., Mehnert, H.H., Obradovich, J.D., 1967. Age of volcanic activity in the San Juan Mountains, Colorado. U.S. Geol. Surv. Prof. Pap. 575-D, 47-55.

Turner G., Huneke, J.C., Podosek, F.A., Wasserburg, G.J., 1971. ^{40}Ar-^{39}Ar ages and cosmic ray exposure ages of Apollo 14 samples. Earth Planet. Sci. Lett. 12, 19-35.

Verati, C., Bertrand, H., Feraud, G., 2005. The farthest record of the Central Atlantic Magmatic Province into West Africa craton: Precise ^{40}Ar/^{39}Ar dating and geochemistry of Taoudenni basin intrusives (northern Mali). Earth Planet. Sci. Lett. 235, 391-407.

Villa I.M., Grobety, B.H., Kelley, S.P., Trigila, R., Wieler, R., 1996. Assessing Ar transport paths and mechanisms in the McClure Mountains hornblende. Contributions to Mineralogy and Petrology 126, 67-80.

Villeneuve M.E., Sandeman, H., Davis, W.J., 2000. A method for intercalibration of U-Th-Pb and ^{40}Ar-^{39}Ar ages in the Phanerozoic. Geochim. Cosmochim. Acta 64, 4017-4030.

Webb A.W., McDougall, I., 1967. A comparison of mineral and whole rock potassium-argon ages of Tertiary volcanics from central Queensland, Australia. Earth Planet. Sci. Lett. 3, 41-47.

Whitby J.A., Gilmour, J.D., Turner, G., Prinz, M., Ash, R.D., 2002. Iodine-Xenon dating of chondrules from the Qingzhen and Kota Kota enstatite chondrites. Geochim. Cosmochim. Acta 66, 347-359.

Yibas B., Reimold, W.U., Armstrong, R., Koeberl, C., Anhaeusser, C.R., Phillips, D., 2002. The tectonostratigraphy, granitoid geochronology and geological evolution of the Precambrian of southern Ethiopia. Journal of African Earth Sciences 34, 57-84.

Zartman R.E., 1964. A geochronologic study of the Lone Grove Pluton from the Llano Uplift, Texas. Journal of Petrology 5, 359-408.

Figure and table captions

Figure 1. Probability density distribution diagram of $^{40}Ar^{*}/^{39}Ar_{k}$ ratios (F-value) of Hb3gr and FCs calculated using Sircombe et al. (2004). Numbers of analysis for each standard are indicated for each of the three irradiations. Arrows indicate the width at the middle-height of the peaks and percentages represent the relative width compared to the peak value allowing fast comparison between the different F-values.

Figure 2. A) Age vs. number of analysis for Hb3gr (n=72). Individual errors are quoted at 1σ. Gray diamond: grains from irradiation MC34 (n=15); white diamond: MC36 (n=29) and black diamond: MC37 (n=28). Outliers outside the 3σ confidence level of the weighted-mean (n=2) and pseudo-outliers at ~2σ and "visually discordant" (n=4) are indicated. B) $^{40}Ar/^{39}Ar$ age-probability density distribution diagram for the three irradiations calculated excluding two (>3σ) outliers. Dotted line: MC34 (n=14); Dotted-dashed line: MC36 (n=28); dashed line: MC37 (n=28). The solid line represents the calculation including all 70 Hb3gr grains. The age derived from the intercalibration-factor (see text) is indicated, and it includes all sources of error.

Table 1. $^{40}Ar/^{39}Ar$ analytical data for Hb3gr and FCs.

$^{40}Ar^{*}$= radiogenic Ar; ^{37}Ar and ^{39}Ar produced by neutron interference with Ca and K respectively. Decay constants are from Steiger and Jager (1977). Errors on the discrimination are not reported but are considered to be ±0.5%. Ages obtained for Hb3gr are derived using an age of 28.02 Ma for FCs (Renne et al, 1998). J-value is indicated for each irradiation and is referenced to FCs. Correction factors for interfering isotopes were $(^{39}Ar/^{37}Ar)_{Ca} = 7.06x10^{-4}$ (± 4%), $(^{36}Ar/^{37}Ar)_{Ca} = 2.79x10^{-4}$ (± 3%) and $(^{40}Ar/^{39}Ar)_{K} = 2.97x10^{-2}$ (± 3%). Analytical uncertainties on ages in this table are 1σ.

Table 2. Summary of $^{40}Ar^{*}/^{39}Ar_{K}$ (F-value) results for Hb3gr and FCs.

F-values were calculated using the weighted-mean and error of the weighted-mean. Irradiation duration, standard deviation (1σ) and MSWD are indicated. n: number of analysis for each suite.

Table 3. Summary of R-values for each individual irradiation.

R values were calculated using the Hb3gr and FCs F-values ratios given in Table 2. Error on each R-value is the error of the weighted-mean on the F-values of Hb3gr and FCs propagated into the calculation.

Table 4. A) Summary of the global R-value and associated age proposed for Hb3gr relative to FCs (28.02 Ma).

Results from different calculations based on the 3 R-values of Table 3 are shown. These calculations include arithmetic and weighted-mean with, error of the weighted-men, standard error of the mean and standard deviation (1σ). Relative errors are indicated in brackets. Ages calculated from the corresponding R-value are indicated (1σ) both excluding and including error on the decay constant (σλ). B). similar as Table 4A, but using Hb3gr as fluence monitor (1072 Ma; Turner et al., 1971) and FCs as the intercalibrated standard.

Figure1

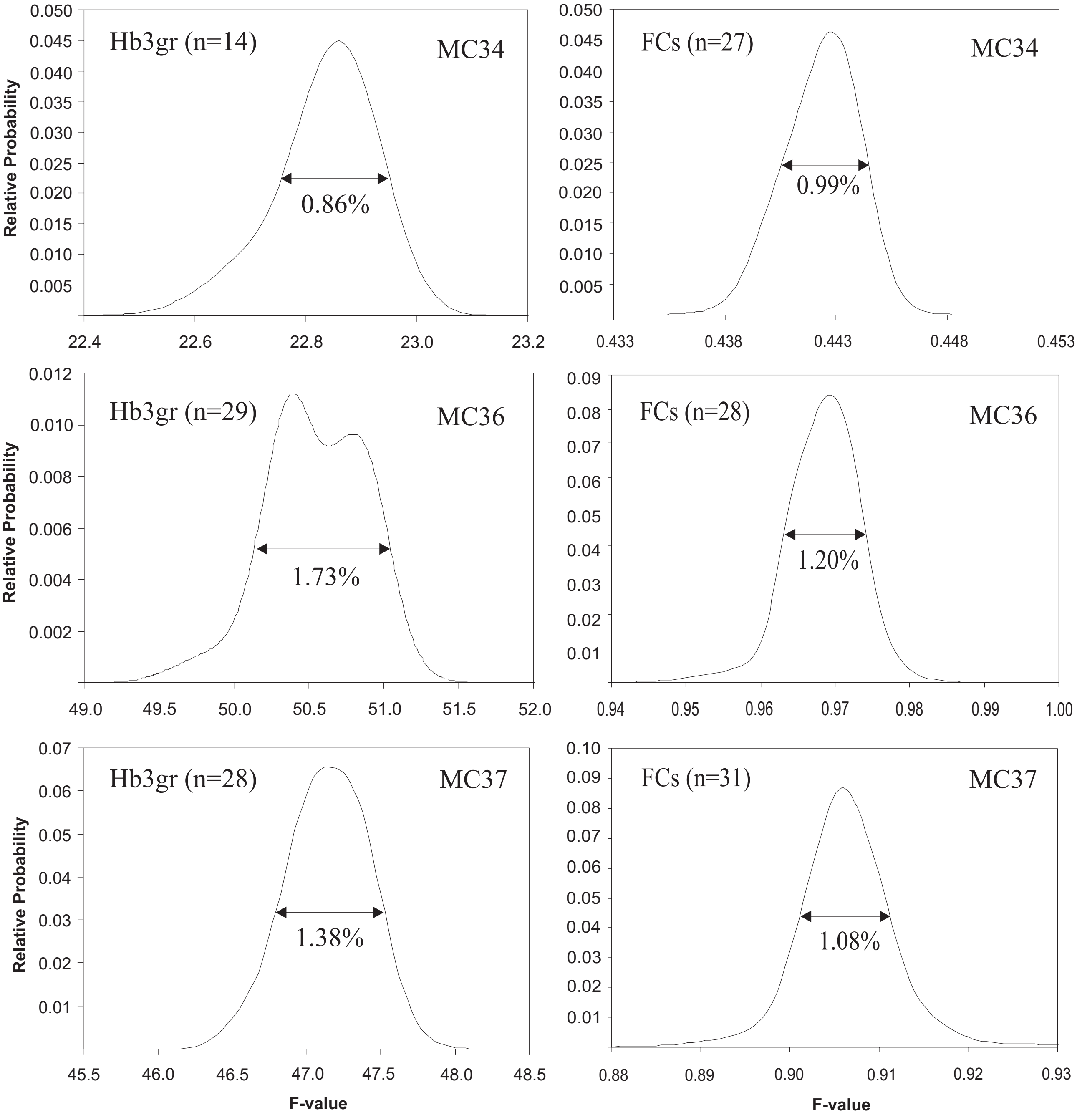

Fig. 1 : Jourdan et al.

Figure2

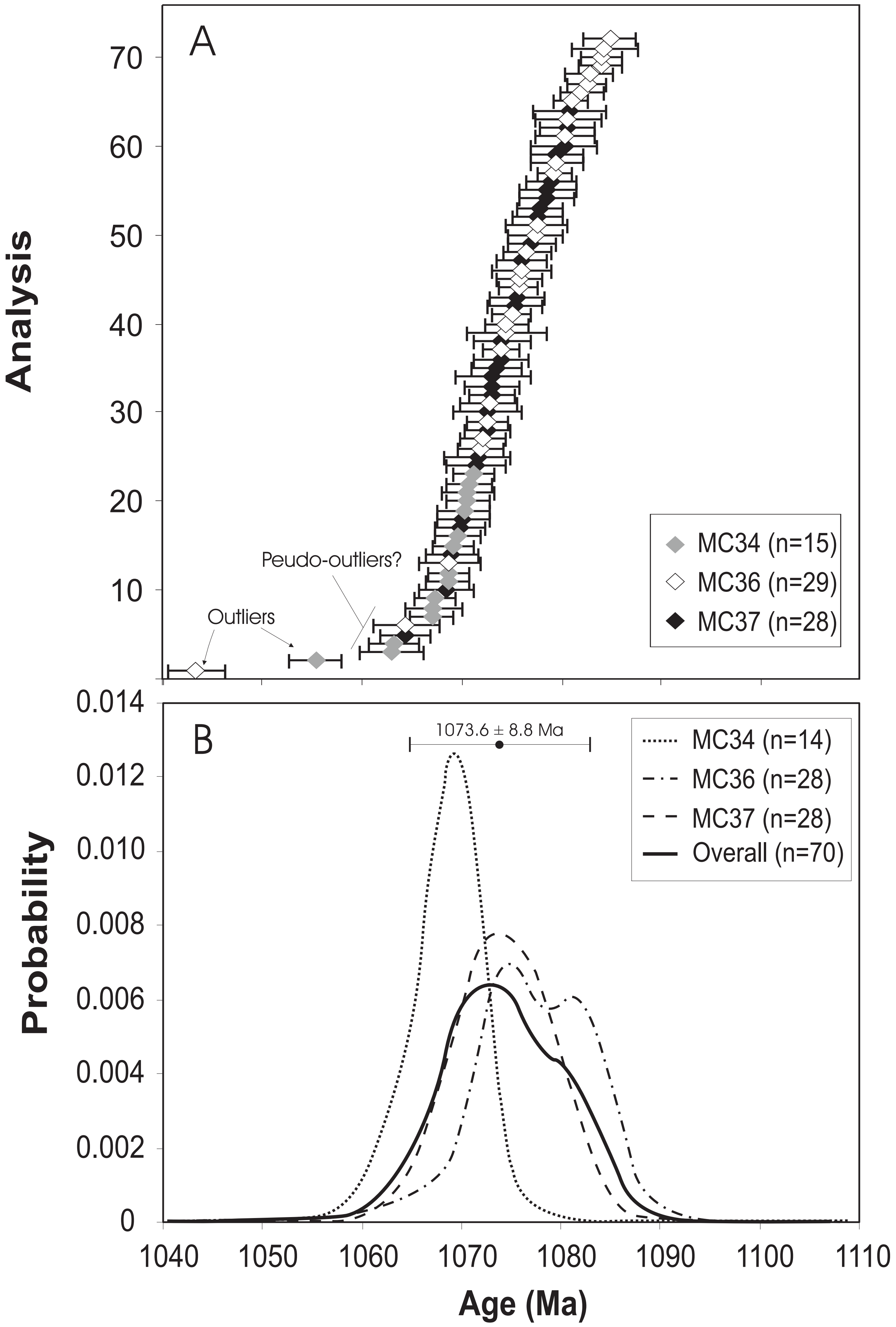
A
Analysis
70
60
50
40
30
20
10
Peudo-outliers?
Outliers
MC34 (n=15)
MC36 (n=29)
MC37 (n=28)
B
Probability
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0
1073.6 ± 8.8 Ma
MC34 (n=14)
MC36 (n=28)
MC37 (n=28)
Overall (n=70)
1040
1050
1060
1070
1080
1090
1100
1110
Age (Ma)

Table1

Standard	Package number	Sample name	Discrimination value	Atmospheric contamination (%)	$^{37}\mathrm{Ar}_{\mathrm{Ca}}/^{39}\mathrm{Ar}_{\mathrm{K}}$	$^{40}\mathrm{Ar}^{*}/^{39}\mathrm{Ar}$	Error	Age (Ma)	Error (1σ)
MC34 (J=0.035381 ±0.000033*)*									
Hb3gr	*1*	*1*	*1.00624*	*0.79*	*3.205*	*22.689*	*0.070*	*1063.2*	*2.5*
Hb3gr	*1*	*2*	*1.00624*	*0.92*	*3.146*	*22.681*	*0.090*	*1062.9*	*3.2*
Hb3gr	*1*	*3*	*1.00624*	*1.12*	*3.309*	*22.466*	*0.072*	*1055.3*	*2.6*
Hb3gr	1	4	1.00624	0.59	3.168	22.888	0.074	1070.2	2.6
Hb3gr	1	5	1.00624	0.79	3.156	22.857	0.056	1069.1	2.0
Hb3gr	1	6	1.00624	0.84	3.416	22.841	0.059	1068.6	2.1
Hb3gr	1	7	1.00624	0.79	3.282	22.801	0.083	1067.2	2.9
Hb3gr	1	8	1.00624	0.67	3.163	22.904	0.064	1070.8	2.3
Hb3gr	1	9	1.00624	0.52	3.416	22.898	0.073	1070.6	2.6
Hb3gr	1	10	1.00624	0.62	3.292	22.870	0.067	1069.6	2.4
Hb3gr	1	11	1.00624	0.60	3.023	22.844	0.060	1068.7	2.2
Hb3gr	1	12	1.00624	0.45	2.922	22.898	0.062	1070.6	2.2
FCs	2	e1	1.00624	0.73	0.007	0.443	0.001	-	-
FCs	2	e2	1.00624	0.31	0.008	0.443	0.001	-	-
FCs	2	e4	1.00624	0.66	0.008	0.441	0.001	-	-
FCs	2	e5	1.00714	0.90	0.007	0.441	0.002	-	-
FCs	2	e6	1.00714	0.58	0.007	0.442	0.001	-	-
FCs	2	e7	1.00714	0.40	0.009	0.443	0.001	-	-
FCs	2	e8	1.00714	1.08	0.009	0.441	0.002	-	-
FCs	2	e9	1.00714	0.85	0.008	0.440	0.001	-	-
FCs	2	e10	1.00714	0.76	0.008	0.442	0.002	-	-
FCs	2	e11	1.00714	1.04	0.009	0.444	0.001	-	-
FCs	2	e12	1.00714	0.85	0.008	0.442	0.001	-	-
FCs	2	e13	1.00714	0.63	0.008	0.442	0.001	-	-
FCs	2	e14	1.00714	1.08	0.007	0.443	0.001	-	-
FCs	2	e15	1.00714	0.49	0.007	0.444	0.001	-	-
FCs	2	e16	1.00714	0.84	0.007	0.441	0.001	-	-
FCs	2	e17	1.00714	0.42	0.008	0.444	0.001	-	-
FCs	2	e18	1.00714	0.22	0.007	0.444	0.001	-	-
FCs	2	e19	1.00714	0.97	0.008	0.440	0.001	-	-
FCs	2	e20	1.00714	1.61	0.008	0.443	0.001	-	-
FCs	2	e21	1.00714	0.39	0.006	0.443	0.001	-	-
FCs	2	e22	1.00714	0.41	0.008	0.443	0.002	-	-
FCs	2	e23	1.00714	0.51	0.008	0.442	0.001	-	-
FCs	2	e24	1.00714	1.00	0.008	0.442	0.001	-	-
FCs	2	e25	1.00714	0.58	0.011	0.442	0.001	-	-
FCs	2	e26	1.00714	0.53	0.008	0.443	0.001	-	-
FCs	2	e27	1.00714	0.52	0.007	0.443	0.001	-	-
FCs	2	e28	1.00714	0.53	0.007	0.442	0.001	-	-
Hb3gr	3	D1	1.00827	0.90	3.101	22.804	0.060	1067.3	2.1
Hb3gr	3	D2	1.00827	0.63	3.1	22.916	0.060	1071.2	2.1
Hb3gr	3	D3	1.00827	0.29	3.099	22.796	0.061	1067.0	2.2
MC36 (J=0.016162 0.000019)									
FCs	1	X1	1.00776	0.86	0.007	0.968	0.003	-	-
FCs	1	X2	1.00776	0.52	0.006	0.973	0.002	-	-
FCs	1	X3	1.00776	0.50	0.007	0.969	0.002	-	-
FCs	1	X4	1.00776	0.76	0.008	0.969	0.003	-	-
FCs	1	X5	1.00776	0.89	0.005	0.964	0.002	-	-
FCs	1	X6	1.00776	2.50	0.011	0.964	0.002	-	-
FCs	1	X7	1.00921	1.08	0.007	0.970	0.004	-	-
FCs	1	X8	1.00921	1.54	0.006	0.958	0.006	-	-
FCs	1	X9	1.00921	0.55	0.008	0.971	0.005	-	-
FCs	1	X10	1.00921	0.78	0.007	0.970	0.004	-	-
FCs	1	X11	1.00921	0.67	0.008	0.968	0.003	-	-
FCs	1	X12	1.00921	2.33	0.007	0.970	0.006	-	-
FCs	1	X13	1.00921	1.62	0.008	0.969	0.003	-	-
FCs	1	X14	1.00921	0.63	0.006	0.972	0.004	-	-
FCs	1	X15	1.00921	3.37	0.007	0.972	0.002	-	-
Hb3gr	2	Y1	1.00948	0.86	3.357	50.016	0.194	1068.8	3.1
Hb3gr	2	Y2	1.00948	0.56	3.275	50.248	0.126	1072.5	2.0
Hb3gr	2	Y3	1.00948	0.56	3.129	50.559	0.193	1077.5	3.1
Hb3gr	2	Y4	1.00948	0.56	3.087	50.465	0.189	1076.0	3.0
Hb3gr	2	i6	1.01188	0.98	3.109	50.368	0.246	1074.4	4.0
Hb3gr	2	I7	1.01132	0.57	3.301	50.259	0.174	1072.7	2.8
Hb3gr	2	I8	1.01132	0.37	3.154	50.887	0.156	1082.7	2.5
Hb3gr	2	I9	1.01132	0.53	3.13	50.370	0.131	1074.5	2.1
Hb3gr	2	i10	1.01132	0.68	3.118	50.225	0.146	1072.1	2.4
Hb3gr	2	i12	1.01132	0.45	3.187	50.773	0.111	1080.9	1.8
Hb3gr	2	I13	1.01132	0.81	3.173	50.962	0.130	1084.0	2.1
Hb3gr	2	i14	1.01132	0.31	3.162	50.961	0.138	1083.9	2.2

Standard	Package number	Sample number		Atmospheric contamination (%)	$^{37}Ar_{Ca}/^{39}Ar_K$	$^{40}Ar^*/^{39}Ar$	Error	Age (Ma)	Error (1σ)
Hb3gr	2	i15	1.01132	0.25	3.325	50.984	0.210	1084.3	3.4
Hb3gr	2	i16	1.01113	0.78	2.959	50.456	0.143	1075.8	2.3
Hb3gr	2	i17	1.01113	0.72	3.175	50.681	0.162	1079.5	2.6
Hb3gr	2	i18	1.01113	0.65	3.156	50.444	0.122	1075.7	2.0
Hb3gr	2	i19	1.01113	0.51	3.231	50.209	0.141	1071.9	2.3
Hb3gr	2	i20	1.01113	0.90	3.253	50.546	0.169	1077.3	2.7
Hb3gr	2	I21	1.01113	0.46	3.075	50.341	0.113	1074.0	1.8
Hb3gr	*2*	*i22*	*1.01113*	*1.22*	*3.385*	*49.747*	*0.207*	*1064.4*	*3.4*
Hb3gr	2	i23	1.01113	0.69	3.047	50.401	0.126	1075.0	2.0
Hb3gr	2	i23	1.01113	0.83	3.305	50.736	0.190	1080.3	3.0
Hb3gr	2	i25	1.01113	0.54	3.219	50.842	0.136	1082.0	2.2
Hb3gr	2	i26	1.01113	0.44	3.323	51.016	0.161	1084.8	2.6
Hb3gr	2	i27	1.01113	0.48	3.075	50.874	0.117	1082.5	1.9
Hb3gr	2	i28	1.00919	0.28	3.468	50.497	0.145	1076.5	2.3
Hb3gr	2	i29	1.00919	0.29	3.209	50.669	0.107	1079.3	1.7
Hb3gr	*2*	*i30*	*1.00919*	*0.52*	*2.797*	*48.451*	*0.170*	*1043.4*	*2.8*
Hb3gr	2	i31	1.00919	0.78	3.323	50.756	0.211	1080.7	3.4
FCs	3	Z1	1.00483	0.57	0.007	0.970	0.004	-	-
FCs	3	Z2	1.00483	0.46	0.007	0.968	0.004	-	-
FCs	3	Z3	1.00483	0.58	0.007	0.971	0.005	-	-
FCs	3	Z4	1.00483	0.68	0.007	0.967	0.005	-	-
FCs	3	Z5	1.00483	1.34	0.007	0.968	0.004	-	-
FCs	3	Z6	1.00483	0.69	0.007	0.966	0.003	-	-
FCs	3	Z7	1.00915	0.76	0.007	0.970	0.002	-	-
FCs	3	Z8	1.00915	1.28	0.007	0.966	0.004	-	-
FCs	3	Z9	1.00915	0.52	0.007	0.972	0.004	-	-
FCs	3	Z10	1.00915	1.24	0.007	0.962	0.005	-	-
FCs	3	Z11	1.00915	0.85	0.006	0.966	0.004	-	-
FCs	3	Z12	1.00705	0.36	0.007	0.971	0.004	-	-
FCs	3	Z13	1.00705	1.46	0.008	0.966	0.004	-	-
FCs	3	Z14	1.00705	0.52	0.006	0.971	0.005	-	-
MC37 (J=0.0172168±0.000018)									
Hb3gr	1	X1	1.00885	0.24	3.176	47.435	0.152	1079.5	2.6
Hb3gr	1	X2	1.00885	0.32	3.462	47.200	0.160	1075.5	2.8
Hb3gr	1	X3	1.00885	0.42	3.137	46.871	0.141	1069.8	2.4
Hb3gr	1	X4	1.00885	0.94	3.281	47.509	0.214	1080.8	3.7
Hb3gr	1	X5	1.00885	0.47	3.101	46.966	0.174	1071.5	3.0
Hb3gr	*1*	*X6*	*1.00885*	*0.83*	*3.156*	*46.552*	*0.140*	*1064.3*	*2.4*
Hb3gr	1	X7	1.00885	0.45	3.614	47.115	0.163	1074.0	2.8
Hb3gr	1	X8	1.00885	0.61	3.288	46.889	0.154	1070.1	2.7
Hb3gr	1	X9	1.00885	0.92	3.266	46.972	0.192	1071.6	3.3
Hb3gr	1	X10	1.00885	1.06	3.489	46.789	0.162	1068.4	2.8
Hb3gr	1	X11	1.00885	0.48	3.152	47.029	0.198	1072.6	3.4
Hb3gr	1	X12	1.00885	0.42	3.365	47.381	0.170	1078.6	2.9
Hb3gr	1	X13	1.00885	0.71	3.205	47.062	0.221	1073.1	3.8
Hb3gr	1	X14	1.00885	0.68	3.373	47.476	0.188	1080.2	3.2
Hb3gr	1	X15	1.00885	0.69	3.166	47.108	0.164	1073.9	2.8
Fcs	2	Y1	1.00770	0.62	0.008	0.904	0.003	-	-
Fcs	2	Y2	1.00770	0.84	0.007	0.907	0.002	-	-
Fcs	2	Y3	1.00770	1.00	0.008	0.906	0.002	-	-
Fcs	2	Y4	1.00770	1.66	0.008	0.897	0.004	-	-
Fcs	2	Y5	1.00770	0.67	0.007	0.904	0.002	-	-
Fcs	2	Y6	1.00770	1.02	0.008	0.918	0.010	-	-
Fcs	2	Y7	1.00770	0.91	0.008	0.905	0.003	-	-
Fcs	2	Y8	1.00770	0.62	0.007	0.903	0.003	-	-
Fcs	2	Y9	1.00770	1.06	0.007	0.902	0.002	-	-
Fcs	2	Y10	1.00770	1.27	0.007	0.900	0.002	-	-
Fcs	2	Y11	1.00770	0.31	0.007	0.910	0.002	-	-
Fcs	2	Y12	1.00770	0.07	0.007	0.915	0.003	-	-
Fcs	2	Y13	1.00770	0.37	0.008	0.909	0.003	-	-
Fcs	2	Y14	1.00770	1.66	0.008	0.906	0.002	-	-
Fcs	2	Y15	1.00770	0.82	0.007	0.905	0.003	-	-
Fcs	2	Y17	1.00770	0.68	0.009	0.906	0.003	-	-
Fcs	2	Y18	1.00770	0.31	0.009	0.910	0.002	-	-
Fcs	2	Y19	1.00770	0.29	0.007	0.908	0.002	-	-
Fcs	2	Y20	1.00770	0.49	0.009	0.910	0.004	-	-
Fcs	2	Y21	1.00770	0.25	0.007	0.911	0.002	-	-
Fcs	2	Y22	1.00770	0.67	0.007	0.907	0.003	-	-
Fcs	2	Y23	1.01141	0.99	0.008	0.903	0.002	-	-
Fcs	2	Y24	1.01141	0.65	0.009	0.912	0.004	-	-
Fcs	2	Y25	1.01141	0.83	0.008	0.905	0.004	-	-
Fcs	2	Y26	1.01141	0.58	0.008	0.906	0.004	-	-
Fcs	2	Y27	1.01141	1.88	0.012	0.899	0.009	-	-

Standard	Package number	Sample number		Atmospheric contamination (%)	$^{37}Ar_{Ca}/^{39}Ar_{K}$	$^{40}Ar^{*}/^{39}Ar$	Error	Age (Ma)	Error (1σ)
Fcs	2	Y28	1.01141	0.75	0.007	0.906	0.002	-	-
Fcs	2	Y29	1.01141	0.69	0.007	0.905	0.003	-	-
Fcs	2	Y30	1.01141	0.56	0.007	0.905	0.005	-	-
Fcs	2	Y31	1.01141	1.10	0.008	0.906	0.005	-	-
Fcs	2	Y32	1.01141	0.15	0.007	0.911	0.002	-	-
Hb3gr	3	Z1	1.00885	0.80	3.327	46.822	0.156	1069.0	2.7
Hb3gr	3	Z2	1.00885	0.69	3.117	47.026	0.129	1072.5	2.2
Hb3gr	3	Z3	1.00885	0.60	3.067	47.059	0.162	1073.1	2.8
Hb3gr	3	Z4	1.00885	0.51	3.328	47.493	0.163	1080.5	2.8
Hb3gr	3	Z5	1.00885	0.22	3.213	47.337	0.138	1077.8	2.4
Hb3gr	3	Z6	1.00885	0.27	3.105	47.082	0.142	1073.5	2.4
Hb3gr	3	Z7	1.00885	0.29	2.925	47.051	0.131	1072.9	2.3
Hb3gr	3	Z8	1.00770	0.31	3.141	47.371	0.160	1078.4	2.7
Hb3gr	3	Z9	1.00770	0.34	3.385	47.194	0.160	1075.4	2.7
Hb3gr	3	Z10	1.00770	0.38	3.077	47.230	0.143	1076.0	2.5
Hb3gr	3	Z11	1.00770	0.27	3.181	47.322	0.148	1077.6	2.6
Hb3gr	3	Z12	1.00770	0.47	3.34	47.284	0.139	1076.9	2.4
Hb3gr	3	Z13	1.00770	0.62	3.136	47.401	0.149	1078.9	2.6

Table 2

Irradiation	Standard	n	Duration (h)	F-value ($^{40}Ar^{*}/^{39}Ar_{K}$)	Error of the weighted mean	Standard deviation (1σ)	Relative Standard Deviation(%)	MSWD
MC34	FCs	27	150	0.4424	± 0.00020 (± 0.05%)	0.001144	*0.26%*	1.19
MC34	Hb3gr	14	150	22.842	± 0.017 (± 0.08%)	0.074712	*0.33%*	1.07
MC36	FCs	28	70	0.9686	± 0.00058 (± 0.06%)	0.002750	*0.28%*	0.96
MC36	Hb3gr	28	70	50.566	± 0.028 (± 0.05%)	0.315936	*0.62%*	4.13
MC37	FCs	31	70	0.9064	± 0.00046 (± 0.05%)	0.004396	*0.48%*	1.98
MC37	Hb3gr	28	70	47.134	± 0.030 (± 0.06%)	0.240521	*0.51%*	2.36

Calculation	$R_{FCs}^{Hb\,3\,gr}$	Error	Standard deviation	Relative standard deviation
MC34	51.632	0.046	0.215	0.42%
MC36	52.204	0.042	0.358	0.69%
MC37	51.999	0.042	0.366	0.70%

Table 3

Table 4A

Calculation	R^{Hb3gr}_{FCs}	Error	Age Hb3gr (Ma)	Error (1σ; excluding σλ))	Error (1σ; including σλ)
Arithmetic mean (± standard deviation)	51.945	± 0.290 (± 0.56%)	1073.6	± 6.5 (± 0.60%)	± 9.5 (± 0.88%)
(± standard error of the mean)		± 0.167 (± 0.33%)		± 5.3 (± 0.49%)	± 8.8 (± 0.82%)
Weighted mean (± weighted mean error)	51.962	± 0.025 (±0.05%)	1073.9	± 4.6 (± 0.43%)	± 8.4 (± 0.78%)

Table 4B

Calculation	R^{FCs}_{Hb3gr}	Error	Age Fcs (Ma)	Error (1σ; excluding σλ))	Error (1σ; including σλ)
Arithmetic mean (± standard deviation)	0.01925	± 0.00011 (±0.56%)	27.95	± 0.23 (0.83%)	± 0.32 (1.16%)
(± standard error of the mean)		± 0.00006 (±0.33%)		± 0.19 (0.68%)	± 0.30 (1.06%)
Weighted mean (± weighted mean error)	0.01924	± 0.00001 (±0.05%)	27.94	± 0.17 (0.61%)	± 0.28 (1.02%)