Modelling effect of sericitization of plagioclase on the $^{40}$K/$^{40}$Ar and $^{40}$Ar/$^{39}$Ar chronometers: implication for dating basaltic rocks and mineral deposits

CHRISTÉLE VERATI$^{1*}$ & FRED JOURDAN$^{2}$

$^{1}$Université de Nice Sophia Antipolis, GEOAZUR, Bât 1, 250 rue Albert Einstein, Les Lucioles 1, Sophia-Antipolis 06560 Valbonne, France

$^{2}$Western Australian Argon Isotope Facility, JdL Centre & Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

*Corresponding author (e-mail: verati@unice.fr)

Abstract: The $^{40}$Ar/$^{39}$Ar technique is the most commonly used technique to date basaltic rocks. For basaltic rocks older than about 30 Ma, the dating of plagioclase separates is preferred over groundmass as the latter is susceptible to containing cryptic alteration due to fluid circulations, difficult if not impossible to remove during sample preparation. Alteration under such metamorphic conditions successively forms K-rich sericite after plagioclase. Owing to its transparency, plagioclase allows a distinction to be made optically between partially–completely altered grains and fresh grains. However, practice shows that grains that contain less than about 1% of sericite are hard to identify under the stereomicroscope. Owing to the high K$_2$O content (c. 10 wt%) of sericite, such compromised grains can have dramatic effects on the age determination of plagioclase. Here, we investigate and quantify the effect of sericite on the $^{40}$Ar/$^{39}$Ar age determination of plagioclase using a numerical model with multiple variable parameters. We show that the most influential parameter is the time difference between the crystallization of plagioclase and the sericitization event. We also show that for some continental flood basalts, even 0.1 wt% of sericite can bias the apparent age of a plagioclase separate by several hundred thousand years. The presence of sericite can be identified using a combination of Ca/K ratios, age spectra, and $^{39}$Ar and $^{37}$Ar degassing curves obtained during a conventional $^{40}$Ar/$^{39}$Ar step-heating procedure. When the age of the fresh plagioclase and its Ca/K ratio are known, the percentage of sericitization and the age of the alteration event can be estimated. Ultimately, above approximately 65% of sericitization, the apparent age measured on the altered plagioclase is within $\pm$1% of the age of the alteration event, with implications for accurately dating low-temperature metamorphism and mineral deposit formations.

Supplementary material: Further details of calculation are available at www.geolsoc.org.uk/SUP18609.

$^{40}$Ar/$^{39}$Ar dating of low-K$_2$O basalt has always proved to be a challenging, yet very important, task when it comes to studying the timing of basaltic volcanic events (e.g. large igneous provinces, oceanic island basalts or lunar maria). Many studies have demonstrated a much better reliability and accuracy of the $^{40}$Ar/$^{39}$Ar technique over ‘conventional’ K–Ar dating, as only the former approach can unambiguously demonstrate that a given sample is free of alteration and does not contain excess or inherited $^{40}$Ar. Whereas alteration can be circumvented by using relatively young (i.e. few million years old, Ma) rocks, the absence of excess $^{40}$Ar$^+$ is impossible to demonstrate using the K–Ar technique alone (e.g. McDougall & Harrison 1999). Dating basaltic rocks of a few tens or even hundreds of Ma is a risky business as alteration can shift the isotopic ‘age’ by few Ma to tens of Ma compared to the eruption age (see examples in Courtillot et al. 2010). Much more robust is the $^{40}$Ar/$^{39}$Ar technique as it allows powerful statistical tests to be made of the reproducibility of the age of a sample age using the step-heating approach.

More recently, better accuracy of plagioclase over groundmass $^{40}$Ar/$^{39}$Ar dating has been demonstrated, at least for rocks older than few tens of Ma, due to the unavoidable cryptic and pervasive alteration of these rocks (Hofmann et al. 2000; Jourdan et al. 2007a, b). Contrary to groundmass, plagioclase allows the optical separation of altered grains from fresh grains due to its transparency (Fig. 1, see the discussion below). Nevertheless, owing to its very low content in K$_2$O (often <0.1 wt%), plagioclase is extremely sensitive to alteration and, in particular, to sericitization, where sericite is a replacement phase introduced from...
during open-system alteration. Plagioclase replacement by sericite occurs during the fluid alteration of magmatic rocks under low-pressure–low-temperature metamorphism; that is, under zeolite–lower greenschist facies conditions (i.e. from 100 to 300 °C, <10 kbar). Owing to the high content of sericite in K$_2$O (c. 10 wt%), only minute quantity of this phase is required to overprint the $^{40}$Ar/$^{39}$Ar age signal of the plagioclase and so compromise the validity of the age.

Very few detailed, although mostly unpublished, K–Ar age mixing models were proposed for sericitized plagioclase (Lippolt & Siebel 1991; Schwarz 2001; Schwarz & Lippolt 2002; Goll et al. 2003), as well as direct K–Ar analytical data on quite pure sericite (Watanabe et al. 1998; Brockamp et al. 2003; Zelazniewicz et al. 2003). Some $^{40}$Ar/$^{39}$Ar geochronological studies used sericitized plagioclase to elucidate the age of low-grade metamorphism. This approach has met variable success depending of the amount of sericite replacement that occurred after plagioclase (Aguirre et al. 1999; Boven et al. 2001, 2002; Fuentes et al. 2005; Oliveros et al. 2008b, c; Jourdan et al. 2009a).

In this study, we provide theoretical models showing: (1) how sericitization modifies the K–Ar and $^{40}$Ar/$^{39}$Ar systematic dating of plagioclase, and, ultimately, how it can affect the accuracy of plagioclase (and groundmass) ages; (2) how and why the sercite signature can be identified using the $^{40}$Ar/$^{39}$Ar age spectrum; and (3) how completely sericitized plagioclase can be used for accurately dating greenschist facies metamorphic events and hydrothermal fluid systems relevant to the study of the timing of ore deposit formations.

**Petrological features of the sericitization**

Sericitization is a process of alteration in low-temperature conditions (<300 °C) encountered commonly during hydrothermal alteration in an epithermal context or during greenschist metamorphism. Sercite KAl$_3$Si$_3$O$_{10}$(OH,F)$_2$ replaces plagioclase by mineralogical substitution and/or fills microfractures within the plagioclases (Fig. 1). Sericitization can correspond to a punctual instantaneous event, a long-term episode or a multistage process. But, unfortunately, these processes are often impossible to differentiate in thin section.

Strongly sericitized (>50%) plagioclase grains commonly have a milky-white appearance (cloudy) under a binocular stereomicroscope (Fig. 1), and are easily discernible. Although major sercici replacement is easily identified in thin section (Fig. 1), it is very difficult to evaluate the minimum amount of sericite that can be detected with the human eye using a stereomicroscope. For instance, it is possible that a sericitization of less than 1–2% cannot be detected during hand-picking, even for those with an experienced eye, and especially when sercite is located within small cracks (Fig. 1).

Considering the relatively low potassium content of plagioclase (often K$_2$O <0.1 wt%), fine alteration, hardly discernible during hand-picking, could have significant effects on the measured K–Ar and $^{40}$Ar/$^{39}$Ar ages, yielding anomalously young ages, often disturbed age spectra and also, in extreme cases, well-defined ‘alteration plateau’ ages (e.g. Jourdan et al. 2003; Baksi 2007a; Pati et al. 2010).

**Two-component mixing model**

In order to evaluate the age reduction of the sericitized plagioclase, we propose a mathematical model based on a two-component mixture between unaltered plagioclase and sercite, bearing in mind that sericitization occurs in a single brief stage. Note that the proposed model does not include any thermally activated diffusive loss of $^{40}$Ar* from plagioclase caused by the hydrothermal circulation or lower greenschist conditions. Whereas diffusive loss inevitably occurs in many cases, most of the age reduction is generally controlled by sercite formation rather than by Ar loss.

Using the K–Ar age equation, for a given K content in plagioclase ($^{40}$K$_{Pl}$), radiogenic $^{40}$Ar in sercite-free plagioclase with an age $t$ is:

$$^{40}Ar = \frac{\lambda}{\lambda - \lambda_{40}} K_{Pl} (e^{\lambda t} - 1).$$

For a plagioclase that is sericitized at $t'$ ($t' < t$), with $X$% of sercite in the mixture, for a given K

---

**Fig. 1.** Typical examples of plagioclase–sercite replacement (samples are from Chili, Botswana and Karoo volcanics). (a0) Photograph of typical plagioclases during hand-picking under binocular microscope. 1, 2 and 3 correspond to very transparent unaltered plagioclase, cloudy highly sericitized plagioclase and moderately altered plagioclase, respectively. (a1) Sercite-free very transparent grains of plagioclases in thin section, well recognized during hand-picking (1 in a0). (a2) Strongly sericitized plagioclase (sercite >50%) in thin section, well recognized during hand-picking (2 in a0). (a3) Diffusely sericitized plagioclase (sercite >30%) in thin section potentially recognized during hand-picking (3 in a0). (a4) & (a5) Slightly sericitized plagioclase (sercite <5%) in thin section hardly recognized during hand-picking. (b) Example of sercite patchy replacement in plagioclase. (c) Example of sercite filling fractures within the plagioclase. Pl, plagioclase; Ser, sercite.
content in sericite ($^{40}\text{K}_{\text{Ser}}$), the total amount of K content in the mixture ($^{40}\text{K}_{\text{Tot}}$), as well as the total amount of radiogenic $^{40}\text{Ar}$ ($^{40}\text{Ar}_{\text{Tot}}$) in the mixture, are:

$$^{40}\text{K}_{\text{Tot}} = (1 - X)^{40}\text{K}_{\text{Pl}} + X^{40}\text{K}_{\text{Ser}} \quad \text{with} \quad ^{40}\text{Ar}_{\text{Tot}} = ^{40}\text{Ar}_{\text{Pl}} + ^{40}\text{Ar}_{\text{Ser}}.$$  

We obtain:

$$^{40}\text{Ar}_{\text{Tot}} = \frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Pl}}(e^{\lambda t'} - 1) + \frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Ser}}(e^{\lambda t''} - 1).$$  

(3)

We can define the apparent age $t''$ of the two-component mixture (sericitized plagioclase) as follow:

$$^{40}\text{Ar}_{\text{Tot}} = \frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Tot}}(e^{\lambda t''} - 1).$$  

(4)

Previous equations may be combined to give:

$$\frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Tot}}(e^{\lambda t''} - 1) = \frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Pl}}(e^{\lambda t'} - 1) + \frac{\lambda_e}{\lambda} ^{40}\text{K}_{\text{Ser}}(e^{\lambda t''} - 1).$$  

(5)

We deduce that the apparent K–Ar age $t''$ of the mixing is:

$$t'' = \frac{1}{\lambda} \ln \left( 1 + \left(\frac{^{40}\text{K}_{\text{Pl}}}{^{40}\text{K}_{\text{Tot}}}(e^{\lambda t'} - 1) + \left(\frac{^{40}\text{K}_{\text{Ser}}}{^{40}\text{K}_{\text{Tot}}}(e^{\lambda t''} - 1) \right) \right) \right)$$  

(6)

where $^{40}\text{K}_{\text{Pl}}$ is the $^{40}\text{K}$ content of fresh plagioclase, $^{40}\text{K}_{\text{Ser}}$ is the $^{40}\text{K}$ content of sericite, $^{40}\text{K}_{\text{Tot}}$ is the $^{40}\text{K}$ content of the mixture, $t$ is the K–Ar magmatic age of the plagioclase, $t'$ is the K–Ar age of the sericitization event and $\lambda$ is the total $^{40}\text{K}$ decay constant (here $5.544 \times 10^{-10}$; Steiger & Jäger 1977).

The percentage of K–Ar age reduction (AR) is:

$$\text{AR} = \frac{t - t''}{t}.$$  

The $^{40}\text{K}_{\text{Pl}}/^{40}\text{K}_{\text{Tot}}$ and $^{40}\text{K}_{\text{Ser}}/^{40}\text{K}_{\text{Tot}}$ ratios in equation (6) can be developed taking into account the chemical composition of plagioclase and sericite; that is, $\%\text{K}_2\text{O}$, $\%\text{CaO}$ and the Ca/K ratio (identified in the $^{39}\text{Ar}/^{39}\text{Ar}$ technique by $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_k$). Detailed equations are reported in the Appendix.

Finally, we obtain the following equations that quantify the two theoretical ratios reported in equation (6):

$$\frac{^{40}\text{K}_{\text{Ser}}}{^{40}\text{K}_{\text{Tot}}} = \frac{XB}{X^B + (1 - X)A \times (\%\text{CaO})_p \times (\text{K}/\text{Ca})_p \times M_p}$$  

(7)

$$\frac{^{40}\text{K}_{\text{Pl}}}{^{40}\text{K}_{\text{Tot}}} = \frac{(1 - X) \times \left( A \times (\%\text{CaO})_p \times (\frac{\text{K}}{\text{Ca}})_p \times M_p \right)}{X^B + (1 - X)A \times (\%\text{CaO})_p \times (\frac{\text{K}}{\text{Ca}})_p \times M_p}$$  

(8)

where $A=\left( M_{\text{K}_{2}\text{O}}/(2 \times M_{\text{CaO}}) \right)$; $B=\left( \%\text{K}_2\text{O}_{\text{Ser}} \times M_{\text{Ser}} \right)$.

The variables are $X$ (percentage of sericite in the mixing), $M_p$ (molecular weight of plagioclase), $(\text{Ca/K})_p$ and $(\%\text{CaO})_p$, $M_p$, $(\text{Ca/K})_p$ and $(\%\text{CaO})_p$ are interdependent (see the Appendix for further explanation). $A$ and $B$ are known values related to the chemical composition of sericite and the molecular weight of implied oxides.

**K–Ar age perturbation during the sericitization process**

Using equations (1)–(3), we can calculate an age reduction (AR) for a given altered plagioclase. The variable parameters are: (1) the age of the plagioclase, $t$; (2) the age of the sericite (alteration event, $t'$); (3) the Ca/K ratio of the plagioclase; and (4) the amount of alteration. In Figure 2, as an exercise, we plotted three curves showing the AR v. percentage of sericitization reported for an An$_{70}$ and for $t'$ being 10% younger than the fresh plagioclase. The three curves correspond to three different chemical compositions of plagioclase; that is, three different Ca/K ratios. For all values of theoretical $t$, ranging from 100 ka to 1 Ga, AR values display imperceptible variations (and, thus, not shown). For a common basaltic plagioclase (An$_{70}$), our model confirms that a few percentage of fine alteration, hardly discernible during the hand-picking, has a dramatic effect on the measured K–Ar ages of the plagioclase (Fig. 2). The age reductions (AR) of the sericitized plagioclase are correlated with the Ca/K ratio of the fresh feldspar. If sericite is 10% younger than plagioclase and represents more than 10% of the total plagioclase aliquot, the K–Ar age decrease can range from 7 to 10%, depending on the Ca/K ratio of plagioclase. Furthermore, a sericitization of less than 1% can also significantly modify the K–Ar ages of the feldspar. For instance, a plagioclase with a Ca/K
ratio of 36 and 100 Ma in age provides an apparent K–Ar age of 98 Ma with minute sericitization of only 0.5% (using an age of alteration of 90 Ma: Figs 2 & 3). In extreme cases, plagioclase with an age of 500 Ma that underwent partial alteration (1%) at 0 Ma would have a shift in its apparent age by 170 Ma (not shown).

Influence of the plagioclase composition

Figure 2 shows that the higher the Ca/K ratio of the unaltered plagioclase, the lower is the age reduction for a same amount of sericitization. For instance, a K-poor An70 displays an age reduction of less than 2% with a sericitization of 1%, whereas analysis of a K-poor An70 almost reached the age of the sericite for the same degree of alteration (Fig. 3). If we consider a Ca-poor (and, hence, K-very poor) plagioclase (i.e. albite end member), the effect of sericitization on the age reduction is more important. The curves of the decreasing K–Ar ages are quite similar for a K-poor An70 (Fig. 3a) and a K-rich An05 (Fig. 3c) plagioclase (Fig. 3).

Influence of the time span between plagioclase and sericite crystallization

The age difference between magmatism and alteration is the main parameter influencing the calculated K–Ar age reduction (Fig. 4a). When the alteration is contemporaneous with the time of magmatic emplacement (i.e. syn-eruptive sericite: e.g. Jourdan et al. 2009a), the decrease in the K–Ar age is obviously equal to zero whatever the amount of sericitization. When the alteration is contemporaneous with the present day, the K–Ar decrease curve displays the maximal values for a given percentage of sericitization. For a difference in age of 5% between crystallization and alteration, the related AR is 2% for a low percentage of alteration of 1% (Fig. 4b). In short, the younger the sericitization event, the greater is the decrease in the K–Ar age of plagioclase, for a given degree of alteration.

Consequences for K–Ar dating of Large Igneous Provinces (LIPs)

Plagioclase has been widely used for the dating of major flood basalt volcanism, such as the Decan, Ethiopian or Siberian traps, or the Karoo or Central Atlantic Magmatic Province, in order to determine the timing and duration of such huge volcanic activities (Deckart et al. 1997; Hofmann et al. 1997, 2000; Marzoli et al. 1999, 2011; Courtillot et al. 2000; Hames et al. 2000; LeGall et al. 2002; Knight et al. 2003; Jourdan et al. 2004, 2005, 2009a; Verati et al. 2005, 2007). According to the brevity of most of these events (<1–2 Ma),

\[
\text{Age of the alteration : } -10\% \text{ / age of unaltered plagioclase} \\
\text{Age of the unaltered plagioclases : can be 100 Ka to 1 Ga} \\
\text{(imperceptible variations on the diagram)}
\]

- An70
  - K-poor (Ca/K = 239)
  - Common (Ca/K = 36)
  - K-rich (Ca/K = 14)

\[
\text{Percent K-Ar or } ^{40}\text{Ar}/^{39}\text{Ar Age Reduction (AR parameter in %) v. % sericitization, for three different altered plagioclases: a K-poor (high Ca/K > 100), an intermediate (common Ca/K of 36) and a K-rich one (Ca/K < 15). Curves are defined with a theoretical An70 plagioclase, and an age difference of 10% between alteration and plagioclase crystallization events. An AR = 0 means that the K–Ar chronometer in plagioclase is not perturbed by the sericitization event. All curves show that a sericitization of more than 10% strongly affects the K–Ar age of plagioclase, which tends rapidly to the value of the alteration age.}
\]
the time resolution required to study these events necessitate that the internal precision of the ages must be, at very least, better than 1% (2σ) but ideally approaching 0.5–1 Ma to be considered useful. We thus investigate when and how the sericitization could disturb this required time precision. In Figure 5, we report, for several flood basalt provinces, on the value of sericitization that causes 1% and 10% of AR. For all of the volcanism events, 1% of sericitization implies an age reduction of more than 1%, and thus more than the minimum time precision required. For the Deccan traps (with a common K content for plagioclase, with a mean Ca/K ratio of 36), only 0.35% of sericite is required to bias the measured age by 1%, whereas an even smaller degree of alteration (<0.05%, definitely imperceptible) is sufficient in the case of the Rajahmundry traps (K-poor plagioclase, with a mean Ca/K ratio of 200). Using a classical K–Ar method for volcanic rocks older than about 20–30 Ma is clearly unsuitable, given that undetectable alteration might easily overprint the magmatic age of plagioclase (and even more for the groundmass) and that the presence of such alteration is not directly recognizable using the K–Ar technique.

Effects of the plagioclase–sericite replacement in Ar/Ar results

A better way to test whether plagioclase recorded a true emplacement age or if it is affected by alteration

Fig. 3. AR parameter v. % sericitization ranging from 0 to 1% (detail of Fig. 2). Curves for An70 are the same as those reported in Figure 2, with the three different Ca/K ratios. Curves for An05 plagioclase (Ca-poor, Na-rich) are also reported for comparison.
is by using the $^{40}\text{Ar}/^{39}\text{Ar}$ method. The $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_{\text{K}}$ ratio, related apparent ages and degassing curves of individual argon isotopes are three useful ways of identifying the presence of sericite in plagioclase.

**Detection of sericitization in degassing curves**

In Figure 6, we reported unpublished data of plagioclases from the CAMP that have more than 2% sericite, as identified in thin section. Related degassing curves represent the relative abundance of argon degassed (mV) for each argon isotope, normalized to the increment in temperature (DT) for each step to avoid dependency on the heating schedule. The complex degassing history can be interpreted as sericite microfractures or $^{40}\text{Ar}$* diffusion loss in the early part of the age spectrum, and sericite patchy replacements in the mid–high temperature steps. Indeed, the sericite degassing curve for $^{39}\text{Ar}$ (one sharp peak at 1050–1200 °C with a high activation energy of $c. 67 \text{ kcal/mol;}$ Harrison et al. 2009) is different to the relatively smooth curve of pure plagioclase identified by the $^{37}\text{Ar}_{\text{Ca}}$ (two peaks at around 900 and 1300 °C, and a lower activation energy of c. 40 kcal/mol; Cassata et al. 2009). A perceptible sericitization in thin section ($X > 2\%$) provides a clear $^{39}\text{Ar}$ peak between (and clearly resolved from) the two main ‘smooth’ peaks of plagioclase. This is also clearly identified by an age reduction for these steps (Fig. 6).
age reduction is also clearly correlated with a decrease in $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_{\text{K}}$. When the Ca/K of plagioclase is homogenous, and if $^{39}\text{Ar}$ and $^{37}\text{Ar}$ are covariant, the $^{39}\text{Ar}_{\text{K}}$ degassed by plagioclase dominates the $^{39}\text{Ar}_{\text{K}}$ of the sericite. However, when the relative amount of $^{39}\text{Ar}_{\text{K}}$ becomes greater than $^{37}\text{Ar}_{\text{Ca}}$, and $^{39}\text{Ar}_{\text{K}}$ and $^{37}\text{Ar}_{\text{Ca}}$ are no longer covariant, this probably indicates that most of the $^{39}\text{Ar}_{\text{K}}$ now comes from the sericite during this particular phase of the degassing process, ultimately causing an apparent age reduction. However, owing to the facts that (1) sericite is directly intergrown with plagioclase, and (2) the variable sericite grain sizes have variable closure temperatures, the argon diffusion of sericite will be intimately linked with the argon diffusion of plagioclase during the entire step-heating process. Therefore, sericite will contribute to variably reduce the $^{40}\text{Ar}/^{39}\text{Ar}$ age along the *entire* age spectrum. In other words, no step can reach the true age of the volcanism. Furthermore, diffusive $^{40}\text{Ar}$ loss from plagioclase due to the rise in temperature associated with a given alteration event will also contribute to reduce the individual step ages, although the latter effect is not included in our current model. As a result, only a minimum qualitative age for the eruption can be estimated from the oldest steps of the age spectrum. For example, Figure 6b shows a minimum age of $\geq 190$ Ma, whereas the true emplacement age is known to be approximately 199 Ma, based on neighbouring well-dated lava flows.

**Determination of the sericitization age**

If we know the age of fresh plagioclase, and its Ca/K ratio, and if the latter is constant within the plagioclase, we then can estimate the percentage of sericitization by taking into account the integrated Ca/K of the mixture (Ca/K$_{\text{mixture}}$) (see the section on ‘Determination of the sericitization value’ in the Appendix). In practice, this exercise is rendered difficult by the fact that the Ca/K ratio is variable at the single grain level. Nevertheless, for homogenous plagioclase, we are able to estimate the alteration age $t'$ (see the section on ‘Estimate of the age $t'$ of the alteration in $\text{Ar}/\text{Ar}$ spectra’ in the Appendix) and the percentage of alteration. For the $^{40}\text{Ar}/^{39}\text{Ar}$ experiment on CAMP basalts reported in Figure 6, we obtain approximately 3% for the value of alteration, with an estimated age of sericitization of 174 Ma, in accordance with some alteration plateau ages obtained from some strongly sericitized plagioclase (Jourdan et al. 2003).

When the sericitization is less apparent in the $^{40}\text{Ar}/^{39}\text{Ar}$ spectra, we still can provide a rough estimate of the sericite/plagioclase content. Plagioclase samples from the Karoo Province (Fig. 7)
yielded a plateau age (essentially mimicking a plateau age) of 179.9 ± 0.9 Ma (2σ; but note that the error boxes in Fig. 7 are given at 1σ) with 100% of cumulated 39Ar. However, some individual steps show lower apparent ages correlated to slight 37ArCa/39ArK depletion, probably associated with some sercite present in the system. If we remove these steps from the plateau age calculation, the new corrected plateau age (180.5 ± 0.6 Ma) is now 0.3% older. According to equations (A10)–(A15) (see the sections on ‘Determination of the sericitization value (A15)’) and (‘Estimate of the age t of the alteration in Ar/Ar spectra’ in the Appendix), such a value corresponds to pass a simple x2-test, leading to an abnormally high mean square weighted deviate (MSWD) and absolute P values lower than 0.05 (e.g. see the detailed description by Baksi 2007a and Jourdan et al. 2009b), indicating discordant results. It has also been proposed that altered plagioclase exhibits an unusually large amount of 36Ar, which can be quantified by the alteration index proposed by Baksi (2007a).

Systematic leaching using a dilute acid (e.g. HF, HNO3) during plagioclase preparation, especially more commonly in use during the last 10–15 years, can help in removing part of the alteration products within the plagioclase, while leaving the latter intact. Nevertheless, the extreme sensitivity of plagioclase to minute amount of sercite renders plagioclase dating a hard task. As a result, many plagioclase 40Ar/39Ar data in the literature do not reflect the true crystallization age of the rock (e.g. Baksi 2007b; Nomade et al. 2007). Using some of these criteria, some authors (e.g. Hofmann et al. 2000; Jourdan et al. 2005; Nomade et al. 2007; Baksi 2007b; Evins et al. 2009; Reichow et al. 2009; Cucciniello et al. 2013) have reinvestigated the 40Ar/39Ar age database of several LIPs. The main filtering parameters used were: (1) the selection of 40Ar/39Ar age data measured exclusively on plagioclase for relatively old LIPs (≥50 Ma); and (2) removal of dates obtained on data that did not satisfy the χ2-test and, thus, did not show well-developed plateaus. Baksi (2007b) also used the alteration index to test the freshness of the mineral post-analysis, although the presence of alteration usually resulted in disturbed age spectra failing the χ2-test anyway. In all cases, the filtered ages showed a much more restricted duration of activity for a given type of magmatic unit. For example, Jourdan et al. (2007a) showed that the 1.4 km-thick Lesotho lava pile was emplaced in a time span shorter than <0.8 Ma, below the resolution of the 40Ar/39Ar technique (at least when using plagioclase). These results when compared to other magmatic events within the Karoo provinces suggested an overall prolonged activity over several Ma, with different short-lived volcanic centres active at different times (Jourdan et al. 2008). Similarly, Marzoli et al. (2011), using the most recent 40Ar/39Ar database of CAMP, showed that the onset and main peak volcanic activity was nearly synchronous over the entire province, although different geochemical signatures from different sub-provinces could be correlated with resolvable differences in the times of eruptions. These authors also suggested that diachronous magmatism could be related to the northwards rift–drift transition during the break-up of Pangea. Rigorous statistical filtering and selection of the most robust data can significantly reduce the number of available ages and even leave some provinces with only a few valid 40Ar/39Ar ages (e.g. Kalkarindji: Evins et al. 2009). However, such an approach allows the removal of all dates that do not strictly represent crystallization ages of plagioclase, and therefore produces more coherent and internally consistent results. In most cases, much more precise time resolutions of different magmatic events allows key points inherent to LIP investigations to be studied.

Consequences of 40Ar/39Ar dating of LIPs

40Ar/39Ar results obtained for plagioclase from basaltic rocks from large igneous provinces (LIPs) can only be understood if one recognizes and takes into account the effect of alteration of plagioclase. Previously, we have shown that a tilda-shape pattern observed on a plagioclase 40Ar/39Ar age spectra and/or a Ca/K plots, as well as a decoupling of the 38Ar and 37Ar degassing curves (Fig. 6), signal the presence of sercite in the plagioclase separate. Thanks to the ability of the 40Ar/39Ar system to recognize disturbances, the main consequence of sericitization of plagioclase will be the departure of individual step age from a statistically concordant population; that is, from a well-defined plateau age. In addition to the tilda-shape pattern, sericitization from a non-synchronous alteration event can be easily recognized as step ages will fail to pass a simple χ2-test, leading to an abnormally high mean square weighted deviate (MSWD) and absolute P values lower than 0.05 (e.g. see the detailed description by Baksi 2007a and Jourdan et al. 2009b), indicating discordant results. It has also been proposed that altered plagioclase exhibits an unusually large amount of 36Ar, which can be quantified by the alteration index proposed by Baksi (2007a).
Fig. 6. Experimental Ar/Ar dating on bulk plagioclases from the Central Atlantic Magmatic Province (CAMP; by courtesy of C. Rapaille). Selected plagioclases are sericitized (apparent sericitization in thin section of more than 2%). The Ca/K ratio (90) as well as the age of fresh plagioclase (199 Ma) is reported. Reported numbers in (c), from 1 to 6, are related to the numbers of the steps shown in (a) and (b). (a) & (b) $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_{\text{K}}$ spectrum and $^{40}\text{Ar}/^{39}\text{Ar}$ age
such as the timing of the onset and end of the LIP magmatism, the duration of the peak activity of the volcanism, identifying magmatic centre migrations, and testing true synchronicity between LIPs and mass extinctions. At the other end of the spectrum, it is worth noting that completely sericitized plagioclase yielding robust plateau ages can provide time constraints on major hydrothermal events, such as continental rifting.

As our knowledge of the effect of alteration on plagioclase (and other minerals and groundmass) is improving, so is our understanding of what $^{40}$Ar/$^{39}$Ar data of a particular plagioclase sample truly means. Only by applying rigorous filtering criteria on what is an acceptable ‘age’, will $^{40}$Ar/$^{39}$Ar dating of plagioclase reach its full potential in the study of LIPs.

**Implications for zeolite/pumpellyite/greenschist facies dating**

Low-degree metamorphism is difficult to date because few related metamorphic minerals are available for geochronology. Yet, it has an important application to date important events, such as the formation of many ore deposits. As far as the $^{40}$Ar/$^{39}$Ar technique is concerned, most analyses attempted so far have been carried out on sericite, adularia, alunite, celadonite and clays, and will be briefly described below.

**Fig. 7.** Experimental Ar/Ar dating on bulk plagioclases from the Karoo Province (data in Jourdan et al. 2005). Selected plagioclases are apparently not sericitized (imperceptible sericitization in thin section). The Ca/K ratio (33) of fresh plagioclase is reported.

**Fig. 6.** (Continued) spectrum, as a function of the percentage of $^{39}$Ar released. The Ca/K ratio is proportional to the measured $^{37}$Ar$_{Ca}/^{39}$Ar$_K$ ratio, with the relationship: Ca/K = 1.83 × ($^{37}$Ar$_{Ca}/^{39}$Ar$_K$). (c) Relative degassing curves of $^{37}$Ar$_{Ca}$ and $^{39}$Ar$_K$ as a function of the experimental temperature of each step. Temperatures are also reported.
In principle, typical K-rich zeolite minerals could also be used as potential low-temperature dateable minerals (WoldeGabriel et al. 1996; Hall et al. 1997; Parry et al. 2001), but low retentivity of argon, and saturation of these minerals by active gases, makes zeolite difficult to date in practice. Clay dating by $^{40}\text{Ar}/^{39}\text{Ar}$ has also been attempted using encapsulation to prevent $^{39}\text{Ar}$ recoil loss (e.g. Dong et al. 1995; Haines & Van der Pluijm 2008). However, in this case, the emplacement age of the clay is best defined by the total gas age of the experiment, making the step-heating approach irrelevant, and where similar results can be obtained using the conventional K–Ar technique (Clauer et al. 2008). Few K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ analyses of celadonite are available, and whether this mineral can provide meaningful ages remains to be seen (Oliveros et al. 2008a; Jourdan unpublished data). Adularia has been used in numerous $^{40}\text{Ar}/^{39}\text{Ar}$ dating studies to constrain the age of fluid flow and associated mineralization (e.g. Oliveros et al. 2008b, c; Marton et al. 2010; Verati et al. this volume, in press), and generally provides robust plateau ages.

The sericitization process occurs at the same $P$–$T$ conditions for all of these minerals and, hence, when sericite is dated using $^{40}\text{Ar}/^{39}\text{Ar}$, it can provide the age of the associated metamorphic and/or hydrothermal and/or mineralization events, with the advantage that sericite occurs in a K-rich alteration phase associated with moderately hot fluids and that the isotopic system is generally closed to subsequent alteration. Of course, the latter statement is true provided that the rock does not subsequently reach temperature conditions higher than the closure temperature of sericite (Jourdan et al. 2009a).

For plagioclase (that contains more than 1% of sericite), the time span between magmatism and metamorphism is the main parameter that affects the plagioclase K–Ar age. Although the K–Ar age of sericite can only be found experimentally with 100% of sericitization, a degree of sericitization can only be established when ≥85% sericitization occurred, which should ultimately be tested at first using electron probe and X-ray diffraction (XRD) techniques and then confirmed by the $[\text{Ca}/\text{K}]_{\text{Ar}}$ ratio. In theory, $[\text{Ca}/\text{K}]_{\text{Ar}}$ ratios of pure sericite phase should tend towards 0 but, in practise, it is possible that some Ca is left behind during the sericitization process, yielding to a non-null ratio. For example, Ca/K ratios reported for completely sericitized plagioclase purposely selected show values generally below ≤1 (Oliveros et al. 2008b, c; Jourdan et al. 2009a), whereas sericite directly deposited by fluid flow yielded Ca/K values well below ≤0.1 (e.g. Jian-Wei et al. 2006; Chi et al. 2008). A clear Ca/K cut-off value for what constitutes >85% sericitization (cf. the discussion above) is therefore hard to estimate at this stage, and more data are required before such a value can be established. Nevertheless, an alteration origin and the high K content of sericite allows the K–Ar system to be insensitive to further perturbation, making it an excellent tool for dating alteration events.

As said previously, because the $^{40}\text{Ar}/^{39}\text{Ar}$ technique enables the production of $^{39}\text{Ar}$ age spectra, we can quantify the amount and the age of a sericitization event if we know the formation age of the fresh plagioclase along with its Ca/K ratio, even if the $^{37}\text{Ar}/^{39}\text{Ar}_{\text{K}}$ and age spectra are strongly affected. In practice, a limiting factor is related to the understanding of the Ca/K and the age of plagioclase before the metamorphism event. In different geological contexts, we are often able to have a good understanding of the nature of the protolith, particularly if it only suffered a low degree of metamorphism. For instance, acid plutonic rocks commonly have Na-rich plagioclases (with low Ca/K), whereas basaltic rocks display Ca-rich plagioclases (with high Ca/K). The magmatic age of the protolith can be measured using a radio-isotopic method resistant to low-degree metamorphism, such as zircon U–Pb dating.

At the present stage, further studies are necessary to refine our understanding of the behaviour of the K–Ar system during plagioclase sericitization, including: (1) phase mixing experiments (e.g. Van-Laningham & Mark 2011) between plagioclase and muscovite (in progress); and (2) modelling of the diffusion of different sericite–plagioclase argon reservoirs during the step-heating process.

**Conclusion**

In this study, we investigate the effect of sericitization on the $^{40}\text{Ar}/^{39}\text{Ar}$ age determination of plagioclase using a numerical model including multiple-variable parameters. The most important conclusions are as follows.

- Although sericitization of plagioclase below 1% is hard to detect using a stereomicroscope, it can have dramatic consequences on the apparent $^{40}\text{Ar}/^{39}\text{Ar}$ age measured on a plagioclase separate. We show that, in some realistic cases, even ≤0.1–0.2% of sericite can shift the apparent age by several hundred ka and even several Ma.
The presence of sericite within plagioclase can
be estimated. When the Ca/K ratio and the crystallization age of fresh plagioclase are known, and the Ca/K ratio of the plagioclase is constant, the amount of sericitization of an altered aliquot of plagioclase and the age of the alteration event can be estimated.

The presence of sericite within plagioclase can be identified using a combination of [Ca/K]_Ar ratios, age spectra, and ⁴⁰Ar and ³⁷Ar degassing curves, all produced during a conventional ⁴⁰Ar/³⁹Ar step-heating procedure.

Ultimately, above 65% of sericitization of plagioclase, the ⁴⁰Ar/³⁹Ar age measured on the plagioclase-sericite mixture will be within ±1% of the age of the alteration event. The two ages will be identical above 85 wt% of sericitization. Dating highly sericitized plagioclase is therefore an important tool for dating low-temperature metamorphic events and mineral deposits, especially since the K–Ar system of the sericite is generally immune to further alteration.

Rigorous statistical filtering of plagioclase ⁴⁰Ar/³⁹Ar Ar data from large igneous provinces allows the effect of alteration on the age database to be largely minimized if not completely removed, and allows the true crystallization ages of dated magmatic units to be accessed.

The authors are grateful to G. Feraud, R. Hassani, M. Besnard, C. Rapaille and V. Oliveros for their help at various stages of this study. D. N. Barfod and S. VanLa-ningham are thanked for their constructive and much appreciated reviews.

Appendix

Detailed equations for the determination of ⁴⁰K content in mineral

Considering M as the molecular weight (in g/mol), the percentage of K content expressed in g/g of mineral i is:

\[ \% K_{(g/g)} = \frac{(\% K_2O) \times M_K \times 2}{M_{K_2O}}. \]  \hspace{1cm} (A1)

The percentage of K content expressed in mol/mol of mineral i is:

\[ \% K_{(mol/mol)} = \frac{\% K_{(mol)}}{M_K} = \frac{(\% K_2O) \times M_i \times 2}{M_{K_2O}}. \]  \hspace{1cm} (A2)

The percentage of ⁴⁰K content determination using a ⁴⁰K/ ⁴₀K ratio of 0.01167 × 10⁻² (Garner et al. 1975), expressed in mol/mol of mineral i, is:

\[ \% {\text{⁴⁰K}}_{(mol/mol_i)} = \frac{(\% K_2O) \times M_i \times 2}{M_{K_2O}} \times (0.01167 \times 10^{-2}). \]  \hspace{1cm} (A3)

The percentage of ⁴⁰K content expressed in mol/mol of the mixture, where X is the percentage of sericite in the mélange, is:

\[ \% {\text{⁴⁰K}}_{(mol/mol_{mix})} = X \% {\text{⁴⁰K}}_{(mol/mol_i)}. \]  \hspace{1cm} (A4)

Numerical application for the ⁴⁰Kser

- \( M_{\text{Ser}} \) is the molecular weight of empirical sericite (KAl_3Si_3O_10(OH)_2) (=398.31 g/mol);
- \( M_{K_2O} \) is the molecular weight of K_2O (=94.2 g/mol);
- \( M_K \) is the molecular weight of K (=39.1 g/mol);
- \( ⁴⁰K/K = 0.01167 \times 10^{-2}; \)
- \( % K_2O = 11.82\% \);
- \( % K = 9.82\% \);
- equation (A1): \((\% K \,(g/g)) = 0.098\% \);
- equation (A2): \((\% K \,(mol/mol_{ser})) = 0.999\% \);
- equation (A3): \( % ⁴⁰K \,(mol/mol_{ser}) = 1.166 \times 10^{-4}\% \).

Note that the ‘sericite’ term is used as a general description for fine-grained phyllosilicate replacement phases. Sericite does not have a fixed composition and can be reported as paragonite, illite or hydromuscovite. The majority of sericite is K-bearing but is clearly not fixed exactly at 11.82% K_2O, as used in the present model (pure muscovite). It is an adjustable parameter in the model that can be given by an in situ microprobe analysis.

Numerical application for the ⁴⁰KPl. Unlike the sericite, which has a fixed chemical composition, plagioclases have various Ca, Na and, thus, K contents. Thus, we have to determine the percentage of K_2O in plagioclase with regard to the various Na and Ca contents.

The structural formula of plagioclases can be expressed as:

\[ \text{Na}_{(4-y)} \text{Ca}_{(1-y)} \text{K}_y \text{Al}_{(2-\text{y})} \text{Si}_{(2+\text{y})} \text{O}_8. \]

For each x and y value – that is for each plagioclase composition ranging from pure end-member of albite (An_0) to anorthite (An_100) – we can calculate the proportion of K related to those of Ca and Na. The K content in common plagioclase rarely exceeds 5% of the K-rich end-member (see Fig. A1). We can realistically consider that the stoichiometric index, y, ranges from 0 to 0.05.

Thus, we can model various composition of plagioclases, based on their structural formula which gives us
the related (1) molecular weight, (2) the %K₂O and (2)
the Ca/K of the plagioclase (see Table A1 and Figs A2
& A3; see also the section on ‘Relationship between
%wt K₂O, %wt CaO and Ca/K in plagioclase’ later in
this Appendix for detailed explanations). For example,
y values ranging from 0.001 to 0.05 implies that related
K₂O contents for classical plagioclases range from
0.0017 to 0.87% using an An₅₀ value for this plagioclase
(Fig. A2). For an An₅₀, calibrated values are shown in
Figure A3.

By knowing the molecular weight and related %wt
K₂O for all of the theoretical plagioclases, we can apply
the previous equations (A1)–(A3) (see Table 1A).

Equations (A1)–(A3) are applied, where
\[ M_{K_2O} \] is molecular weight of K₂O (= 94.2 g/mol),
\[ M_K \] is the molecular weight of K (= 39.1 g/mol) and
\[ 40K/K = 0.01167 \times 10^{-2} \]
(Garner et al. 1975).

**Detailed equations for the determination of**
\[ (^{40}K_{Ser}/^{40}K_{tot}) \] and \[ (^{40}K_{Pl}/^{40}K_{tot}) \]
in the mixture

Using equations (A4) and (2), \[ ^{40}K_{tot} = (1 - X)^{40}K_{Pl} + X^{40}K_{Ser} \], we determine the two ratios for the mixture as following:

\[
^{40}K_{Ser}/^{40}K_{tot} = \frac{X(\%K_2O_{Ser} \times M_{Ser} \times 2 \times 0.0001167)}{(1 - X)(\%K_2O_{Pl} \times M_{Pl} \times 2 \times 0.0001167) + X(\%K_2O_{Ser} \times M_{Ser})}
\]

and also:

\[
^{40}K_{Pl}/^{40}K_{tot} = \frac{(1 - X)(\%K_2O_{Pl} \times M_{Pl})}{(1 - X)(\%K_2O_{Pl} \times M_{Pl}) + X(\%K_2O_{Ser} \times M_{Ser})}
\]

**Relationship between %wt K₂O, %wt CaO and Ca/K in plagioclase**

It is obvious that these three chemical parameters are not
independent in plagioclase, such as shown in Figures A2
& A3. In equations (A5) and (A6) the Ca/K ratio is
missing, although it is very important in Ar/Ar dating.

| Plagioclase          | Example 1 | Example 2 | Example 3 |
|----------------------|-----------|-----------|-----------|
|                      | K-rich An₅₀ | K-poor An₅₀ | Classical An₅₀ |
| Structural formula   | K₀₀₅Na₀₄₅Ca₀₅ | K₀₀₀Na₀₄₉Ca₀₅ | K₀₀₁Na₀₄₉Ca₀₅ |
| y (stoichiometric index) | 0.05   | 0.001    | 0.01     |
| %wt K₂O             | 0.869    | 0.017    | 0.174    |
| Molecular weight (g/mol) | 271.13 | 270.23   | 270.40    |
| Related mass ratio Ca/K | 10    | 500      | 50       |
| Equation (A1)       | 0.72140  | 0.01411  | 0.14444  |
| Equation (A2)       | 5.0024   | 0.0975   | 0.9989   |
| Equation (A3)       | 5.84 × 10⁻⁴ | 1.14 × 10⁻⁵ | 1.17 × 10⁻⁴ |
Fig. A2. Related molecular weight, %wt K₂O and Ca–K values in the case of An₅₀.

Fig. A3. Related molecular weight, %wt K₂O and Ca–K values in the case of An₀₅.
because it is related to the $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_{\text{K}}$ ratio measured during the degassing process of analysed minerals.

If we apply equations (A1) and (A2) for Ca in plagioclase:

$$
\% \text{Ca}_{(g/\ion{O}{})} = \left( \frac{(\% \text{CaO})_{\text{pl}} \times M_{\text{Ca}}}{M_{\text{CaO}}} \right) \quad \text{and}
$$

$$
\% \text{Ca}_{(\text{mol/mol})} = \left( \frac{(\% \text{CaO})_{\text{pl}} \times M_{\text{pl}}}{M_{\text{CaO}}} \right).
$$

We can determine the (Ca/K)$_1$ mass ratio or the (Ca/K)$_2$ molar ratio as following:

$$
\left( \frac{\text{Ca}}{K} \right)_1 = \frac{(\% \text{CaO})_{\text{pl}} \times M_{\text{Ca}}}{M_{\text{CaO}}} \times \frac{M_{K_{\text{O}}}}{2(\% K_{\text{O}})_{\text{pl}} \times M_{K}} \approx 0.8606 \left( \frac{\% \text{CaO}}{\% K_{\text{O}}}_{\text{pl}} \right).
$$

$$
\left( \frac{\text{Ca}}{K} \right)_2 = \frac{(\% \text{CaO})_{\text{pl}} \times M_{\text{pl}}}{M_{\text{CaO}}} \times \frac{M_{K_{\text{O}}}}{2(\% K_{\text{O}})_{\text{pl}} \times M_{K}} = \frac{(\% \text{CaO})_{\text{pl}} \times M_{K_{\text{O}}}}{2M_{\text{CaO}}(\% K_{\text{O}})_{\text{pl}}} \approx 0.8387 \left( \frac{\% \text{CaO}}{\% K_{\text{O}}}_{\text{pl}} \right).
$$

Consequently, we can write taking into account the molar ratio:

$$
(\% K_{\text{O}})_{\text{pl}} = \frac{M_{K_{\text{O}}}}{2M_{\text{CaO}}} \times (\% \text{CaO})_{\text{pl}} \times \frac{K}{Ca} \approx 0.8606 \%
$$

If we use equation (A7) in equations (A5) and (A6), we obtain the final equations used in our model:

$$
(\text{Ca/K})_{\text{sericite}} = \frac{X(\% K_{\text{O}})_{\text{Pl}} \times M_{\text{sericite}}}{(1 - X)((M_{K_{\text{O}}}/2M_{\text{CaO}}) \times (\% \text{CaO})_{\text{pl}} \times (K/Ca)_{\text{pl}} \times M_{\text{pl}}) + X(\% K_{\text{O}})_{\text{sericite}} \times M_{\text{sericite}}}
$$

Fig. A4. Ca–K spectrum (left) of plagioclases from the CAMP; and the theoretical (Ca–K)$_{\text{mel}}$ using equation (A11) (right). The (Ca–K) of the mélange is determined using equation (A10) and corresponds to sericitization of 2.8%.
The %wt CaO for plagioclase is related to the stoichiometric indices or Ca in the structural formula. For our model mixing, we fixed first on An80, An60, or An40 for a given K content (y stoichiometric index) and we calculated the related %wt CaO, Ca/Ca ratio and, thus, the induced molecular weight of the considered plagioclase (see the example in Table 1A). We input these values into equations (A8) and (A9).

**Determination of the sericitization value (X) in 40Ar/39Ar spectra**

With the 37ArCa/39ArK data from a real experiment, we approximate the Ca/K ratio of the mélange (Ca/K)$_{mel}$ (hereinafter defined as "s" parameter) with respect to Ca/K and the related percentage of 39Ar of each temperature step:

$$\left(\frac{\text{Ca}}{K}\right)_{mel} = \sum_{i}^{N} \left(\%\text{Ca}_{i} \times \left(\frac{\text{Ca}}{K}\right)_{i}\right) = s$$  \hspace{1cm} (A10)

where $s$ represents the experimental (Ca/K)$_{mel}$, $i$ is the number of steps and Ca/K is 1.83 $\times$ 37ArCa/39ArK (after McMaster Reactor Facilities).

We can also define the theoretical value of (Ca/K)$_{mel}$ considering the (Ca/K)$_{Pl}$ of the unaltered plagioclase:

$$\left(\frac{\text{Ca}}{K}\right)_{mel} = \left(\frac{\text{Ca}_{Pl}}{K_{Pl}} + \text{K}_{ser}\right) = \left(1 + \left(\text{K}_{ser}/\text{K}_{Pl}\right)\right)^{-1} \hspace{1cm} (\text{CAK})$$  \hspace{1cm} (A11)

Using equations (7) and (8), we can replace K$_{ser}$/K$_{Pl}$ with:

$$\left(\frac{\text{Ca}}{K}\right)_{mel} = \frac{(\text{Ca}_{Pl}/\text{K}_{Pl})}{\left(1 + (X/B/(1 - X))AC\right)} = s$$  \hspace{1cm} (A12)

where $A$ and $B$ are already defined in (7) and (8); $C$ is related to plagioclase chemistry with $C = (\%\text{CaO})_{Pl} \times (K/\text{Ca}_{Pl}) \times M_{Pl}$.

Finally, we obtain:

$$X = \frac{1}{(B/\gamma AC ) + 1} \hspace{1cm} \text{with} \hspace{1cm} (\text{Ca}/K)_{Pl} = \frac{\text{Ca}_{Pl}}{\text{K}_{Pl}}$$

$$\gamma = \frac{\%\text{Ca}_{i} \times (\text{Ca}/K)_{i}}{\sum_{i}^{N} \%\text{Ca}_{i} \times (\text{Ca}/K)_{i}} - 1 \hspace{1cm} (A13)$$

$$= \left(\frac{(\text{Ca}_{Pl}/\text{K}_{Pl})}{s} - 1\right).$$

We use these equations for the 40Ar/39Ar data reported in Figures 6 and 7.

For the CAMP plagioclase (Fig. 6), we find a degree of sericitization of approximately 3% (see Fig. A4). For the Karoo sample, we find a slight sericitization of 0.16% (Fig. 7).

**Estimate of the age $t'$ of the alteration in Ar/Ar spectra**

Using equation (1) in the text, and considering previous the $X$ value in equations (2) and (3), we can write for $t'$:

$$t' = \frac{1}{\Delta} \ln \left[1 + \left(\frac{40\text{K}_{tot}}{40\text{K}_{ser}}\right)\left(e^{\Delta t} - 1\right) - \left(\frac{40\text{K}_{Pl}}{40\text{K}_{ser}}\right)\left(e^{\Delta t} - 1\right)\right]$$  \hspace{1cm} (A14)

where $t$ is the age of the unaltered plagioclase, and $t_{mel}$ is the age of the mélange and thus the total gas age during the entire degassing process (for $i$ temperature steps):

$$t_{mel} = \sum_{i}^{N} \left(\%\text{Ar}_{i} \times t_{i}\right) \hspace{1cm} (A15)$$

For CAMP and Karoo plagioclases, we find an age of sericitization of 176 and 172 Ma, respectively.

**References**

AGUIRRE, L., FERAUD, G., MORATA, D., VERGERA, M. & ROBINSON, D. 1999. Time interval between volcanism and burial metamorphism and rate of basin subsidence in a Cretaceous Andean extensional setting. *Tectonophysics*, 313, 433–447.

BAKSI, A. K. 2007a. A quantitative tool for detecting alteration in undisturbed rocks and minerals—I: water, chemical weathering and atmospheric argon. *In: FOUGLER, G. R. & JURDY, D. M. (eds) The Origin of Melting Anomalies, Plates, Plumes and Planetary Processes*. Geological Society of America, Special Papers, 430, 285–303.

BAKSI, A. K. 2007b. A quantitative tool for detecting alteration in undisturbed rocks and minerals—II: application to argon ages related to hotspots. *In: FOUGLER, G. R. & JURDY, D. M. (eds) The Origin of Melting Anomalies, Plates, Plumes and Planetary Processes*. Geological Society of America, Special Papers, 430, 305–335.

BOVEN, A., PASTEELS, P., KELLEY, S. P., PUNZALAN, L., BIGEN, B. & DEMAIEFFE, D. 2001. 40Ar/39Ar study of plagioclases from the Rogaland anorthosite complex (SW Norway); an attempt to understand argon ages in plutonic plagioclase. *Chemical Geology*, 176, 105–135.

BOVEN, A., PASTEELS, P. et al. 2002. 40Ar/39Ar geochronological constraints on the age and evolution of the Permo-Triassic Emeishan Volcanic Province, Southwest China. *Journal of Asian Earth Sciences*, 20, 157–175.

BROCKAMP, O., CLAUSER, N. & ZUTHER, M. 2003. Authigenic sericite record of a fossil geothermal system: the Offenburg trough, central Black Forest, Germany. *International Journal of Earth Sciences (Geologische Rundschau)*, 92, 843–851.

CASSATA, W. S., RENNE, P. R. & SHUSTER, D. L. 2009. Argon diffusion in plagioclase and implications for thermochronometry: a case study from the Bushveld...
Complex, South Africa. *Geochemica et Cosmochimica Acta*, **73**, 6600–6612.

CLAUER, N., LIEWIG, N., LEDESERT, B. & ZWINGMANN, H. 2008. Thermal history of Triassic sandstones from the Voges Mountains-Rhine Graben rifting area, NE France, based on K–Ar illite dating. *Clay Minerals*, **43**, 363–379.

CHI, G., WATERS, S., DAVIS, W. J., NI, P., CASTONGUAY, S. & HOY, D. 2008. Geologic, geochemical, and Geochronological Constraints on the Genesis of Gold Mineralization at Poplar Mountain, Western New Brunswick, Canada. *Exploration and Mining Geology*, **17**, 101–130.

COURTILLOT, V., GALLET, Y. ET AL. 2000. Cosmic markers, 40Ar/39Ar dating and paleomagnetism of the KT sections in the Anjar Area of the Deccan large igneous province. *Earth and Planetary Science Letters*, **182**, 137–156.

COURTILLOT, V., KRACHVINSKY, V. A., GUIDELLEUR, X., RENNE, P. R. & GLADKOCHEB, D. P. 2010. Preliminary dating of the Viluy traps (Eastern Siberia): eruption at the time of Late Devonian extinction events? *Earth and Planetary Science Letters*, **300**, 239–245.

CUCCIENELLO, C., MELLUSO, L., JOURDAN, F., MAHONEY, J. J., MEISEL, T. & MORR, V. 2013. 40Ar–39Ar ages and isotopic geochemistry of Cretaceous basalts in northern Madagascar: refining eruption ages, extent of crustal contamination and parental magmas in a flood basalt province. *Geology Magazine*, **150**, 1–17.

DECKART, K., FERAUD, G. & BERTRAND, H. 1997. Age of Jurassic continental tholeiites of French Guyana, Surinam and Guinea: implications for the initial opening of the Central Atlantic Ocean. *Earth and Planetary Science Letters*, **150**, 205–220.

DONG, H., HALL, C. M., PEACOR, D. R. & HALLIDAY, A. N. 1995. Mechanism of argon retention in clays revealed by laser 40Ar/39Ar dating. *Science*, **267**, 355–359.

EVINS, L. Z., JOURDAN, F. & PHILLIPS, D. 2009. The Cambrian Kalkarindji large igneous province: extent and characteristics based on new 40Ar/39Ar and geochemical data. *Lithos*, **110**, 294–304.

FUENTES, F., FERAUD, G., AGUIRRE, L. & MORATA, D. 2005. 40Ar/39Ar dating of volcanism and subsequent very low-grade metamorphism in a subsiding basin: example of the Cretaceous lava series from central Chile. *Chemical Geology*, **214**, 157–177.

GARNER, E. L., MURPHY, T. J., GRAMLICH, J. W., PAULSEN, P. J. & BARNES, I. L. 1975. Absolute isotopic abundance ratios and the atomic weight of a reference sample of potassium. *Journal of Research of NIST (U.S.)*, **79A**, 713–725.

GOLL, M., LIPPO, H. J. & HOEFS, J. 2003. Mesozoic alteration of Permian volcanic rocks (Thüringer Wald, Germany): Ar, Sr and O isotope evidence. *Chemical Geology*, **199**, 209–231.

HAINES, S. H. & VAN DER PLUIT, B. A. 2008. Clay quantification of Ar and Ar–Ar dating of synthetic and natural gouge: Application to the Miocene Sierra Mazatán detachment fault, Sonora, Mexico. *Journal of Structural Geology*, **30**, 525–538.

HALL, C. M., HIGUERAS, P. L., KESLER, S. E., LUNAR, R., DONG, H. & HALLIDAY, A. N. 1997. Dating of alteration episodes related to mercury mineralization in Almaden District, Spain, Earth Planet. *Science Letters*, **148**, 287–298.

HAMES, W. E., RENNE, P. R. & RUPPEL, C. 2000. New evidence for geologically instantaneous emplacement of earliest Jurassic Central Atlantic magmatic province basalts on the North American margin. *Geology*, **28**, 859–862.

HARRISON, T. M., CÉLÉRIER, J., AIKMAN, A., HERMANN, J. & HEIZLER, M. T. 2009. Diffusion of 40Ar in muscovite. *Geochemica et Cosmochimica Acta*, **73**, 1039–1051.

HOFMANN, C. 1997. Datation 40Ar/39Ar et paléomagnétisme des traps d’Ethiopie, du Deccan et de Sibérie. PhD thesis, Université Paris 7 – IPGP.

HOFMANN, C., COURTILLOT, V., FERAUD, G., ROCHETTE, P., YIRGU, G., KETEFO, E. & PIK, R. 1997. Timing of the Ethiopian flood basalt event and implications for plume birth and global change. *Nature (London)*, **389**, 838–841.

HOFMANN, C., FERAUD, G. & COURTILLOT, V. 2000. 40Ar/39Ar dating of mineral separates and whole rocks from the Western Ghats lava pile: further constraints on duration and age of the Deccan traps. *Earth and Planetary Science Letters*, **180**, 13–27.

JIAN-WEI, L., VASCONCELOS, P., MEI-FU, Z., XIN-FU, Z. & CHANG-QIAN, M. 2006. Geochronology of the Pengjiakuang and Rushan Gold Deposits, Eastern Jiaodong gold province, Northeastern China: implications for regional mineralization and Geodynamic setting. *Economic Geology*, **101**, 1023–1038.

JOURDAN, F., MARZOLI, A., BERTRAND, H., COSCA, M. & FONTIGNIE, D. 2003. The northernmost CAMP: 40Ar/39Ar age, petrology and Sr–Nd–Pb isotope geochemistry of the Kerforne Dike, Brittany, France. In: HAMES, W. E., MCHONE, J. G., RENNE, P. R. & RUPPEL, C. R. (eds) *The Central Atlantic Magmatic Province: Insights from Fragments of Pangea*. American Geophysical Union, Geophysical Monograph, **136**, 209–226.

JOURDAN, F., FERAUD, G. ET AL. 2004. The Karoo triple junction questioned: evidence from 40Ar/39Ar Jurassic and Proterozoic ages and geochemistry of the Okavango dyke swarm (Botswana). *Earth and Planetary Science Letters*, **222**, 989–1006.

JOURDAN, F., FERAUD, G., BERTRAND, H., KAMPUNZU, A. B., TSHOSO, G., WATKEYS, M. K. & LE GALL, B. 2005. The Karoo large igneous province: brevity, origin, and relation with mass extinction questioned by new 40Ar/39Ar age data. *Geology*, **33**, 745–748.

JOURDAN, F., FERAUD, G., BERTRAND, H. & WATKEYS, M. K. 2007a. From flood basalts to the inception of oceanization: example from the 40Ar/39Ar high-resolution picture of the Karoo large igneous province. *Geochemistry, Geophysics, Geosystems*, **8**, Q02002, http://dx.doi.org/10.1029/2006GC001392.

JOURDAN, F., FERAUD, G., BERTRAND, H., WATKEYS, M. K. & RENNE, P. R. 2007b. Distinct brief major events in the Karoo large igneous province clarified by new 40Ar/39Ar ages on the Lesotho basalts. *Lithos*, **98**, 195–209.

JOURDAN, F., FERAUD, G., BERTRAND, H., WATKEYS, M. K. & RENNE, P. R. 2008. The 40Ar/39Ar ages of the sill complex of the Karoo large igneous province: Implications for the Plinianbachian-Toarcian climate.
K–Ar AND PLAGIOCLASE ALTERATION

change. *Geochemistry Geophysics Geosystems*, 9, Q06009.

Jourdan, F., Marzoli, A. et al. 2009a. 40Ar/39Ar ages of CAMP in North America: implications for the Triassic–Jurassic boundary and the 40K decay constant bias. *Lithos*, 110, 167–180.

Jourdan, F., Renne, P. R. & Reimold, W. U. 2009b. An appraisal of the ages of terrestrial impact structures. *Earth and Planetary Science Letters*, 286, 1–13.

Knight, K. B., Renne, P. R., Halkett, A. & White, N. 2003. 40Ar/39Ar dating of the Rajahmundry Traps, Eastern India and their relationship to the Deccan Traps. *Earth and Planetary Science Letters*, 208, 85–99.

LeGall, B., Tshosho, G. et al. 2002. 40Ar/39Ar geochronology and structural data from the giant Okavango and related mafic dyke swarms, Karoo igneous province, Botswana. *Earth and Planetary Science Letters*, 202, 595–606.

Lippolt, H. J. & Siebel, W. 1991. Evidence for multistage alteration of Schwarzwald lamprophyres. *European Journal of Mineralogy*, 3, 587–601.

Márton, I., Moritz, R. & Spikings, R. 2010. Application of low-temperature thermochronology to hydrothermal ore deposits: formation, preservation and exhumation of epithermal gold systems from the Eastern Rhodopes, Bulgaria. *Tectonophysics*, 483, 240–254.

Marzoli, A., Renne, P. R., Piccirillo, E. M., Ernesto, M., Bellieni, G. & De Min, A. 1999. Extensive 200-million-year-old continental flood basalts of the Central Atlantic Magmatic Province. *Science*, 284, 616–618.

Marzoli, A., Jourdan, F. et al. 2011. Timing and duration of the Central Atlantic magmatic province in the Newark and Culpeper basins, eastern USA. *Lithos*, 122, 175–188.

McDougall, I. & Harrison, T. M. 1999. Geochronology and Thermochronology by the 40Ar/39Ar Method. Oxford University Press, Oxford.

Nomade, S., Knight, K. B. et al. 2007. Chronology of the Central Atlantic Magmatic Province: implications for the Central Atlantic rifting processes and the Triassic–Jurassic biotic crisis. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 246, 326–344.

Oliveros, V., Aguirre, L., Morata, D., Simonetti, A., Vergara, M., Belmar, M. & Calderón, S. 2008a. Geochronology of very low-grade Mesozoic Andean metabasites; an approach through the K–Ar, 40Ar/39Ar and U–Pb LA-ICP-MS methods. *Journal of the Geological Society*, 165, 579–584.

Oliveros, V., Feraud, G., Aguirre, L., Ramirez, L., Fornari, M., Palacios, C. & Parada, M. 2008b. Detailed 40Ar/39Ar dating of geologic events associated with the Mantos Blancos copper deposit, northern Chile. *Mineralium Deposita*, 43, 281–293.

Oliveros, O., Tristá-Aguilera, D., Féraud, G., Morata, D., Aguirre, L., Kojima, S. & Ferraris, F. 2008c. Time relationships between volcanism–plutonism–alteration–mineralization in Cu-stratabound ore deposits from the Michilla mining district, northern Chile: a 40Ar/39Ar geochronological approach. *Mineralium Deposita*, 43, 61–78.

Parry, W. T., Bunds, M. P., Bruhn, R. L., Hall, C. M. & Murphy, J. M. 2001. Mineralogy, 40Ar/39Ar dating andapatite fission track dating of rocks along the Castle Mountain fault, Alaska. *Tectonophysics*, 337, 149–172.

Pati, J. K., Jourdan, F., Armstrong, R. A., Reimold, W. U. & Prakash, K. 2010. First SHRIMP U–Pb and 40Ar/39Ar chronological results from impact melt breccia from the Paleoproterozoic Dhala impact structure, India. In: Gibson, R. L. & Reimold, W. U. (eds) *Large Meteorite Impacts and Planetary Evolution IV*. Geological Society of America, Special Papers, 465, 571–591.

Reichow, M. K., Pringle, M. S. et al. 2009. The timing and extent of the eruption of the Siberian Traps large igneous province: implications for the end-Permian environmental crisis. *Earth and Planetary Science Letters*, 277, 9–20.

Schwarz, H. 2001. Argon-Geochemie von Mineralien hydrothermaler Bildung (Zoilithe; Serizite in Plagioklas). Unpublished PhD thesis, Ruprecht-Karls-University, Heidelberg.

Schwarz, H. & Lippolt, H. J. 2002. Dating of hydrothermal alteration by the 40Ar/39Ar step heating method using plagioclase–sericite intergrowth. *Geochimica et Cosmochimica Acta*, 66, 692.

Steiger, R. H. & Jäger, E. 1977. Subcommission on geochronology: convention of the use of decay constants in geo- and cosmochronology, *Earth and Planetary Science Letters*, 36, 359–362.

VanLaningham, S. & Mark, D. F. 2011. Step heating of 40Ar/39Ar standard mineral mixtures: investigation of a fine-grained bulk sediment provenance tool. *Geochimica et Cosmochimica Acta*, 75, 2324–2335.

Verati, C., Bertrand, H. & Feraud, G. 2005. The farthest record of the Central Atlantic Magmatic Province into West Africa craton: precise 40Ar/39Ar dating and geochemistry of Taoudenni basin intrusives (northern Mali). *Earth and Planetary Science Letters*, 235, 391–407.

Verati, C., Rapaille, C., Féraud, G., Marzoli, A., Bertrand, H. & Youbi, N. 2007. 40Ar/39Ar ages and duration of the Central Atlantic Magmatic Province volcanism in Morocco and Portugal and its relation to the Triassic–Jurassic boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 244, 308–325.

Verati, C., Patrier-Mas, P., Lardeaux, J. M. & Bouchot, V. In press. Timing of geothermal activity in an active island-arc volcanic setting: First 40Ar/39Ar dating from Bouillante geothermal field (Guadeloupe, French West Indies) In: Jourdan, F., Mark, D. F. & Verati, C. (eds) *Advances in 40Ar/39Ar Dating: from Archaeology to Planetary Sciences*. Geological Society, London, Special Publications, 378, http://dx.doi.org/10.1144/SP378.19

Watanabe, M., Hoshino, K., Kagami, H., Nishido, H. & Sugiyama, M. 1998. Rb–Sr, Sm–Nd and K–Ar systematic of metamorphosed pillowed basalts and associated Besshi-type deposits in the Sanbagawa Belt, Japan. *Mineralium Deposita*, 34, 113–120.

WoldeGabriel, G., Brontx, D. E. & Byers, F. M. 1996. Mineralogy and temporal relations of coexisting authigenic minerals in altered silicic tuffs and their
utility as potential low-temperature dateable minerals. 
*Journal of Volcanology and Geothermal Research*, **71**, 155–165.

Zelazniewicz, A., Marheine, D. & Oberc-Dziedzic, T. 2003. A late Tournaisian synmetamorphic folding and thrusting event in the eastern Variscan foreland: 
*40Ar/39Ar* evidence from the phyllites of the Wolsztyn-Leszno High, western Poland. *International Journal of Earth Sciences (Geologische Rundschau)*, **92**, 185–194.