Neutron-induced $^{37}$Ar recoil ejection in Ca-rich minerals and implications for $^{40}$Ar/$^{39}$Ar dating

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Abstract: The $^{40}$Ar/$^{39}$Ar dating technique requires the transformation of $^{39}$K into $^{39}$Ar by neutron activation. Neutron activation has undesirable secondary effects such as interfering isotope production, and recoil of $^{39}$Ar and $^{37}$Ar atoms from their (dominant) targets of K and Ca. In most cases, the grains analysed are large enough (>50 µm) such that the amount of target atoms ejected from the grains is small and has a negligible effect on the ages obtained. However, increasing needs to date fine-grained rocks requires constraining, and in some cases correcting for, the effect of nuclear recoil. Previous quantitative studies of recoil loss focus mostly on $^{39}$Ar. However, $^{37}$Ar loss can affect the ages of Ca-rich minerals via interference corrections on $^{39}$Ar (and, to a lesser extent, $^{39}$Ar), yielding lower $^{40}$Ar*/$^{39}$ArK and, thus, an age spuriously too young. New results focused on $^{37}$Ar recoil by measuring the apparent age of multi-grain populations of Ca-rich minerals including Fish Canyon plagioclase (FCp) and Hb3gr hornblende, with discrete sizes ranging from 210 to <5 µm. We use previous results on sandine grains to correct for the $^{39}$Ar recoil loss. For the finest fractions, FCp and Hb3gr apparent ages are younger than the $^{39}$Ar recoil-corrected ages expected for these minerals, with a maximum deviation of $-40\%$ (FCp) and $-21\%$ (Hb3gr) reached for grains below 5 µm. We calculate $^{37}$Ar-depletion values ranging from approximately 30 to 91% and from approximately 28 to 98% for plagioclase and hornblende, respectively. This results in $x_0$ values (mean thickness of the partial depletion layer) of 3.3 ± 0.4 µm (2σ; FCp) and 3.6 ± 1.4 µm (Hb3gr), significantly higher than suggested by current models. The reason for the substantial $^{37}$Ar loss is not well understood, but might be related to the radiation damage caused to the mineral during irradiation. $x_0$ ($^{39}$Ar) and $x_0$ ($^{37}$Ar) values obtained in this study, along with crystal dimensions, can be used for correcting $^{40}$Ar/$^{39}$Ar ages from $^{37}$Ar and $^{39}$Ar recoil loss. We also discuss the relevance of our results to vacuum-encapsulation studies and isotopic redistribution in fine-grained minerals.

Supplementary material: Annex 1, 2 and 3 are available at www.geolsoc.org.uk

Background

$^{39}$Ar irradiation-induced recoil

The $^{40}$Ar/$^{39}$Ar dating technique is one of the most trusted dating techniques in the geological community. One of the downsides of $^{40}$Ar/$^{39}$Ar dating, however, is the necessity to bombard $^{39}$K with fast neutrons to convert the former into $^{39}$Ar via the reaction ($^{39}$K(n, p)$^{39}$Ar). This reaction has an undesirable effect as it recoils the daughter atom over a short distance (Turner & Cadogan 1974; Foland et al. 1984). This effect is well known and has been studied over more than three decades through experimental measurements (e.g. Turner & Cadogan 1974; Hess & Lippolt 1986; Villa 1997; Paine et al. 2006; Jourdan et al. 2007) and theoretical modelling (Onstott et al. 1995; Renne et al. 2005).

In theory, the effect of $^{39}$Ar recoil on $^{40}$Ar/$^{39}$Ar ages becomes noticeable when the grains analysed are smaller than approximately 50 µm (e.g. Paine et al. 2006). $^{39}$Ar recoil is responsible for the ejection of $^{39}$Ar out of the grains, yielding spuriously older ages, and/or $^{39}$Ar redistribution within the lattice of the grain, yielding complex age spectra. $^{39}$Ar recoil makes dating fine-grain material, such as cryptocrystalline rocks, altered minerals and clay material, a challenge (e.g. Foland et al. 1993; Hall et al. 1997; Haines & van der Pluijm 2008).

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In order to quantify recoil, Turner & Cadogan (1974) introduced the $x_0$ value, which corresponds to the thickness of the partial depletion layer surrounding the grain affected by recoil ejection loss. A similar method of quantifying recoil has been proposed by Jourdan et al. (2007) with the $d_0$ value; $d_0$ is the thickness of the nominal outer boundary layer completely depleted by recoil loss and is represented as a virtual 0-concentration layer in the outermost part of the grain. The benefit of $d_0$ over $x_0$ is that the former allows the calculation of the proportion of $^{39}$Ar lost for any size fraction and mineral shape directly. A relationship between the two values is given by:

$$d_0 = \frac{1}{2} x_0. \quad (1)$$

Experimental and theoretical studies suggest a mean thickness of the partial depletion layer ($x_0$) of approximately 0.08 $\mu$m (e.g. Turner & Cadogan 1974; Onstott et al. 1995) for silicates. This value corresponds to a mean recoil distance for the $^{39}$Ar atoms of approximately 0.16 $\mu$m, with values ranging from 0.14 to 0.18 $\mu$m depending on the mineral compositions (Renne et al. 2005). More recently, Paine et al. (2006) and Jourdan et al. (2007) directly measured the recoil-induced loss in biotite and sanidine grains, with a $x_0$ value ranging from about 210 to <5 $\mu$m. These studies showed that the loss effect is dependent on the mineral analysed. The $x_0$ value of 0.070 ± 0.024 $\mu$m measured for sanidine is in excellent agreement with previous estimations. The $x_0$ value of biotite is about an order of magnitude higher than sanidine, with a $x_0$ value of 0.92 ± 0.12 $\mu$m (cf. discussion in Jourdan et al. 2007). A comprehensive description of the $^{39}$Ar recoil effect is given, for instance, by Onstott et al. (1995), Renne et al. (2005) and Jourdan et al. (2007).

The specific case of $^{37}$Ar recoil

One overlooked effect of the neutron activation is the recoil of $^{37}$Ar (e.g. Jourdan et al. 2007 and references therein). $^{37}$Ar is produced from calcium by the reaction $^{40}$Ca($n, \alpha$)$^{37}$Ar. $^{37}$Ar$_{Ca}$ is unstable and decays with a half-life of 35.1 days (Renne & Norman 2001). Monitoring the $^{37}$Ar is crucial in Ca-rich samples as it allows for the correction for Ca-induced interferences on $^{36}$Ar produced by $^{40}$Ca($n, \alpha$)$^{36}$Ar and $^{39}$Ar $^{40}$Ca($n, \alpha$)$^{39}$Ar. ($^{36}$Ar/$^{39}$Ar)$_{Ca}$ is constant for a given neutron energy spectrum as both activation products derive from the same Ca isotope ($^{40}$Ca), whereas ($^{39}$Ar/$^{37}$Ar)$_{Ca}$ may vary between samples due to small enrichments of $^{40}$Ca* in old, K-rich samples.

Fortunately the latter effect is negligible in all but extreme cases. Values of ($^{39}$Ar/$^{37}$Ar)$_{Ca}$ and ($^{36}$Ar/$^{37}$Ar)$_{Ca}$ of $(7.60 \pm 0.09) \times 10^{-4}$ and $(2.70 \pm 0.02) \times 10^{-4}$, respectively, for the TRIGA reactor (Oregon State University, USA) have been determined reproducibly for over more than a decade (Renne et al. 2005). These ratios are obtained by using reference material usually irradiated along with the standards and samples. The assumption is made that all the $^{37}$Ar is derived from calcium.

The $^{39}$Ar$_K$ corrected for the $^{39}$Ar$_{Ca}$ contribution is given by:

$$^{39}$Ar$_{K} = ^{39}$Ar$_{m} - ^{37}$Ar$_{Ca} \left( \frac{^{39}Ar}{^{37}Ar} \right)_{Ca} \quad (2)$$

where $^{39}$Ar$_K$ is the $^{39}$Ar produced from $^{39}$K, $^{39}$Ar$_{Ca}$ is the total $^{39}$Ar measured, and $^{37}$Ar$_{Ca}$ is the total $^{37}$Ar$_{raw}$ measured and decay-corrected back to the time of irradiation. ($^{39}$Ar/$^{37}$Ar)$_{Ca}$ is the production ratio determined from irradiated standard materials.

The $^{36}$Ar$_{atm}$ is corrected for the $^{36}$Ar$_{Ca}$ contribution and is particularly important for the correction on trapped atmospheric argon given by the following combined equation:

$$^{40}$Ar* = $^{40}$Ar$_{m} - ^{39}$Ar$_{K} \left( \frac{^{40}Ar}{^{39}Ar} \right)_K - \left( \frac{^{40}Ar}{^{36}Ar} \right)_{atm} \times \left[ ^{36}$Ar$_{m} - ^{37}$Ar$_{Ca} \left( \frac{^{36}Ar}{^{37}Ar} \right)_{Ca} \right] \quad (3)$$

where $^{40}$Ar* is the radiogenic $^{40}$Ar, $m$ denotes measured, ($^{40}$Ar/$^{39}$Ar)$_K$ is the production ratio of K and ($^{40}$Ar/$^{36}$Ar)$_{atm}$ is the argon atmospheric composition. During this study, we used a value of 295.5 (Nier 1950) in our calculations (mass spectrometer discrimination and air corrections). We note that a more accurate value of 298.6 ± 0.3 has recently been determined by Lee et al. (2006), but using either value will have no influence on the results of our experiments (Renne et al. 2010). ($^{36}$Ar/$^{37}$Ar)$_{Ca}$ is the production ratio of Ca.

Based on preliminary recoil-experiment results on a plagioclase–sanidine mixture, Jourdan et al. (2007) suggested that $^{37}$Ar recoil effects might be much more important than their $^{39}$Ar counterparts for very fine-grain Ca-rich material, and might bias the age towards younger ages through interference correction disturbances. In addition, they showed that the $Q$ value (energy measurement) of 1.7483 MeV involved in the $^{40}$Ca($n, \alpha$)$^{37}$Ar nuclear reaction indicates that this reaction is much more prone to recoil than the $^{40}$Ca($n, \alpha$)$^{36}$Ar reaction,
with a $Q$ value of $-6.9912 \pm 0.0005$ MeV (see the values compiled by Renne et al. 2005). The decoupling of the $^{37}\text{Ar}_\text{Ca}$ and $^{36}\text{Ar}_\text{Ca}$ concentration within the grain due to ejection loss of $^{37}\text{Ar}_\text{Ca}$ by recoil will, therefore, produce spurious corrections to the $^{40}\text{Ar}^\ast$. Equations (2) and (3) show that $^{37}\text{Ar}$ recoil loss will induce an anomalously low $^{40}\text{Ar}^\ast / ^{39}\text{Ar}_K$ ratio and, thus, bias the age towards younger values.

Here, we carried out $^{40}\text{Ar}/^{39}\text{Ar}$ measurement on Ca-rich minerals to test the effect of the $^{37}\text{Ar}$ recoil loss on $^{40}\text{Ar}/^{39}\text{Ar}$ ages. We studied multi-grain aliquots of hornblende and plagioclase with discrete sizes ranging from 210 to $<5 \mu$m, and we calculated the $d_0$ and $x_0$ values of $^{37}\text{Ar}$ for these two minerals.

**Sample description**

**Fish Canyon plagioclase (FCp)**

FCp comes from the same tuff as widely used Fish Canyon sanidine (FCs) standards (e.g. Renne et al. 1998). The plagioclase grains are slightly zoned and have a homogenous composition of An33$\pm$1 (e.g. Johnson & Rutherford 1989), although some An60 zones have been detected (Bachmann et al. 2002). The plagioclase has a CaO and K$_2$O mean composition of 6.60 wt% and 0.79 wt%, respectively, and a Ca/K atomic ratio of approximately 7 (Johnson & Rutherford 1989). Recent $^{40}\text{Ar}/^{39}\text{Ar}$ measurements by Bachmann et al. (2007) yielded an apparent plateau age of 28.26 $\pm$ 0.20 Ma (2$\sigma$) and an apparent total fusion mean age of 28.31 $\pm$ 0.22 Ma ($n = 3$), relative to FCs at 28.02 Ma (Renne et al. 1998) and using the decay constants of Steiger & Jäger (1977). However, these ages were interpreted as reflecting minor inherited $^{40}\text{Ar}^\ast$ in FCp and not the true age of the plagioclase and Fish Canyon tuff eruption. As a side product of this study, we have measured the age of FCp relatively to FCs. We used 10 multi-grain aliquots of the three coarsest plagioclase fractions, with grains ranging between $>150$ and 85 $\mu$m ($n = 10$). These grain sizes are considered large enough to remain unaffected by the effect of recoil loss (Paine et al. 2006; Jourdan et al. 2007). The 10 FCp aliquots yielded apparent ages ranging from 27.83 $\pm$ 0.26 to 28.12 $\pm$ 0.25 Ma (2$\sigma$). These data are largely concordant within error, with a MSWD of 0.46 and $P$ of 0.90, and yield a weighted mean age of 28.00 $\pm$ 0.08 Ma (2$\sigma$), indistinguishable from the age of the FCs monitor. Interestingly, our particular batch of FCp does not contain any inherited $^{40}\text{Ar}^\ast$ compared to FCp investigated by Bachmann et al. (2007), and shows that, in this case, plagioclase and sanidine both record the age of the Fish Canyon tuff eruption.

Using the recently published value of the K decay constants (Renne et al. 2010, 2011) yields an absolute age of 28.29 $\pm$ 0.08 Ma. Nevertheless, the accurate age of FCp is not essential for this study as the ages obtained for the various fractions is normalized to the mean age obtained for the three coarser fractions, and only the departure from this baseline value will be of interest to study recoil effects.

**Hb3gr hornblende**

The Hb3gr hornblende comes from the Lone Grove pluton (Texas, USA) and is used as a fluorescence monitor for dating samples generally older than few hundred million years (e.g. Zartman 1964; Turner et al. 1971). The Hb3gr standard has been selected in this study as the hornblende shows a homogenous chemical composition with constant K$_2$O (1.46 $\pm$ 0.06 wt%) and CaO (10.49 $\pm$ 0.22 wt%) values, Ca/K ratio (6.19 $\pm$ 0.25) (Jourdan & Renne 2007) and is homogenous in age at the single-grain level, with a good reproducibility from grain to grain and with a $F$ value ($^{40}\text{Ar}^\ast / ^{39}\text{Ar}_K$) mean standard deviation of 0.49%. Hb3gr yielded a $^{40}\text{Ar}/^{39}\text{Ar}$ age of 1074 $\pm$ 11 Ma (2$\sigma$; Jourdan et al. 2006) using the decay constant of Steiger & Jäger (1977) and relative to FCs at 28.02 Ma. The adopted age is in agreement with a primary K/Ar age of 1072 $\pm$ 14 Ma (Turner et al. 1971). As for FCs, the apparent age of the Hb3gr standard has been recently revised using a new set of decay constants (Renne et al. 2010) and has an absolute age of 1081.4 $\pm$ 2.2 Ma, but, as explained for FCp, this is not directly relevant to this study.

**Methods**

**Sample preparation**

FCp comes from a 250–500 $\mu$m plagioclase separate (BYO-Nov97) isolated during the initial preparation of the FC sanidine standard at the Berkeley Geochronology Center, using heavy liquids. Plagioclase grains were further hand-picked, using a binocular microscope, in order to select the more transparent and alteration- and inclusion-free grains. To obtain a pure plagioclase (sanidine-free) fraction, we further picked the plagioclase in clove oil (nominal refractive index of 1.535) under plane polarized light. Under clove oil, plagioclase is easily distinguished from sanidine by using the Becke line test. The plagioclase grains were leached in dilute HF acid (2N) for 5 min and rinsed in distilled water for 20 min. We used a total of 400 mg for this experiment.
The hornblende grains come from a cleaned version of the original Hb3gr provided by C. Roddick and named PP-20. The grains range in size from 200 to 250 μm. White inclusions with an age approximately 7.5% younger (e. 990 Ma) than the nominal age of Hb3gr have been reported by Zartman (1964). However, the inclusion-bearing grains were further removed by stringent hand-picking.

Both FCp and Hb3gr grains were crushed and sieved in discrete size fractions ranging from 150 to <5 μm and from 250 to <5 μm for plagioclase and hornblende, respectively. Below 50 μm, sieving was performed in alcohol to facilitate percolation of the grains through the sieve-cloth. All FCp fractions were analysed as multi-grain aliquots, whereas Hb3gr grains were analysed as single grains from 250 to 150 μm, and as multi-grains below 150 μm to obtain sufficiently large Ar ion beams for optimal precision in the measurement of Ar isotopes. For Hb3gr, each sieved fraction was further removed by stringent hand-picking.

Irradiation

Two irradiations of 10 h (irr. 346-FJ; FCp) and 90 h in duration (irr. 342-FJ; Hb3gr) were performed in the Cd-shielded (to minimize undesirable isotopic interference reactions caused by thermal neutrons) CLICIT facility of the TRIGA reactor at the Oregon State University, USA. For irradiation 346-FJ and 342-FJ, sample batches were loaded into wells within, respectively, three and two aluminium discs of 1.9 cm diameter and 0.3 cm depth. Each batch was loaded separately in one–six individual wells. FCs grains (250–500 μm) were used as the neutron fluence monitor and were loaded in five wells bracketing the fractions of FCp. Grains of Hb3gr (210–250 μm) were loaded into five wells bracketing the various fractions of Hb3gr. Each of the discs was wrapped in Al-foil and placed in a silica tube. Each of the tubes was sealed at atmospheric pressure and sent for irradiation with other unknown samples.

We calculated the J values relative to FCs at 28.02 Ma (Renne et al. 1998) and Hb3gr at 1072 Ma (Turner et al. 1971), and used the decay constants of Steiger & Jager (1977). The J values consist of the weighted mean and standard deviation of J values from bracketing wells across the entire disc. The J values of disc 1 and 2 vary from 0.002652 ± 0.000004 to 0.002656 ± 0.000004 for the FCp experiment, and the J values of the three discs vary from 0.023654 ± 0.000059 to 0.023690 ± 0.000065 for the Hb3gr experiment. The correction factors for interfering isotopes correspond to the weighted mean of 10 years of measurements of K–Fe and CaSi2 glasses, and CaF2 fluorite, in the TRIGA reactor: they are \(\frac{39\text{Ar}}{37\text{Ar}} \text{Ca} = (7.60 \pm 0.09) \times 10^{-4}\), \(\frac{36\text{Ar}}{37\text{Ar}} \text{Ca} = (2.70 \pm 0.02) \times 10^{-4}\); and \(\frac{40\text{Ar}}{39\text{Ar}} \text{K} = (7.30 \pm 0.90) \times 10^{-4}\).

Analytical technique

\(^{40}\text{Ar}/^{39}\text{Ar}\) analyses were performed at the Berkeley Geochronology Center between 5 and 6 months after irradiation. The grains were degassed using a CO₂ laser, and the gas was purified in a stainless steel extraction line using two C-50 getters and a cryogenic condensation trap. Ar isotopes were measured in static mode using a MAP 215-50 mass spectrometer with a Balzers electron multiplier, mostly using 10 cycles of peak-hopping. A more complete description of the mass spectrometers and extraction line is given in Renne et al. (1998). Blank measurements were generally obtained every three samples. All of the results here were obtained by using the conventional \(^{40}\text{Ar}/^{39}\text{Ar}\) value of 295.5 ± 0.5 (Nier 1950) to correct for the instrumental mass discrimination and \(^{40}\text{Ar}\) atmospheric contamination. Mass discrimination was monitored every nine steps using an automated air pipette, and yielded mean values of 1.0051 ± 0.0022 and 1.0078 ± 0.0024 daltons (Da) for the FCp and Hb3gr experiments, respectively.

Our criteria for the plateau and mini-plateau ages are as follows: plateaus and mini-plateau ages are calculated using the mean of all the plateau steps, each weighted by the inverse variance of their error. Integrated ages (that compare with total fusion ages) are calculated using the total gas (i.e. summed volumes) for each Ar isotope.

Results

Fish Canyon plagioclase (FCp)

For each fraction, we obtained total fusion ages for two–eight aliquots. A weighted mean age and associated error were calculated for each size fraction, and are given in Table 1. Total fusion weighted mean ages range from 27.97 ± 0.17 Ma (2σ) for
Table 1. Summary table for FCp. The information for individual fractions includes the number of analyses, the total fusion weighted mean age (2σ), the deviation from the $^{39}$Ar recoil-corrected theoretical age, available plateau age and integrated age.

| Size range (μm) | Total fusion experiments | Step-heating experiments |
|----------------|--------------------------|--------------------------|
|                | $n$ | Mean age ± 2σ (Ma) | Deviation ± 2σ (%) | % $^{39}$Ar | Plateau age ± 2σ (Ma) | Integrated age ± 2σ (Ma) | $F(^{37}$Ar) ± 2σ (%) | $d_0$ (plagioclase) ± 2σ (μm) |
| 210–150        | 3   | 27.97 ± 0.17 | −0.2% ± 0.7 | – | – | – | – | – |
| 150–125        | 3   | 28.02 ± 0.15 | −0.1% ± 0.6 | – | – | – | – | – |
| 125–85         | 4   | 28.01 ± 0.10 | −0.1% ± 0.5 | – | – | – | – | – |
| 85–74          | 4   | 28.10 ± 0.12 | 0.1% ± 0.5 | 100 | 28.19 ± 0.16 | 28.21 ± 0.22 | – | – |
| 74–63          | 4   | 28.14 ± 0.12 | 0.2% ± 0.5 | – | – | – | – | – |
| 63–53          | 3   | 28.07 ± 0.14 | 0.0% ± 0.6 | 100 | 28.13 ± 0.16 | 28.18 ± 0.24 | – | – |
| 53–38          | 8   | 28.26 ± 0.12 | 0.5% ± 0.5 | 100 | 28.14 ± 0.16 | 28.13 ± 0.22 | – | – |
| 38–34          | 2   | 28.24 ± 0.24 | 0.4% ± 0.9 | – | – | – | – | – |
| 34–28          | 4   | 28.35 ± 0.16 | 0.7% ± 0.6 | 64 | 28.42 ± 0.2 | 28.27 ± 0.26 | – | – |
| 28–22          | 3   | 27.78 ± 0.18 | −1.5% ± 0.7 | – | – | – | – | – |
| 22–15          | 5   | 28.41 ± 0.41 | 0.5% ± 1.5 | 100 | 23.6 ± 3.0 | 22 ± 6 | 29 ± 4 | 1.78 ± 0.5 |
| 15–10          | 3   | 26.8 ± 2.0 | −5.6% ± 7.1 | 84 | 28.10 ± 0.34 | 26.7 ± 0.4 | 48 ± 9 | 1.43 ± 0.82 |
| 10–5           | 4   | 28.03 ± 0.29 | −2.1% ± 1.0 | 99 | 27.9 ± 2.0 | 21 ± 8 | 44 ± 4 | 0.6 ± 0.18 |
| <5             | 3   | 17.58 ± 0.69 | −39.8% ± 2.4 | – | – | – | – | 91 ± 2 | 1.63 ± 0.14 |

For each fraction, $^{37}$Ar loss ($F(^{37}$Ar) = depletion factor; %) and resulting total depletion layer thickness ($d_0$ (plagioclase); μm) have been calculated and are indicated at 2σ. % $^{39}$Ar represents the cumulative percentage of $^{39}$Ar released and included in the plateau and mini-plateau age calculations.
Fig. 1. (a) Relationship between the age and the grain size of weighted mean ages (2σ) of FC sanidine. Black-filled circle, total fusion age; green-filled square, plateau age; red-filled circle, integrated age. The nominal age of FCp is indicated by the purple-filled box. The red dashed curve represents the age expected for plagioclase affected by $^{39}$Ar recoil alone. (b) Same as (a) with a magnified scale. (c) Relative age difference between the measured age and the nominal (blue-filled circle) and $^{39}$Ar recoil-corrected (red-filled circle) age of FCp. The error bars include both the analytical measurement and the age of the monitor uncertainties.
be older. We calculated the deviation (\(\Delta_{FCP}\)) from the nominal age of FCp, although we note that the centre of mass of the age tends to be older. We calculated the deviation (\(\Delta_{FCP}\)) from the nominal value by including both the uncertainty on the measured age and on the age of FCp (28.00 ± 0.08 Ma; \(\Delta_{FCP}\) ranges from 0.25 ± 0.64% to 1.46 ± 0.85%). However, previous studies of \(^{39}\)Ar recoil showed that \(^{39}\)Ar loss is proportional to the size of the grains below 50 \(\mu m\); as the grain size diminishes, measured ages will become increasingly older than the nominal age. Recoil loss age correction has been calculated using the correction equation for feldspar rearranged from Jourdan et al. (2007):

\[
t_c \approx t_{FCP} \times 1.03h^{-0.007}
\]

\(\approx t_{FCP} \times (0.16699h^{-0.9918})\)  (4)

where \(t_c\) is the age of FCp corrected to account for \(^{39}\)Ar recoil loss, \(t_{FCP}\) is the nominal age of FCp at 28.00 Ma and \(h\) is the mean length of a parallelepiped grain with dimensions of \(h:1.2h:1.5h\) adopted for feldspar. Note that these equations are approximations and are used for graphical representation only (see the figures in this section).

The apparent ages measured for FCp match to a better extent the theoretical age of FCp if the latter is corrected for \(^{39}\)Ar recoil loss, \(t_{FCP}\) is the nominal age of FCp at 28.00 Ma and \(h\) is the mean length of a parallelepiped grain with dimensions of \(h:1.2h:1.5h\) adopted for feldspar. Note that these equations are approximations and are used for graphical representation only (see the figures in this section).

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fractions, with an age of $909 \pm 27$ Ma corresponding to $D_{\text{HB3gr}}$ and $D_{\text{HB3gr(corr.)}}$ of $2_{-15}^{+15}$ and $2_{-21}^{+2}$, respectively.

The $[\text{Ca}/\text{K}]_{\text{Ar}}$ range from $-1 \pm 7$ to $9 \pm 4$ ($n = 66$; Fig. 2b) with a MSWD and $P$ values of 1.16 and 0.18, respectively, suggesting that the Ca/K composition is homogenous among all aliquots. The $[\text{Ca}/\text{K}]_{\text{Ar}}$ ratios are indistinguishable from the HB3gr $[\text{Ca}/\text{K}]_{\text{EMP}}$ microprobe values, ranging from 5.1 to 6.8 (Jourdan & Renne 2007). No correlation between $[\text{Ca}/\text{K}]_{\text{Ar}}$ and the grain size is observed, although a scatter is present. We note that the $37\text{Ar}_{\text{em}}$ measured (before correction of $37\text{Ar}$ decay) shows a very low ion beam signal for most fractions, rendering the calculation of $[\text{Ca}/\text{K}]_{\text{Ar}}$ a difficult task. Below 5 $\mu$m, the $[\text{Ca}/\text{K}]_{\text{Ar}}$ ratio shows values with large error bars due to a $37\text{Ar}_{\text{em}}$ with a value close to 0 due to the small quantity of material analysed at this size fraction.

**Discussion**

**Recoil in Fish Canyon plagioclase (FCp)**

$37\text{Ar}$ recoil loss. The 28–22 $\mu$m, 10–5 $\mu$m and, especially, the $<5$ $\mu$m fractions show ages statistically younger than what would be expected for ages affected by recoil-induced $39\text{Ar}$ loss alone. As proposed by Jourdan et al. (2007), this effect is likely to be due to $37\text{Ar}$ loss caused by the recoil-induced ejection of $37\text{Ar}$ atoms following the reaction $[^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}]$. $37\text{Ar}_{\text{Ca}}$ loss causes under-correction of the $39\text{Ar}_{\text{Ca}}$ and especially $36\text{Ar}_{\text{Ca}}$, interferences, ultimately yielding a low $40\text{Ar}^{*}/39\text{Ar}_{\text{K}}$ ratio and a younger age (see the detail in Jourdan et al. 2007). To estimate the proportion of $37\text{Ar}$ lost from the grains, we assume that the age shift is entirely due to $37\text{Ar}$ loss and we use the equations of Jourdan et al. (2007), indicated below and adapted for any $40\text{Ar}^{*}/36\text{Ar}$ atmospheric ratios.
Fig. 3. Relationship between the age and the grain size of Hb3gr hornblende. The caption description is similar to that of Figure 1.
Table 2. Summary table for Hb3gr. The caption is similar to that of Table 1

| Size range (μm) | Total fusion experiments | Step-heating experiments | $F(^{37}$Ar) ± 2σ (%) | $d_0$ ± 2σ (μm) |
|----------------|--------------------------|--------------------------|-----------------------|-----------------|
|                | $n$ | Mean age ± 2σ (Ma) | Deviation ± 2σ (%) | % $^{39}$Ar | Plateau age ± 2σ (Ma) | Integrated age ± 2σ (Ma) |                |
| 212+           | 3   | 1075 ± 5         | 0.2% ± 1.1          | –        | –        | –                  | –              |
| 212–180        | 3   | 1072 ± 4         | −0.1% ± 1.1         | –        | –        | –                  | –              |
| 180–150        | 3   | 1076 ± 5         | 0.2% ± 1.1          | –        | –        | –                  | –              |
| 150–125        | 3   | 1068 ± 6         | −0.5% ± 1.2         | –        | –        | –                  | –              |
| 125–106        | 3   | 1071 ± 6         | −0.2% ± 1.2         | –        | –        | –                  | –              |
| 106–85         | 3   | 1071 ± 5         | −0.3% ± 1.1         | –        | –        | –                  | –              |
| 85–74          | 3   | 1065 ± 8         | −0.9% ± 1.3         | –        | –        | –                  | –              |
| 74–63          | 3   | 1079 ± 7         | 0.4% ± 1.2          | –        | –        | –                  | –              |
| 63–53          | 3   | 1065 ± 7         | −1.0% ± 1.2         | –        | –        | –                  | 42 ± 36        |
| 53–38          | 5   | 1071 ± 4         | −0.5% ± 1.1         | 91       | 1068 ± 4 | 1066 ± 3         | 3.5 ± 3.0      |
| 38–34          | 1   | 1075 ± 10        | −0.2% ± 1.4         | –        | –        | –                  | 41 ± 14        |
| 34–28          | 5   | 1072 ± 4         | −0.6% ± 1.1         | –        | –        | –                  | 3.4 ± 1.8      |
| 28–22          | 3   | 1044 ± 46        | −3.3% ± 4.4         | –        | –        | –                  | 28 ± 9         |
| 22–15          | 2   | 1048 ± 67        | −3.1% ± 6.3         | –        | –        | –                  | 49.9 ± 24      |
| 15–10          | 3   | 1065 ± 41        | −2.0% ± 3.9         | –        | –        | –                  | 80 ± 14        |
| 10–5           | 7   | 1069 ± 15        | −2.5% ± 1.7         | 71       | 1074 ± 4 | 1069 ± 4         | 5.7 ± 2.0      |
| <5             | 2   | 909 ± 27         | −18.0% ± 2.6        | –        | –        | –                  | 1.4 ± 1.3      |

F. JOURDAN & P. R. RENNE
First, we calculated the theoretical quantity of \(^{37}\text{Ar}\) that should be present in the sample based on what would be expected to be obtained for the \(^{39}\text{Ar}\) recoil-corrected age of FCp for a given grain size: 

\[
^{37}\text{Ar}_t = \frac{\left( e^{k \text{FCp}} - 1 \right)}{J} \left\{ \begin{array}{l}
\frac{40}{39} \text{Ar} \\
\frac{36}{39} \text{Ar} \end{array} \right\}_\text{K} - \left( \frac{40}{39} \text{Ar} \right)_\text{m} + \frac{40}{36} \text{Ar} \times \left( \frac{36}{39} \text{Ar} \right)_\text{m} \\
+ \frac{40}{36} \text{Ar} \times \left( \frac{36}{39} \text{Ar} \right)_\text{Ca}
\]

where \(^{37}\text{Ar}_t\) is the theoretical relative abundance of \(^{37}\text{Ar}\) expected for a given grain size and proportional to \(^{40}\text{Ar}_m\), \(^{39}\text{Ar}_c\) and \(^{36}\text{Ar}_m\). \(^{40}\text{Ar}_m\) and \(^{36}\text{Ar}_m\) are the measured \(^{40}\text{Ar}\) and \(^{36}\text{Ar}\) (corrected for blank and mass fractionation), respectively. \(k\) is the total decay constant of \(^{40}\text{K}\), and \(J\) is the neutron fluence parameter determined from a co-irradiated standard of known age. \((^{39}\text{Ar}/^{37}\text{Ar})_\text{Ca}, (^{36}\text{Ar}/^{39}\text{Ar})_\text{Ca}\) and \((^{40}\text{Ar}/^{39}\text{Ar})_\text{K}\) are the interference correction factors, the values of which are given in the Methods section. \(^{39}\text{Ar}_c\) is the \(^{39}\text{Ar}\) corrected for recoil-induced depletion of a given size fraction using:

\[
^{39}\text{Ar}_c = \frac{^{39}\text{Ar}_m}{1 - F(^{39}\text{Ar})} = ^{39}\text{Ar}_m \times D_f(^{39}\text{Ar}) \quad (6)
\]
where \( D_1^{(39)\text{Ar}} \) corresponds to the \( ^{39}\text{Ar} \) depletion factor and \( F^{(39)\text{Ar}} \) corresponds to the relative fractional loss of \( ^{39}\text{Ar} \). Both values are related and calculated for a given fraction size, shape and mineral composition. Note that the \( D_i^{(39)\text{Ar}} \) values reported by Jourdan et al. (2007) correspond, in fact, to \( F^{(39)\text{Ar}} \) as per equation (6). In this study, we use the \( F^{(39)\text{Ar}} \) values obtained for sanidine crystals, which should represent a good estimate for plagioclase and hornblende crystals, and can be approximated by:

\[
F^{(39)\text{Ar}} \approx 0.1699e^{-0.991b}.
\]  

(7)

The relative loss of \( ^{39}\text{Ar} \) is then given by:

Relative \( ^{39}\text{Ar} \) fractional loss

\[
= F^{(39)\text{Ar}} = \frac{37\text{Ar}_i - 37\text{Ar}_m}{37\text{Ar}_i}.
\]  

(8)

The \( ^{37}\text{Ar}_c \) corrected (equal to the above theoretical \( ^{37}\text{Ar}_i \)) for recoil-induced depletion for a given size fraction, rearranged from equation (8), is given by:

\[
^{37}\text{Ar}_c = ^{37}\text{Ar}_i = \frac{37\text{Ar}_m}{1 - F^{(37)\text{Ar}}}.
\]  

(9)

where \( F^{(37)\text{Ar}}_{\text{FCP}} \) can be approximated by the following relationship fitted to the depletion trend given by the present data (Fig 4a):

\[
F^{(37)\text{Ar}} \approx 2.1575h^{-0.617}.
\]  

(10)

We calculated the \( F^{(37)\text{Ar}} \) for the four fractions with negative \( \Delta P_{\text{FCP}(\text{corr.})} \): namely 28–22, 15–10, 10–5 and <5 \( \mu \text{m} \). \( F^{(37)\text{Ar}} \) weighted mean values are accompanied by their uncertainty, expressed as the standard error of the mean (i.e. the standard deviation divided by the square root of the number of samples) (Fig. 4a). \( F^{(37)\text{Ar}} \) is inversely proportional to the size of the grain fractions, with \( F^{(37)\text{Ar}} \) ranging from 29 ± 4% (28–22 \( \mu \text{m} \)) to 91.0 ± 1.2% (<5 \( \mu \text{m} \); Table 1).

As stressed during our previous study on \( ^{39}\text{Ar} \) loss (Jourdan et al. 2007), \( ^{39}\text{Ar} \) or \( ^{37}\text{Ar} \) atoms ejected out of the grains by recoil can be reimplanted at the surface of other grains in close contact and, thus, not lost despite ejection. In addition, \( ^{39}\text{Ar} \) and \( ^{37}\text{Ar} \) atoms can be displaced in low-retentivity sites (including the reimplanted atoms) and can be lost by thermal diffusion due to the temperature reached in the reactor or during the extraction line bake-out (in both cases up to c. 200 °C; Dong et al. 1995; McDougall & Harrison 1999), especially for the very fine fractions. However, simple diffusion calculations using standard \( D_o \) (Frequency factor) and \( E_o \) (Activation energy) values for feldspar and amphibole show that spheres of 5 \( \mu \text{m} \) diameter heated for 40 and 100 h, respectively, cause a maximum fractional loss of 0.005% for the feldspar and no loss for the hornblende. Nevertheless, the results obtained in this study indicate the total \( ^{37}\text{Ar} \) loss directly or indirectly caused by the irradiation process, and that we regroup here under the term ‘recoil loss’.

\( ^{37}\text{Ar total depletion thickness.} \) Based on a simple geometric relation, \( F^{(37)\text{Ar}} \) can be converted into \( ^{37}\text{Ar} \) loss from a parallelepiped structure and converted into the thickness \( (d_0) \) of a 0-concentration layer in the outermost part of the parallelepiped grain (Jourdan et al. 2007) as:

\[
F^{(37)\text{Ar}}_{\text{parallelepiped}} = 1 - \left(\frac{L - 2d_0}{Lw} + 2d_0(h - 2d_0)\right). \quad (11)
\]

Equation (11) is solvable analytically as a third degree polynomial. \( L, w \) and \( h \) represent the length, width and height of the grain, respectively:

\[
-8d_0^3 + 4(w + L)d_0^2 - 2(w + L)d_0 + (Lwh(D_{\text{par}})) = 0. \quad (12)
\]

For each grain size, the mean \( d_0 \) value corresponds to the average of the individual \( d_0 \) value calculated for each batch, weighted by the relative error on the ages associated for each batch. Uncertainties are reported as the standard error of the mean (\( 2\sigma \)). For each batch, we used a parallelepiped of dimensions \( h:1.2h:1.5h \). Mean \( d_0 \) values obtained for FCP ranges from 1.6 ± 0.13 to 0.60 ± 0.17 \( \mu \text{m} \) (\( 2\sigma \); Table 1), and yielded a weighted mean and standard error of the mean of 1.27 ± 0.53 \( \mu \text{m} \) (Fig. 5a). The MSWD (31) and \( P (<0.001) \) values obtained for this group indicate that the data belong to more than one population and that the scatter of the data cannot be explained by individual uncertainty alone. A closer look at the \( d_0 \) values suggest that only the 5–10 \( \mu \text{m} \) fraction shows a \( d_0 \) value (0.6 ± 0.1 \( \mu \text{m} \)) that departs from an otherwise homogeneous population. If the 5–10 \( \mu \text{m} \) fraction is omitted in the calculation, the three other \( d_0 \) values give a MSWD of 0.30 and \( P (0.74) \), and a weighted mean and standard error of the mean \( d_0 \) of \( (^{37}\text{Ar})_{\text{FCP}} \) of 1.63 ± 0.21 \( \mu \text{m} \). We shall see that the result obtained for hornblende is similar to this value, further justifying rejection of the \( d_0 \) obtained on the 5–10 \( \mu \text{m} \) fraction.

The weighted mean of the \( d_0 \) value has been tested against the data in Figure 6a. We modelled the relative \( ^{37}\text{Ar} \) loss of a parallelepiped with a
volume of $h:1.2h:1.5h$ for $h$ ranging from 50 to 2 $\mu$m. We used $d_0$ values of $1.63 \pm 0.21$ and $1.27 \pm 0.53$ $\mu$m as widths of constant 0-concentration layers on the outer edge of a grain. Figure 6a shows that both $d_0$ values match well the relative $^{37}$Ar loss of each fractions from which they are derived.

*The problem of the increasing $[Ca/K]_{Ar}$.* As illustrated by the modelled $^{37}$Ar- and $^{39}$Ar-depletion curve in Figure 2a, the $[Ca/K]_{Ar}$ ratio should decrease below the nominal $[Ca/K]_{EMP}$ composition. Such a decrease should start to be apparent below about 25 $\mu$m and reach a $[Ca/K]_{Ar}$ value of 0 for sub-micron grains. The data show a slight decrease in $[Ca/K]_{Ar}$ until approximately 35 $\mu$m, after which the $[Ca/K]_{Ar}$ increases with decreasing size fractions and reaches a maximum of about 5.9 ($+15\%$ increase) for the $<5 \mu$m fraction. Even if no $^{37}$Ar loss were to occur, the Ca/K of homogenous plagioclase should remain sub-stationary, as the $^{39}$Ar depletion is only $3\%$. In any case, nuclear physics laws imply that the recoil distance of $^{37}$Ar atoms must be at least 2–3 times the recoil distance of $^{39}$Ar due to the energy of the reaction (e.g. Turner & Cadogan 1974; Onstott et al. 1995; Renne et al. 2005).

At this stage, two hypotheses are possible: (1) the decreasing age with decreasing fraction is not due to $^{37}$Ar loss but by contamination by a Ca-rich phase with a composition similar to FCp ($[Ca/K]_{EMP} \geq 6$) but with an age significantly younger than FCp. This would imply that the $F(^{37}Ar)$ and $d_0 (^{37}Ar)$ values cannot be calculated for FCP; or (2) a significant part of the $^{37}$Ar$_{Ca}$ is, indeed, ejected from the grain but an extremely Ca-rich

![Figure 5](image-url)
phase is progressively enriched in the small fractions and, despite evidence of the young ages, masks the direct loss of $^{37}$Ar. Apatite and sphene inclusions (Ca-rich, K-free phases) along with plagioclase cores with An75 composition (Ca/K of c. 90) and An60 microlites have all been reported to be abundant for the Fish Canyon tuff (Bachmann et al. 2002). All of these phases have the potential to dramatically increase the Ca/K ratios towards fine fractions, especially as the relatively small Ca-rich inclusions and An75 plagioclase cores get liberated and concentrated during the crushing and sieving processes involved in the small fractions. Importantly, these inclusions do not have the potential to reduce the age of FCp as apatite and sphene do not contain any K, and An75 plagioclase has the same age as FCp. Therefore, we conclude that even though inclusions can explain the increasing trend of [Ca/K]$_{40}$, $^{37}$Ar loss is still required to explain the younger ages.

Fig. 6. (a) Theoretical $F(37\text{Ar})_{\text{FCp}}$ curve calculated for a parallelepiped with dimensions of $h:1.2h:1.5h$ ($h = x$) and $d_0$ ($^{37}$Ar) = 1.63 ± 0.21 μm, and compared with the $F(37\text{Ar})_{\text{FCp}}$ calculated from the data. The error envelope of the curve is indicated at 2σ. For comparison, the $F(39\text{Ar})_{\text{sanidine}}$ model curve using $d_0$ ($^{39}$Ar) = 0.035 μm is shown. (b) Same as (a) for $F(37\text{Ar})_{\text{Hb3gr}}$ and using $d_0$ ($^{37}$Ar) = 1.78 ± 0.58 μm. The red curve (black in the printed version) has been calculated using a parallelepiped with dimensions of $h:1.2h:1.5h$. 

Data

| Outlier |
|---------|
| 0%      |
| 20%     |
| 40%     |
| 60%     |
| 80%     |
| 100%    |

Relative $^{37}$Ar-volume depletion (%)

0 1 02 03 04 05 06 07 0

Relative $^{39}$Ar-volume depletion (%)

D0 = 1.63 ± 0.21 μm

Depletion of $^{37}$Ar (sanidine)

Parallelepiped

$(h:1.2h:1.5h)$

$D_0 = 1.78 ± 0.67 μm$
Recoil in Hb3gr hornblende (Hb3gr)

$^{37}$Ar recoil loss. For Hb3gr, the nine smallest fractions ranging from 63 to $<5$ μm show negative ΔHb3gr(corr.) values (i.e. with ages younger than the $^{39}$Ar recoil-corrected ages of Hb3gr) and offer a better continuity than FCP to study the effect of $^{37}$Ar recoil loss for small fractions (Fig. 3). In the case of Hb3gr, the closure temperature of hornblende (c. 550 °C) is too high to allow any diffusion of $^{37}$Ar due to the temperatures attained within the reactor and during the bake-out of the extraction line.

We calculated the relative $^{37}$Ar loss ($F(37Ar)$) from all aliquots of the different size fractions using equations (5)–(8), assuming that the decrease in age is entirely due to $^{37}$Ar loss. The weighted mean and standard error of the mean of the $F(37Ar)$ values range from 28 ± 9% to 98 ± 4% (Fig. 4b, Table 2). The $F(37Ar)$ values of all but one fraction are proportional to the grain size, and can be approximated by a power-law curve fitted to the data and defined by the following equation:

$$F^{(37}Ar) \approx 1.5h^{-0.3639} \quad (13)$$

where $h$ is the mean size (in μm) of the grains of a given aliquot.

The 22–28 μm fraction (80 ± 14%) lays well above the trend defined by the other eight fractions and is considered here to be an outlier. The smallest fraction ($<5$ μm) shows almost an entire depletion of the $^{37}$Ar within the grain with the ejection of 98 ± 4% of $^{37}$Ar atoms.

$^{37}$Ar total depletion thickness. We calculated the $d_0$ values for each fraction below 63 μm. $d_0$ ranges from 1.4 ± 0.3 to 3.5 ± 5.9 μm (Fig. 5b, Table 2). As mentioned above, the 22–28 μm fraction behaves like an outlier compared to an otherwise homogenous population, and as been excluded from the final calculation of $d_0 (37Ar)_{Hb3gr}$. Weighted mean and standard error of the mean of $d_0$ (Hb3gr) is 1.78 ± 0.67. MSWD and $P$ values of 1.7 and 0.10, respectively, indicate that some scatter is present but still significant that these data might belong to a single population. We further tested the $d_0 (37Ar)_{Hb3gr}$ value by modelling the relative $^{37}$Ar loss of a parallelepiped with dimensions of $h:1.2h:1.5h$, for $h$ ranging from 63 to 0 μm, and a constant 0-concentration layer with a $d_0$ thickness of 1.78 ± 0.67 μm. Figure 6b shows that the model curve offers a reasonable match with the data within uncertainty, in particular with the smallest fractions, whereas the largest fractions show slightly higher $F(37Ar)$ than expected from the model alone. Varying the shape of the parallelepiped does not much affect the model curve, although a slightly better match on coarser fractions is reached for square-shaped grains.

$[Ca/K]_{37Ar}$ Hb3gr shows rather scattered $[Ca/K]_{37Ar}$ values oscillating around 5. The $[Ca/K]$, theoretical curve with $^{37}$Ar, and $^{39}$Ar corrected for recoil loss, using equations (6) and (9), predicts a decrease in $Ca/K$ with decreasing fraction size (Fig. 2b). $[Ca/K]$ is indistinguishable from the $[Ca/K]_{37Ar}$ measured down to 15 μm. Only the 15–10 and 10–5 μm fractions show some significant departure from the curve, with $[Ca/K]_{37Ar} > [Ca/K]$. The <5 μm fraction shows $[Ca/K]_{37Ar} \approx [Ca/K] \approx 0$. $^{37}$Ar raw beams measured for all fractions and before applying the decay correction show values ranging from -0.00005 to 0.0009, (i.e. close to 0), which makes it hard to assess the reliability of the $[Ca/K]_{37Ar}$ ratio in this case. The low $^{37}$Ar raw values are certainly a major cause of the large error associated with $d_0 (37Ar)_{Hb3gr}$ of 1.78 ± 0.68 μm.

Comparison with the theoretical estimation of $^{37}$Ar recoil

According to Turner & Cadogan (1974) and Onstott et al. (1995), the recoil distance calculated for $^{37}$Ar atoms (c. 0.38 μm) during neutron bombardment is about 2.5 times greater than the recoil distance calculated (and experimentally confirmed) for $^{39}$Ar atoms (c. 0.16 μm). It is worth noting that the range of possible recoil distances for individual $^{37}$Ar atoms is larger than for $^{39}$Ar, with recoil distances ranging from 0.2 to 0.6 μm (i.e. with mean range of c. 0.4 μm: Onstott et al. 1995). The difference between $^{37}$Ar and $^{39}$Ar recoil behaviour is due to the larger recoil energy accompanying the reaction with $^{40}Ca$ in comparison with $^{39}K$ (Onstott et al. 1995). The $Q$ value of the reaction $^{39}K(n, p)$ is 0.217 ± 0.005 MeV, whereas the $Q$ value for $^{40}Ca(n, α)$ is almost an order of magnitude higher, with a value of 1.7583 ± 0.0005 MeV (e.g. Renne et al. 2005). As a result, $x_0 (37Ar)$ is predicted by Onstott et al. (1995) to be equal to approximately 0.19 μm.

The $x_0 (37Ar)$ value generally assumed for silicates is approximately 0.07–0.09 μm (Turner & Cadogan 1974; Renne et al. 2005) and has been confirmed by a recent value of 0.07 ± 0.02 μm directly calculated from a range of FC sanidine fractions (Jourdan et al. 2007). However, we saw that the mean $x_0 (37Ar)$ for Ca-rich silicate is approximately 3.3 ± 0.4 μm (calculated as the weighted mean between FCP and Hb3gr), about 50 times larger than $x_0 (37Ar)_{Sanidine}$ but ‘only’ around 3–4 larger than $x_0 (37Ar)_{Biotite}$. Clearly, the $x_0 (37Ar)$ values...
observed for plagioclase and hornblende are much larger than predicted by theoretical models for this type of silicate.

If correct, then why is so much $^{37}$Ar lost from the grains compared to $^{39}$Ar? The total recoil distance of inelastic collisions is a function of the energy of incident neutrons, the stopping power of the medium and the energy involved in the reaction. In the case of plagioclase and sanidine, the stopping power of the medium can be considered as equal, which makes the recoil energy directly dependent on the energy of the incident neutron required for the reactions on $^{40}$Ca and $^{39}$K, and the energy of these reactions. The physics behind these reactions are well known. Accordingly, one of the most straightforward explanations is that ejection due solely to pure nuclear recoil is not the only cause for the $^{37}$Ar loss.

In the case of $x_0$ ($^{39}$Ar)$_{\text{biotite}}$ being more than 10 times larger than $x_0$ ($^{39}$Ar)$_{\text{sanidine}}$, the favoured explanations for such a difference were related to the structure of the mineral itself. Biotite being a sheet silicate, it will have much more abundant fast pathways (e.g. between sheets) than compact tectosilicate, with these pathways acting as short-circuit diffusion for $^{39}$Ar (Paine et al. 2006). In the case of plagioclase and hornblende, the compact structure of these minerals is similar enough to sanidine to rule out a similar explanation for the large $x_0$ ($^{37}$Ar)/$x_0$ ($^{39}$Ar) value. Another possible explanation is that Ca-rich material has a longer stopping distance than Ca-poor material. However, SRIM 2003 simulations used to calculate the stopping range of recoiled $^{39}$Ar and carried out on a variety of slab compositions, albeit with amorphous structure, suggest that Ca-rich and dense material, such as hornblende and anorthite, have a similar if not slightly shorter stopping distance than sanidine for $^{39}$Ar recoil (Renne et al. 2005). As the same behaviour is expected for $^{37}$Ar atoms, the composition is unlikely to play any role in the $x_0$ ($^{37}$Ar) value.

A possibility is that the external layer of the grains might become amorphous due to significant structural radiation damage caused by the nuclear collisions, especially for $^{37}$Ar as the energy of the reaction is exoergic with a $Q$ value of 1.75 MeV. As a consequence, the amorphous external layer could be prone to significant thermal diffusion of the $^{37}$Ar atoms displaced in this layer by recoil, but this effect would certainly also result in an enhanced loss of $^{39}$Ar and, hence, does not seem to provide a suitable explanation.

The exact reason(s) for a large $x_0$ ($^{37}$Ar) value is currently unknown. The physics behind the nuclear recoil process is generally well understood. Yet, our measurements show that a quantity of $^{37}$Ar much larger than expected from recoil alone is lost from the grains, somewhere between the irradiation time and the analysis in the mass spectrometer. Our results are unlikely to be a biased experimentally as two distinct minerals with two distinct irradiation durations (i.e. 10 and 90 h) and distinct neutron doses, and carried out at different times, produced similar results. Our new results are also in agreement with the FCs-p experiments (Jourdan et al. 2007), where a $d_d$ ($^{37}$Ar) upper-limit value of $<3 \mu$m was calculated (i.e. $x_0 < 6 \mu$m). Similarly, the good fit between experiment and model for $^{37}$Ar lost from plagioclase and hornblende seems to preclude a bias of the experiments. The rather unexpected results obtained during this study warrant further investigation of the $^{37}$Ar recoil loss. One of the possible approaches to directly cross-check our results will be to vacuum-encapsulate all of the mineral fractions (e.g. see the detail in Foland et al. 1992) and to carry out complementary experiments by: (1) directly measuring all of the $^{37}$Ar ejected from the various grain fractions and trapped in the capsules; and (2) measuring the isotopic composition of each fraction similar to the present study. However, the downside of these experiments is that the irradiation of the grains must occur under vacuum conditions and will thus produce $^{39}$Ar and $^{37}$Ar values significantly lower than the ones reported in this study due to the re-implantation of the $^{37}$Ar (and $^{39}$Ar) in neighbouring minerals.

$^{37}$Ar and $^{39}$Ar recoil age correction

According to our experiments, a measurable proportion of $^{37}$Ar is lost due to the direct and indirect effects of recoil at small fraction size (Fig. 4), albeit the exact mechanism explaining the large amount of $^{37}$Ar loss is not well understood. In addition, $^{39}$Ar loss has been shown by Paine et al. (2006) and Jourdan et al. (2007) to be mineral dependent, and seems to affect the age results below 50 $\mu$m. Therefore, in order to accurately determine the age of minerals of a given size range below the 50 $\mu$m threshold, one needs to correct for $^{39}$Ar and $^{37}$Ar loss.

The general $^{40}$Ar/$^{39}$Ar age equation is given by:

$$t_c = \frac{1}{\lambda} \ln \left[ 1 + J \left( \frac{^{40}\text{Ar}^*}{^{39}\text{Ar}_K} \right) \right].$$ (14)

$^{40}$Ar* and $^{39}$Ar* need to be corrected from $^{39}$Ar and $^{37}$Ar recoil losses that have a direct ($^{39}$Ar) or indirect effect ($^{37}$Ar) on these isotopes. $^{40}$Ar* and $^{39}$Ar* can be directly corrected from the effects of recoil by combining the general equation (3.42) of McDougall & Harrison (1999), and equations (6) and (9).
of the present study:

\[
\frac{^{40}\text{Ar}}{^{39}\text{Ar}} = \frac{^{40}\text{Ar}_{\text{m}}}{^{39}\text{Ar}_{\text{m}}} \left(\frac{^{36}\text{Ar}_{\text{am}}}{^{39}\text{Ar}_{\text{am}}} \left(1 - F(^{39}\text{Ar})\right) + \frac{^{40}\text{Ar}_{\text{am}}}{^{39}\text{Ar}_{\text{am}}} \left(\frac{^{37}\text{Ar}_{\text{m}}}{^{39}\text{Ar}_{\text{m}}} \left(1 - F(^{37}\text{Ar})\right)\right)\right) - \frac{^{40}\text{Ar}}{^{39}\text{Ar}_{\text{K}}}
\]

where the calculation of \(F(^{39}\text{Ar})\) for a range of crystal size of fixed proportion has been given in Jourdan et al. (2007), and where the same equations can be used to calculate \(F(^{37}\text{Ar})\) using the appropriate \(d_0(^{37}\text{Ar})\).

\(^{39}\text{Ar}\) and \(^{37}\text{Ar}\) recoil-corrected age can then be calculated by combining equations (14) and (15). If the mineral is calcium-free, then equation (15) is equivalent to equation (9) given by Jourdan et al. (2007).

The age correction calculation proposed here can be applied to loose minerals irradiated in an air-filled capsule, as is usually the case for conventional \(^{40}\text{Ar}/^{39}\text{Ar}\) dating. If fine-grained minerals are irradiated as a single compressed pellet or under vacuum, significant amounts of ejected \(^{37}\text{Ar}\) and \(^{39}\text{Ar}\) atoms will be re-implanted in neighbouring grains, resulting in an over-correction for recoil effects on total fusion ages. In this case, \(d_0\) values need to be measured for these specific conditions.

**Implication for \(^{40}\text{Ar}/^{39}\text{Ar}\) geochronology of Ca-rich material**

**Age determination.** \(^{39}\text{Ar}\) recoil-induced loss in minerals can become problematic when it comes to dating fine-grained minerals of \(<50 \mu\text{m}\) (Paine et al. 2006; Jourdan et al. 2007). \(^{37}\text{Ar}\) recoil adds one layer of complexity to the problem for calcium-rich minerals as they will suffer from both \(^{39}\text{Ar}\) and \(^{37}\text{Ar}\) recoil. Until a more sophisticated sample

![Graph](image-url)
irradiation method is available (e.g. Deuteron–Deuteron fusion reactor: Renne et al. 2005), neutron-induced recoil loss has to be taken into account for small grain size. Paradoxically, our results show that the $^{37}$Ar loss will result in a younger age but will, to some extent, compensate the opposite effect of $^{39}$Ar recoil loss. As a result, the measured age of Ca-rich minerals will be close to the nominal age of a mineral at least down to a size fraction of about 10 μm (Figs 1 & 3), but note that this is a first-order approximation only.

**Vacuum encapsulation and age correction.** Ultimately, because of the complexity of the correction problem and the magnification of the uncertainties associated with the recoil correction of grains with a size below 5 μm, dating of fine- to very-fine-grained minerals (e.g. clay and glaucony grains) will require encapsulation of the samples following a standard vacuum-encapsulation method (e.g. Foland et al. 1992; Haines & van der Pluijm 2008). The downside of this approach is that the benefits of age spectrum analysis are sacrificed. This, however, can be circumvented by using samples with different grain sizes or fractions with a different range size, provided that, for each size fraction, the recoil-corrected age can be calculated and then compared to the measured integrated age. If the $^{40}$Ar* distribution in each grain is homogenous, then for each fraction:

$$t_c(h = x) \approx t_{int}(h = x)$$

where $t_c$ is given by combining equations (14) and (15), and $t_{int}$ is the total gas age obtained by integrating the gas measured in the capsule and the sample. This implies that $d_0^{37}$Ar and $d_0^{39}$Ar values are known for samples irradiated under vacuum condition with $d_0^{3x}$Ar$_{atm} > d_0^{3x}$Ar$_{vacuum}$ for $^{37}$Ar and $^{39}$Ar.

If the distribution of $^{40}$Ar* is heterogeneous due to excess $^{40}$Ar* or alteration discretely distributed within the grains, then it is expected that the

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Fig. 8. $^{40}$Ar/$^{39}$Ar and [K/Ca]$_{Ar}$ spectra plotted v. the cumulative percentage of $^{39}$Ar released for a fine-grained Ca-rich melt rock sample (Jourdan unpublished). Errors are quoted at 2σ. The black arrow illustrates the theoretical redistribution of $^{39}$Ar from K-rich to K-poor domains, and the grey arrow shows the $^{37}$Ar redistribution from Ca-rich to Ca-poor sites. Note that neither the low- nor the high-temperature flat sections of the age spectrum are likely to represent the formation age of this rock due to $^{39}$Ar and $^{37}$Ar redistribution within the sample (cf. the discussion in the text).
different size fractions will not follow a recoil-induced power-law age pattern, such as shown in equation (4). At this stage, the validity and applicability of this method remains to be seen and thoroughly tested.

Note on $^{39}$Ar and $^{37}$Ar redistribution in groundmass. Irradiation-induced recoil not only affects minerals with size $<50 \, \mu m$ through $^{39}$Ar and $^{37}$Ar loss, but can also seriously hamper age determination through recoil redistribution of these isotopes within the structure of the minerals or rocks. Any fine-grained structure will undergo recoil redistribution of the $^{39}$Ar and $^{37}$Ar isotopes. In principle, most of $^{39}$Ar is released from K-rich sites at low to middle temperatures, whereas the $^{37}$Ar is produced by Ca-rich sites and released mostly at high temperatures. In a fine-grain basaltic groundmass, recoil redistribution will cause part of $^{39}$Ar$_{Ca}$ to move in Ca-rich sites (e.g. pyroxene) causing the low- and mid-temperature steps to yield apparent ages too old, whereas the $^{39}$Ar$_{K}$ re-implanted in Ca-rich phases will cause the high-temperature steps to be too young (Fig. 7). $^{37}$Ar$_{Ca}$ recoil will exacerbate this effect by enriching the low- and mid-temperature steps in $^{37}$Ar$_{Ca}$ causing over-correction of $^{39}$Ar and $^{40}$Ar (again yielding spuriously old age) and depleting the Ca-rich sites of $^{37}$Ar$_{Ca}$, with a result similar to that observed during $^{39}$Ar loss (Fig. 8). As a consequence, when recoil redistribution affects the argon isotopes in the groundmass, this will result in a tilde-shaped spectrum such as the one exemplified in Figure 8. In most cases, two pseudo-flat sections will be formed with a relatively old mid-temperature section and a younger high-temperature section. As seen previously, none of these sections will reflect the true age of the groundmass with mid- and high-temperature ‘mini-plateau’ being too old and too young, respectively.

Conclusion

We carried out total fusion and step-heating Ar isotope measurements on multi-grain populations of Fish Canyon plagioclase (FCp) and Hb3gr hornblende, with discrete sizes ranging from 210 to $<5 \, \mu m$. Our results show that the smallest fractions yielded younger ages than expected for minerals affected by $^{39}$Ar recoil loss alone. We propose that $^{37}$Ar loss may seriously bias the age measured for a mineral towards younger ages through the interference of correction disturbances on $^{39}$Ar and $^{38}$Ar isotopes. For both FCp and Hb3gr, the smallest fraction ($<5 \, \mu m$) shows the highest departure from the theoretical $^{39}$Ar recoil-corrected age, with $\Delta$FCp(corr.) of $-40 \pm 4\%$ and $\Delta$Hb3gr(corr.) of $-21 \pm 2\%$. The age deviations are best explained by ejection of $^{39}$Ar out of the grains during nuclear reactions or subsequent loss of the displaced atoms by diffusion. Relative $^{37}$Ar loss calculated for each mineral is proportional to the grain size, and ranges from approximately 30 to 91\% for FCp and from about 28 to 98\% for Hb3gr. The $^{37}$Ar loss is used to calculate the mean size of a partial depletion layer $x_0$ ($^{37}$Ar) with two concordant values of 3.3 $\pm$ 0.4 (FCp) and 3.6 $\pm$ 1.4 $\mu m$ (Hb3gr). The reason for such a massive $^{37}$Ar loss is not well understood. It can tentatively be attributed to the formation of an external amorphous layer as the result of significant structural radiation damages, and prone to significant thermal diffusion of the $^{37}$Ar atoms displaced into this layer by recoil. The extreme depletion values obtained in this study warrant further investigation of Ca-rich crystals. In any case, using $x_0$ ($^{39}$Ar) and $x_0$ ($^{37}$Ar), and approximate crystal dimensions, the age of a given mineral can be corrected from the effects of $^{39}$Ar and $^{37}$Ar loss. We also propose a method based on our approach to test the validity of ages obtained via the vacuum-encapsulation method. Finally, our results highlight the problem of $^{37}$Ar (and $^{39}$Ar) redistribution in fine-grained Ca-rich samples.

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