

**A quantitative tool for detecting alteration in undisturbed rocks  
and minerals – I: water, chemical weathering and atmospheric argon.**

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## ABSTRACT

Alteration of undisturbed igneous material used for argon dating work, is the most common cause of incorrect (low) estimates of the time of crystallization. Identification of alteration has relied on qualitative and subjective (optical) methods. For  $^{40}\text{Ar}/^{39}\text{Ar}$  dating, I introduce a new parameter the alteration index (A.I.) - to *quantitatively* assess alteration. This looks to the quantity of  $^{36}\text{Ar}$  (atmospheric argon) released in such studies. A non-dimensional parameter is used, relating the  $^{36}\text{Ar}$  levels to that of  $^{39}\text{Ar}$  for K-rich phases (K-feldspar, biotite, whole-rock basalt), and to  $^{37}\text{Ar}$  for Ca-rich phases (plagioclase feldspar and hornblende). Water contains large amounts of dissolved argon derived from the atmosphere. During chemical weathering,  $^{36}\text{Ar}$  carried by water is introduced into the silicate phases of rocks. All common alteration minerals contain water; their  $^{36}\text{Ar}$  contents are  $\sim 100 - 1000$  times higher than in anhydrous silicate phases. Incipient alteration, undetected by current tests, is unequivocally recognized by the A.I. method. In  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating studies, the plateau steps (if any) release argon from the least altered sites. The A.I. of plateau steps for fresh, subaerial, material yields the cut-off value for detecting alteration. *Partial loss of  $^{40}\text{Ar}^*$  from altered samples, may result in statistically acceptable plateaus, that underestimate the true crystallization age by  $\sim 2 - 10\%$ .* Many ages are invalid as accurate estimates of the age of crystallization (a) based on statistical analysis of the apparent ages on plateau/isochron plots and/or (b) plateau ages derived from altered phases within the sample. At subduction zones, the hydrated slab cycles substantial quantities of (atmospheric) argon into the mantle. Monitoring  $^{36}\text{Ar}$  levels in (mafic and intermediate) rocks should serve as a sensitive tool in elucidating the role of water driven off the subducted slab, in triggering magmatism in convergent zone settings.

*“It is my intention to cite experience, then to show by reasoning why this experience is constrained to act in this manner. And this is the rule according to which speculators as to natural effects have to proceed” (Leonardo da Vinci, ca. 1513).*

## INTRODUCTION

Obtaining precise and accurate radiometric data plays a critical role in earth sciences in unravelling the timing, duration, and rates of geological processes/phenomena. The most widely used techniques are the argon dating methods, utilizing the presence of measurable quantities of potassium in most rocks and minerals, and the wide temporal range (~2 ka to 4.5 Ga – Renne et al., 1997; Renne, 2000) to which the method has been utilized. The  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating technique (Merrihue and Turner, 1966), permits evaluation of the possible (partial) loss of  $^{40}\text{Ar}^*$ , and/or the presence of excess argon in terrestrial material (Lanphere and Dalrymple, 1971, 1976). The reproducibility of the resulting step ages determines the accuracy and precision of ages as estimates of the time of crystallization of igneous rocks and minerals. Numerous  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating ages in the literature do not meet the basic “mathematical” requirements in this regard. All such ages should be statistically acceptable at the 95% confidence level. Many “ages” related to hotspot generated rocks, have been shown to be statistically invalid (Baksi, 1999, 2005a).

For the argon dating methods the daughter product is a gas, and can escape from rocks/ minerals under various physico-chemical conditions. The effect of raising the ambient temperature, leading to diffusion loss of  $^{40}\text{Ar}^*$  and lowered K-Ar dates, has been known for many decades (e.g. Hart, 1964). Effort has been directed to recover accurate time and (cooling) rate information (see McDougall and Harrison, 1999, and references therein). Alteration (chemical weathering), ubiquitous in geological materials, can lead to lowered argon ages by the formation of “leaky” (altered) minerals that do not retain 100% of argon over geological time, or by episodic loss of  $^{40}\text{Ar}^*$  at the time of the weathering processes (see reviews in Dalrymple and Lanphere, 1969; McDougall and Harrison, 1999).

Arguably, the outstanding achievement of the argon dating methods was the establishment of the geomagnetic polarity time scale (GPTS), which led to the plate tectonic revolution (Glen, 1982). The K-Ar based GPTS (Fig. 1) was based on dating specimens (primarily whole-rock

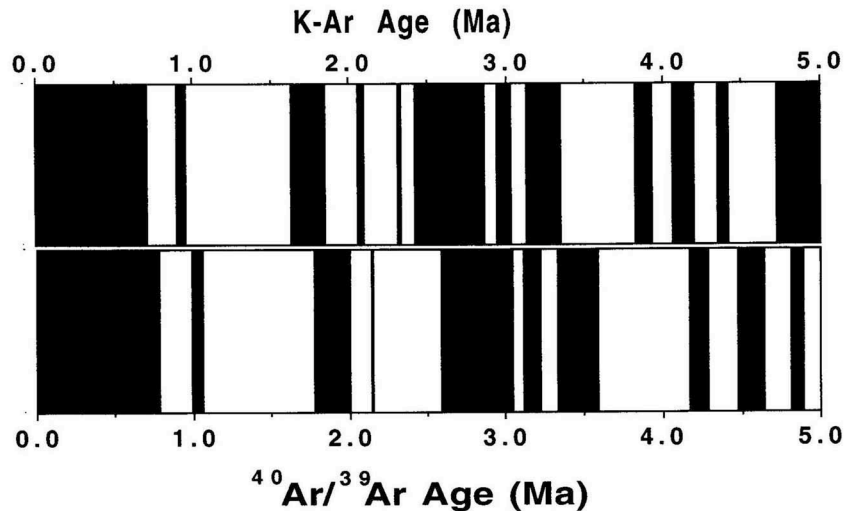


Figure 1. The geomagnetic polarity time scale for 5-0 Ma; black = normal polarity, white = reversed polarity. The K-Ar based version yields ages for chron boundaries that are 5-7% younger than based  $^{40}\text{Ar}/^{39}\text{Ar}$  dating. This results, in part, from K-Ar dates on altered subaerial whole-rock basalts (see text). K-Ar scale from Harland et al. (1990);  $^{40}\text{Ar}/^{39}\text{Ar}$  scale from Baksi (1995).

basalts and sanidine separates) carefully selected for freshness on the basis of petrographic examination (e.g. McDougall and Chamalaun, 1966). Recent astrochronological and  $^{40}\text{Ar}/^{39}\text{Ar}$  dating studies have shown that the K-Ar derived GPTS underestimates the ages of most geomagnetic reversals over the past ~5 Ma by 5-7% (Fig. 1). The low (incorrect) K-Ar dates result, in part, from dating altered whole-rock material which had suffered minor (~5-7%) loss of  $^{40}\text{Ar}^*$  (Baksi, 1995). *The most careful selection of fresh samples (based on optical methods) for very young subaerial rocks is, inadequate.* Dating (older) submarine material that has been in an environment suited for alteration/weathering, for tens of millions of years, is fraught with problems. Thus, the age of the bend in the Hawaiian-Emperor Chain based on whole-rock material (Dalrymple and Clague, 1976), indicated an age of ~43 Ma; recent work on mineral separates suggests it is ~15% older (Sharp and Clague, 2006).

The  $^{36}\text{Ar}$  content of analyses has been used as a guiding factor to detecting alteration (Baksi, 1974a; Roddick, 1978). The method remains underutilized, perhaps due to the lack of a firm theoretical basis for such usage. Herein, this technique will be placed on a *quantitative* basis; the

causes of a marked increase in  $^{36}\text{Ar}$  contents during alteration will be investigated. “The effects of weathering and alteration usually can be recognized in hand specimens or thin sections” (Dalrymple and Lanphere, 1969, p. 146). Advances in this respect have been considerable (see Devigne, 1998), but the method remains semi-quantitative (at best), and its applicability varies widely. The partial loss of an inert gas ( $^{40}\text{Ar}^*$ ) from rocks/minerals (often at the sub parts per trillion level), must be traced by sensitive tools. Chemical methods seem well suited; the water content of mafic whole-rocks have been utilized with limited success (e.g. Kaneoka, 1972). Diffusion loss of  $^{40}\text{Ar}^*$  at the ppt level, is being sought by tools that operate, at best, at the ppm level. The argon data itself, the quantity of one isotope ( $^{36}\text{Ar}$ ) routinely measured in gas samples, is best suited for detecting alteration. Other causes may cause lowered argon ages, including devitrification and exsolution processes. Weathering may cause *partial* loss of  $^{40}\text{Ar}^*$ , as the breakdown of the mineral lattice is incomplete. Occasionally, weathering associated with hydrothermal solutions leads to “ages” that are too old; these will not be investigated herein.

I first review the statistical rules to be observed, then proceed to examine the role of  $^{36}\text{Ar}$  in the understanding of alteration/weathering effects. Ages must be listed with estimated errors, both of which are statistically robust. Only such radiometric “numbers” should be used to derive the timing, and rates of various geological phenomena/ processes. I shall denote (in figures/ tables) and list errors at the one sigma level. Ages are reported relative to the calibrations of Renne et al. (1998) and where necessary, converted to the decay constants, isotopic abundances, listed by Steiger and Jager (1977). All plateau/isochron ages with probability values  $< 0.05$  ( $2\sigma$  or 95% confidence interval) are rejected as accurate estimates of crystallization age. In cases where the goodness of fit parameter (hereinafter  $F$ ) is  $> 1$ , but the corresponding probability value is  $> 0.05$ , the error in the plateau age is multiplied by  $F^{1/2}$  (cf. Roddick, 1978).

## METHODOLOGY

### *Statistical tests.*

The  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating method gives a series of apparent ages, which are then examined to recover possible crystallization ages for igneous rocks. The data sets are often examined on an isochron plot. The goodness of fit parameter (York, 1969), is calculated for the resulting straight line, bearing in mind the number of data points involved. This (F) parameter is used with Chi Square Tables, to arrive at the probability that the scatter of the points around the isochron, results (entirely) from the experimental errors in measurement of the isotopic ratios (peaks). If this probability value is  $< 0.05$ , excess scatter of the data points is demonstrated - geological error is present. For most undisturbed igneous phases, violation of the “closed system” assumption has occurred, indicating gain or loss of the parent/daughter after formation (time  $t = 0$ ). For argon dating work, the most common cause is loss of the gaseous daughter product.

Many igneous rocks/minerals show little or no excess  $^{40}\text{Ar}$ , as evidenced by isochron plots, yielding initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios (on isochron plots) that are statistically indistinguishable from the atmospheric argon value (295.5 – Nier, 1950). For such material, the use of the age spectrum is justified (see Dalrymple, 1991). Statistics for data evaluation are similar to those applied to isochrons (see Baksi, 2005a), and are easier to understand/evaluate for the average reader. Age spectra with “plateau” sections that show statistically defined variations at the 95% confidence level, can be identified, if the age spectrum is drawn to a proper scale (see [www.mantleplumes.org/ArAr.html](http://www.mantleplumes.org/ArAr.html)). Readers can satisfy themselves to the probable validity of the “plateau age” and if necessary, turn to the detailed examination of the isotopic data sets. *It is critical that authors/journals make all such data available within the manuscript itself or at a supplementary site that can be accessed by readers.* The basics of testing the robustness of isochron data were placed on a firm footing over three decades ago. Berger and York (1970) examined the factors underlying the scatter of points in

their replicate analyses of a whole-rock basalt. Important cases where these principles were disregarded, will be outlined below.

***<sup>36</sup>Ar – the key to detecting alteration in rocks and minerals.***

In K-Ar work, the <sup>36</sup>Ar (atmospheric argon) seen in analyses, is derived from two sources. (a) The “initial” argon within the sample itself and (b) “blank” drawn from the fact that the atmosphere contains ~0.003% of <sup>36</sup>Ar. Careful control of blanks is a prerequisite to using the level of <sup>36</sup>Ar in analyses for quantitative purposes. For much of the early (pre 1980) work this is not the case, though it was demonstrated that such data sets could be achieved with diligent vacuum techniques (Hayatsu and Carmichael, 1970, 1977; Baksi, 1973, 1974a, b; Hayatsu and Palmer, 1975; Hall and York, 1978). With the advent of micro-dating techniques and the utilization of ultra-sensitive mass spectrometers with low and controlled levels of blank (York et al., 1981, 1984), <sup>36</sup>Ar levels in analyses reflect that within the sample itself.

Over three decades ago, it was noted that altered whole-rock basalts showed considerably higher amounts of <sup>36</sup>Ar than fresh material (Baksi, 1974a, b). Fresh whole-rock basaltic material subjected to K-Ar dating, show  $\sim 2 \times 10^{-10} \text{ cm}^3 \text{ STPg}^{-1}$  of <sup>36</sup>Ar (Baksi, 1974a, b; Hall and York, 1978). More felsic material is expected to contain ~3 times as much <sup>36</sup>Ar (e.g. Lux, 1987). Both fresh and marine water contain large amounts of dissolved argon drawn from the atmosphere that currently contains ~0.93% of argon (Kellas, 1895). During chemical weathering, silicate phases interact with water; the latter contains  $\sim 1 \times 10^{-6} \text{ cm}^3 \text{ STPg}^{-1}$  of dissolved <sup>36</sup>Ar (Bieri et al., 1968), >1,000 times higher than in fresh anhydrous silicates. Large amounts of all three isotopes of argon are transferred over to the (altered) mineral, and its isotopic composition should reflect that of the atmosphere at the time of alteration. Since the <sup>40</sup>Ar<sub>At</sub> level cannot be detected uniquely, i.e. distinguished from <sup>40</sup>Ar\*, <sup>36</sup>Ar (which is ~5 times more plentiful than <sup>38</sup>Ar) will be used to detect alteration. The <sup>36</sup>Ar content of a rock/mineral is sharply raised during the alteration/weathering process. Incipient alteration, unobservable by other (chemical or optical) techniques can be pinpointed by a marked increase in the <sup>36</sup>Ar content of the

rock/mineral. This will form the basis of detecting alteration in rocks and minerals. The role of water in raising the  $^{36}\text{Ar}$  level in rocks was recognized over 20 years ago (Baksi, 1982), in seeking to explain K-Ar isochron results (Hayatsu and Carmichael, 1970) on interbedded sediments and basalts from Cape Breton Island, Canada.

The level of atmospheric argon observed in rocks and minerals used for K-Ar dating, varies widely. I shall refer to this component by looking to  $^{36}\text{Ar}$  in the sample (see Fig. 2). McDougall and Harrison (1999) observe that high levels of atmospheric argon are seen in platy minerals (such as micas) as compared to those with prismatic habits. I note a marked correlation between the level of structural water in the material, and its  $^{36}\text{Ar}$  content. The lowest levels are seen in anhydrous material (K-feldspar, plagioclase feldspar, whole-rock basalt), somewhat higher levels in minerals containing low levels of water (hornblende), and the highest levels in those containing high levels of water (micas). Alteration products contain higher amounts of structural water than the parent fresh material, and carry significantly higher levels of  $^{36}\text{Ar}$ . Figure 2 shows a wide variation – an order of magnitude or more - in the  $^{36}\text{Ar}$  contents of all minerals. These variations result in (large) part from dating of samples that have suffered alteration; values for fresh anhydrous minerals should fall close to (or lower than) the minimum values seen in Figure 2. In particular, plagioclase feldspar and whole-rock basalts, commonly used for argon dating work, are prone to alteration. Leaching the crushed samples in acid in an ultrasonic bath, is successful in removing alteration products, and improves the quality of the results. The acid reacts with (and removes) surface alteration and penetrates into microfractures where incipient alteration has taken place.



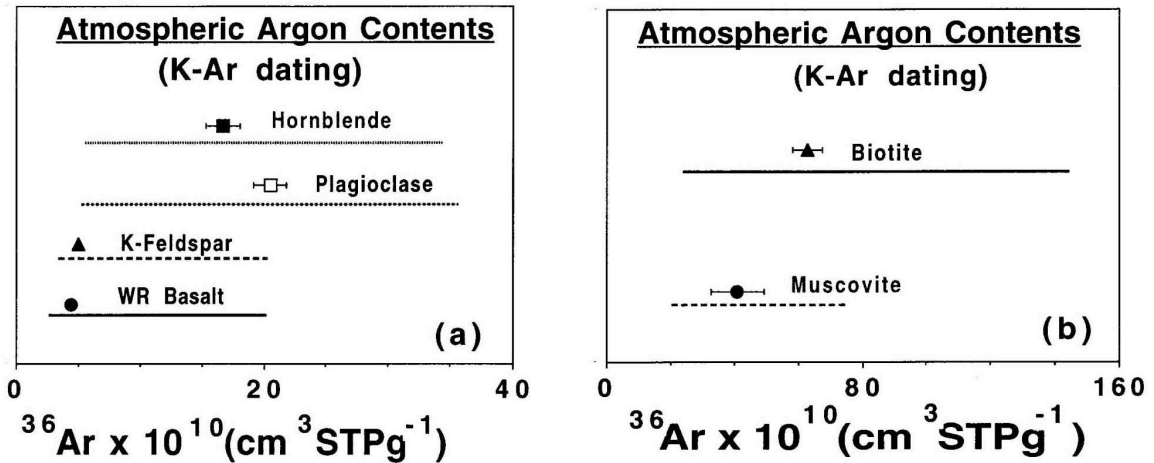


Figure 2. The atmospheric argon contents of various silicate phases as obtained from K-Ar dating studies (modified from McDougall and Harrison, 1999). Results shown in units of  $^{36}\text{Ar}$ , with the mean and standard error on the mean (SEM), along with a line showing the range of values listed in McDougall and Harrison (1999) – single outliers omitted for clarity. (a) Listing for anhydrous silicate phases and hornblende – the large range of values in each case is thought to result from dating of altered material (see text). (b) Results for hydrated phases – the micas. The latter contain  $\sim 10$  times more  $^{36}\text{Ar}$  than the anhydrous phases, resulting from the high solubility of (atmospheric) argon in water.

In  $^{40}\text{Ar}/^{39}\text{Ar}$  dating work, the weight of the sample utilized, and the quantity of gas released in each step, are often not enumerated; further, the K content of the material is generally not measured. It is then not possible to calculate the absolute amount of  $^{36}\text{Ar}$  released in either stepheating or total fusion studies. The neutron irradiation of the specimen produces  $^{39}\text{Ar}$  from  $^{39}\text{K}$ , as well as  $^{37}\text{Ar}$  from  $^{40}\text{Ca}$ . The quantity of these isotopes of argon, routinely measured during mass spectrometry, permits calculation of the K and Ca content of the specimen. The efficiency of production of  $^{39}\text{Ar}_K$  and  $^{37}\text{Ar}_{Ca}$  are dependent on the total neutron flux to which the sample was exposed, measured by J, the irradiation parameter. I shall utilize the quantity of these isotopes released in each step (normalized for the level of neutron irradiation) as a proxy for the weight of the sample under study. The  $^{36}\text{Ar}$  measured must be corrected for blanks, and contributions from side (interfering) reactions for argon produced from calcium and chlorine within the sample. Ideally, one should measure the quantity of  $^{36}\text{Ar}$  released (in  $\text{cm}^3 \text{STPg}^{-1}$  or  $\text{molesg}^{-1}$ ) in all argon dating experiments.

### ***Setting up the alteration index.***

A single parameter for detecting alteration in all rocks and minerals may not be feasible. I look to establishing the modalities for silicates commonly used for argon dating. It involves *quantitatively* assessing the amount of  $^{36}\text{Ar}$  present in the material under study. Typical calculations are shown in the Appendix.

***Whole-rock basalts.*** Fresh whole-rock basalts in K-Ar work, wherein careful vacuum techniques were utilized, contain  $\sim 2 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$  of  $^{36}\text{Ar}$  (Baksi, 1974a, b; Hall and York, 1978). In K-Ar dating, a wide range of values is noted (Fig. 2), resulting from analysis of partially altered rocks. In basalts, the fine-grained mesostasis carries most of the K (Mankinen and Dalrymple, 1972). On alteration, this forms clay minerals that contain substantially greater amounts of  $^{36}\text{Ar}$ . I shall relax the upper cut off value to  $6 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$  of  $^{36}\text{Ar}$  in K-Ar analyses to denote use of fresh material for dating purposes. This method has been used with success to narrow down the range of “good” K-Ar dates for tholeiitic rocks (Baksi, 1987, 1989; Baksi and Hoffman, 2000).

Plateau sections in  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating studies of undisturbed rocks and minerals are taken to reflect crystallization ages (see McDougall and Harrison, 1999). However, numerous cases in the literature show otherwise. *Recovery of statistically acceptable  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages, shown to be considerably younger than crystallization values, prompted a search for a technique to detect alteration in rocks and minerals.* A significant question is how to recognize correct  $^{40}\text{Ar}/^{39}\text{Ar}$  ages. This is best attempted by comparison with ages obtained by more robust techniques such as U-Pb dating. Ages may differ by  $\sim 1\%$ , due, in part, to errors in the currently used values of the decay constants in argon work and/or the ages of the monitors (standards) that are utilized (Min et al., 2000, Renne, 2000). For young rocks, comparison may be possible with the results obtained by the astrochronological approach (Baksi et al., 1992; Renne et al., 1994; Baksi, 1994), or to historical notes (Renne et al., 1997).

In incremental heating studies on whole-rocks, non-plateau steps with low (incorrect) ages invariably show higher amounts of  $^{36}\text{Ar}$  than the plateau steps.  $^{40}\text{Ar}/^{39}\text{Ar}$  dating results for the Gettysburg Sill, northeastern USA, illustrate important features. The age spectra for three specimens yield different plateau ages, all valid from the statistical viewpoint (Fig. 3a). The age of 200 Ma (Baksi, 2003) is close to the U-Pb age (201 Ma – Dunning and Hodych, 1990). The other “ages” (Sutter and Smith, 1979) are significantly younger, resulting from partial loss of  $^{40}\text{Ar}^*$  from altered sites in the material dated. To verify this assertion, a suitable alteration index (A.I.) needs to be set up - I utilize the  $^{36}\text{Ar}/^{39}\text{Ar}$  ratio, corrected for  $^{36}\text{Ar}_{\text{Ca}}$ . All values are normalized to  $J = 0.0100$ , measuring the production of  $^{39}\text{Ar}$  from  $^{39}\text{K}$ . Figure 3b shows the results for the Gettysburg Sill samples. The plateau steps in the work of Sutter and Smith (1979) show  $\sim 20 - 50$  times more  $^{36}\text{Ar}$  than unaltered GS-14 (Baksi, 2003) and are clearly altered. The K content of these rocks is taken to be subequal. In wider application, the K content of basalts used for argon dating may vary by a factor of  $\sim 10$  (0.2% - 2.0% K). This will lead to a similar variation in A.I., resulting from differing K contents, and not alteration effects. Whenever possible, the A.I. must be adjusted for K contents and I utilize an intermediate value of  $K = 0.65\%$ . In the absence of this correction, a variation of  $\sim 3$  in the A.I. would result, reflecting K contents, compared to the 10 - 1000 increase caused by the presence of altered material. The latter may be removed by acid leaching. Use of HF on material with ferromagnesian phases can cause loss of  $^{40}\text{Ar}^*$  without a concomitant loss of K, and the use of  $\text{HNO}_3$  (Baksi and Archibald, 1997), is recommended.

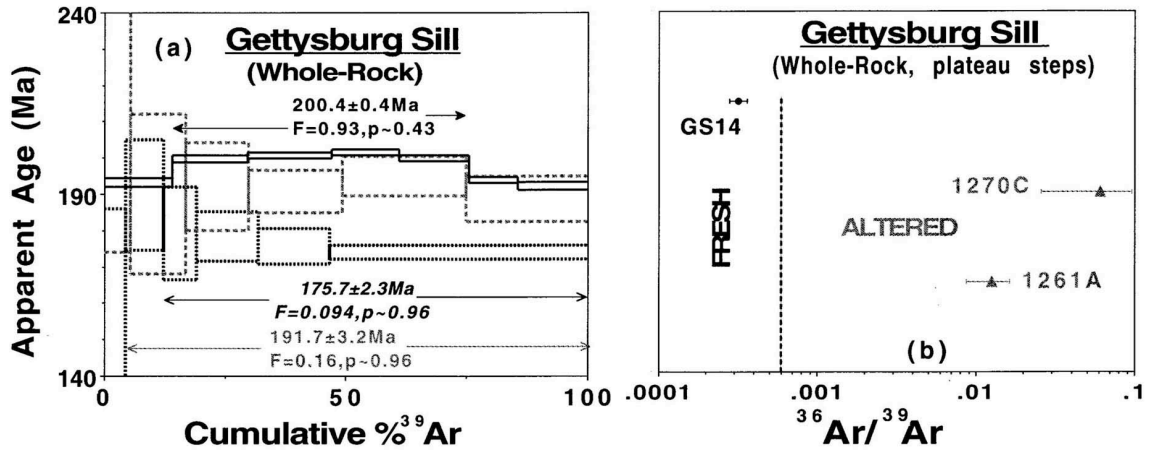


Figure 3. <sup>40</sup>Ar/<sup>39</sup>Ar dating results for whole-rock samples from the Gettysburg Sill. (a) Age spectra for three splits; plateau sections delineated by arrows, F = goodness of fit parameter, p = probability of occurrence. One specimen (solid lines – Baksi, 2003) yields the correct age of ~200 Ma. Two samples (shown with dotted lines - Sutter and Smith, 1979), yield statistically acceptable plateau but are measurably younger. (b) Assessment of the alteration state for the *plateau steps* of all three samples. Average A.I. values and the associated standard error on the mean (SEM) are shown on a *log* scale. Sample GS14 of Baksi (2003), shows ~20 – 50 times less <sup>36</sup>Ar than samples 1261A and 1270C of Sutter and Smith (1979). The latter are clearly altered, even for the plateau (best) sites (see text).

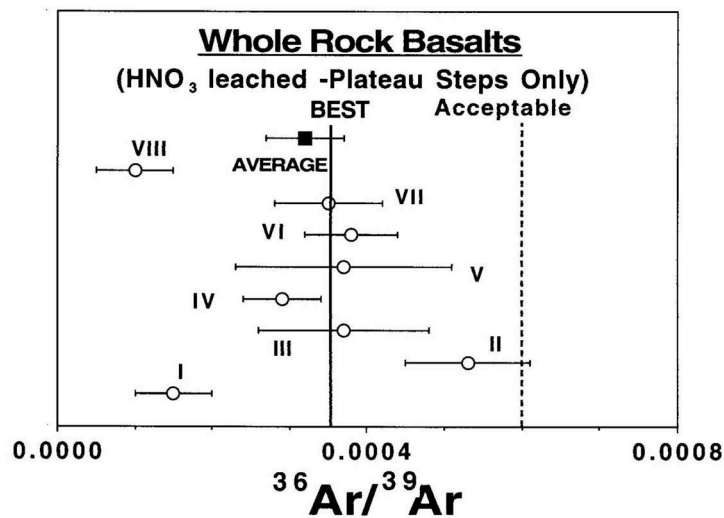


Figure 4. Assessing the A.I. for fresh whole-rock basalts, (average values and SEM shown on a *linear* scale). The average A.I. value is ~0.00035 and the cut-off for fresh samples is relaxed to < 0.0006. Source of data (I through VIII, respectively): alkali basalts ~0.8 Ma – Baksi et al. (1992); tholeiite ~1.8 Ma – Baksi (1994); tholeiites ~2.15 Ma – Baksi and Hoffman (2000); alkali basalts ~9.7 Ma – Baksi et al. (1993); tholeiites ~65 Ma – Baksi (2001); andesitic basalt, alkali basalt, tholeiite (~116 to 119 Ma – Rajamhal Traps, India) – Baksi (unpubl data).

To derive a cutoff value for the A.I. on fresh basalts, I look to <sup>40</sup>Ar/<sup>39</sup>Ar stepheating work on a variety of subaerial whole-rocks ranging in age from < 1 Ma to ~120 Ma, and with K contents

varying from ~ 0.1 to 3.0%. All samples were washed with HNO<sub>3</sub>, and yielded plateau ages for a substantial fraction of the gas released. The A.I. (Fig. 4) shows a relatively small range, illustrating the efficacy of our approach. The average value of ~0.00035, is in agreement with that noted in the work of Hall and York (1978) on ~50 ka (fresh) rocks. Whole-rock basalts exhibiting A.I. > 0.0006 are altered. The Gettysburg Sill samples of Sutter and Smith (1979) exhibit A.I. values 20 - 100 higher, and are highly altered. The <sup>36</sup>Ar content of the rocks used in Figure 4, leads to an average value of ~4 x 10<sup>-10</sup> cm<sup>3</sup>STPg<sup>-1</sup>; a tholeiite (RM82-5) from the Rajmahal Traps, India, contains 90% less <sup>36</sup>Ar. These values are within the guidelines developed over the years for fresh samples. It is critical that the stepheating process, at intermediate and high laboratory extraction temperatures, is able to derive argon from (relatively) unaltered sites, verifiable by noting their A.I.. Whole-rock diabase intrusions from the Newark Trend Basins, USA (Sutter and Smith, 1979), show A.I. > 0.006, ten times the cutoff value. The plateau steps in these experiments typically contain > 100 x 10<sup>-10</sup> cm<sup>3</sup>STPg<sup>-1</sup> of <sup>36</sup>Ar. These rocks are grossly altered and the conclusions of Sutter and Smith (1979) regarding the timing of their intrusion, and the opening of the central Atlantic Ocean, must be discounted.

***Plagioclase feldspar.*** In K-Ar work, this mineral should show low <sup>36</sup>Ar contents since it is anhydrous (see Fig. 2a). It alters readily to form clay minerals. The latter are hydrous and contain considerably higher amounts of <sup>36</sup>Ar. The large range of <sup>36</sup>Ar values noted in K-Ar dating of this mineral (Fig. 2a), results from analysis of altered material. Thus, analyses on plagioclase separates from the Deccan Traps, India (Courtilot et al., 1986), show a correlation between increase in <sup>36</sup>Ar contents (alteration) and lowered K-Ar dates (Fig. 5).

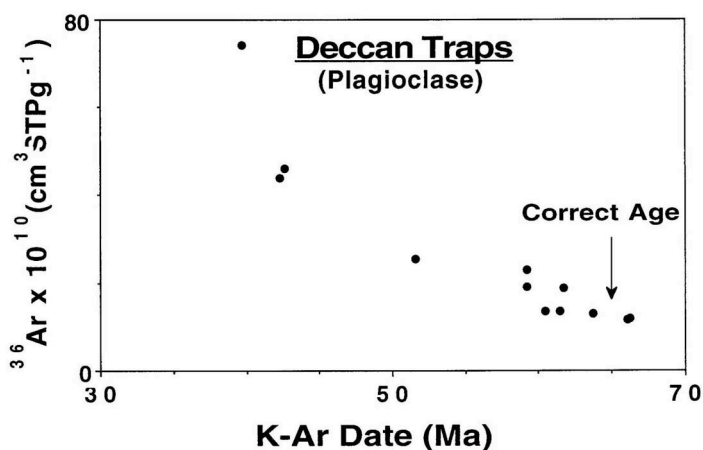


Figure 5. K-Ar dates on plagioclase separates from the Deccan Traps (Courtilot et al., 1986) assessed for alteration. Samples yielding “ages” < 65 Ma, exhibit large amounts of  $^{36}\text{Ar}$ , are altered and have suffered partial loss of  $^{40}\text{Ar}^*$ .

The  $^{40}\text{Ar}/^{39}\text{Ar}$  study of Knight et al. (2003) on the Rajahmundry Traps, India, is our starting point; plagioclase separates were leached with  $\text{HNO}_3$  prior to analysis and gave plateau ages of  $\sim 65$  Ma. Utilizing the A.I. developed above, it is noted the non-plateau steps show high levels of  $^{36}\text{Ar}$  (see Fig. 6a). The age spectrum technique helps obtain a plateau age from the best (least altered) sites. Two specimens (RA99.02 and 99.06/2) are altered (throughout) – (see Baksi, 2005b), and are not considered further. There is considerable variation (factor of  $\sim 10$ ) in the A.I. for the best phases (plateau steps) for the different samples (Fig. 6a), resulting from differing K contents. To overcome this problem, a new A.I. for low-K, high-Ca samples is defined,  $^{36}\text{Ar}/^{37}\text{Ar}$ . The calcium content of the plagioclase serves as a proxy for the weight of the sample. For most plagioclase from mafic rocks, the Ca content varies by about a factor of 2 ( $\sim \text{An}_{40}$  to  $\text{An}_{80}$ ). Figure 6b looks to this new A.I. for the Rajahmundry samples. The data sets are tightened up considerably; the total variation is a factor of  $\sim 3$ . Changes caused by alteration raise the A.I. by a factor of  $\sim 10 - 1000$ .

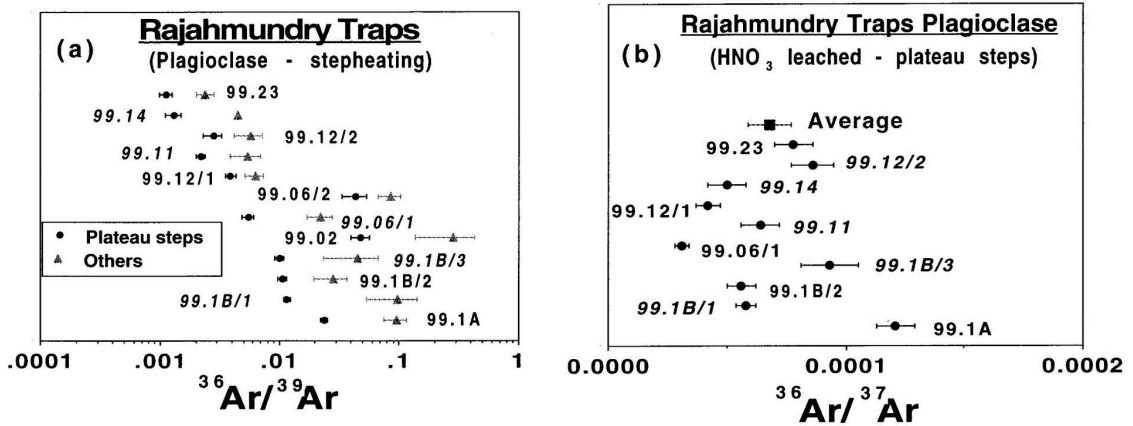


Figure 6.  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating studies on HNO<sub>3</sub> leached plagioclase separates from the Rajahmundry Traps, India (data from Knight et al. 2003). Average A.I. values shown with associated SEM. (a) Results assessed for their  $^{36}\text{Ar}$  content (normalized to  $^{39}\text{Ar}$ ) on a *log* scale. The plateau steps show significantly lower amounts of  $^{36}\text{Ar}$  than other steps. The A.I. for the plateau steps differ considerably. (b)  $^{36}\text{Ar}$  levels normalized to  $^{37}\text{Ar}$  (see text); plateau step averages, with associated SEM, shown on a *linear* scale. The range of A.I. is reduced considerably.

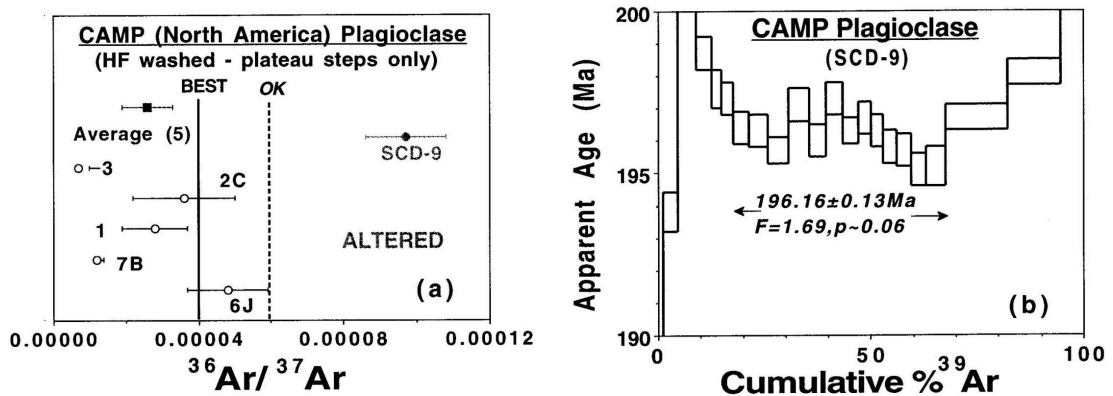


Figure 7. (a) Assessment of the A.I. for HF leached plagioclase from CAMP rocks (data from Hames et al., 2000). Averages and SEM for plateau steps shown on a *linear* scale. Five samples yield a low A.I. cut-off ( $\sim 0.00004$ ) for fresh samples; SDC-9 shows a higher A.I. value. (b) The age spectrum for SDC-9 (symbols and legends as in Fig. 3a), yields a barely acceptable plateau and an “age” that is  $\sim 4$  m.y. too young (see text). This sample is altered; a hard cut off value for A.I.  $< 0.00006$  excludes altered plagioclase.

Alteration products in plagioclase separates can be removed by acid leaching of crushed material (see Dalrymple and Lanphere, 1969). Plagioclase separates from the Central Atlantic Magmatic Province (CAMP) rocks in Africa and North America, have been analyzed in various forms. HF treated samples (Hames et al., 2000) show the lowest  $^{36}\text{Ar}$  concentrations (Fig. 7a). Five samples yield plateau ages of 199-201 Ma and low A.I.. A sixth sample, SDC-9, shows higher A.I., and yields a barely acceptable plateau age that is measurably younger at  $\sim 196$  Ma (Fig. 7b). This sample

is altered, shows disturbance even in the best (“plateau”) steps, and helps to form a sharp A.I. cutoff ( $<0.00006$ ) for fresh plagioclase. The (acid) untreated CAMP plagioclase samples of Deckart et al. (1997) show much higher A.I. (Fig. 8a),  $\sim 10$ – $100$  times that of fresh samples. Their “ages” are not proper plateaux as based on statistical observations, and are thought to be  $\sim 5$ – $10$  m.y. too young (Baksi, 2003). The hot  $\text{HNO}_3$  leached CAMP plagioclase samples of Verati et al. (2005) show lower values of A.I. (Fig. 8b), but are 3–5 times that of the freshest samples; plateau ages are older than those of Deckart et al. (1997). The quantity of (low temperature) gas in each set of experiments that do not constitute the plateau and are derived from altered (high A.I.) sites, varies substantially. For untreated samples this constitutes  $\sim 20\%$  (Deckart et al., 1997), falling to 3–8% for the  $\text{HNO}_3$  leached samples (Verati et al., 2005), and  $< 2\%$  for the HF leached samples (Hames et al., 2000). The A.I. values of Hames et al. (2000) are somewhat lower than the  $\text{HNO}_3$  washed samples of Knight et al. (2003) on the Rajahmundry Traps. The latter chose not to leach their samples with HF since this often produces “fluffy” material on the outside of the plagioclase crystals that are difficult to date properly (P.R. Renne, pers. comm., 2006). The Rajahmundry Trap rocks may contain higher amounts of  $^{36}\text{Ar}$ , as they were formed from intracanyon flows in estuarine/shallow marine conditions (Baksi et al., 1994; Baksi, 2001, 2005b).

I recommend an A.I. cutoff value  $< 0.00006$  for screening plagioclase samples. Values  $< 0.00004$  (Fig. 7a, based on the work of Hames et al., 2000) denote the freshest material. Samples with A.I. values  $> 0.00006$ , show alteration, and yield lower ages (see specimen SDC-9 above). The A.I. method shows different degrees of alteration for plagioclase samples used for defining the CAMP event. Samples washed in  $\text{HNO}_3$  yield statistically valid plateau ages, but may be marginally too young. Until these ages can be verified by some other technique, it is premature to attempt fine resolution of the duration of the CAMP event in North America, Africa, South America and Europe. Alternately, only the ages of samples showing of A.I.  $< 0.00006$  (washed in HF?) serve as accurate estimates of the time of crystallization. The results of Hames et al. (2000) on  $\sim 200$  Ma samples, yield



$^{36}\text{Ar}$  values of  $\sim 1 \times 10^{-10} \text{ cm}^3\text{STP g}^{-1}$  lower than the minimum values observed in K-Ar dating (Fig. 2a). The  $\sim 1.2$  Ma Alder Creek (rhyolite) plagioclase (Nomade et al., 2005) shows  $^{36}\text{Ar} \sim 0.5 \times 10^{-10} \text{ cm}^3\text{STP g}^{-1}$ . This is  $<20\%$  of the lowest value noted in K-Ar dating (see Fig. 2a).

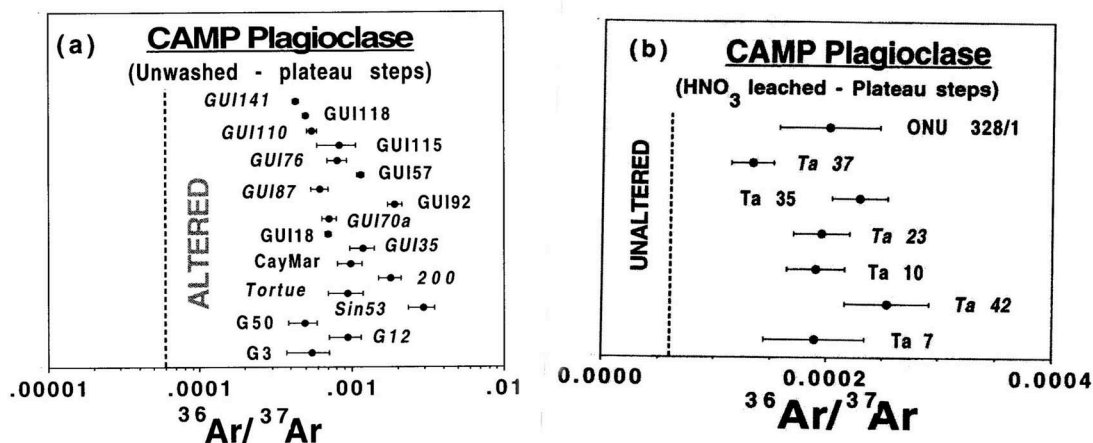


Figure 8. A.I. values for CAMP plagioclase samples. (a) Average and SEM for plateau steps shown on a *log* scale for acid unwashed samples (Deckart et al. 1997). These show  $\sim 10 - 100$  times higher amounts of  $^{36}\text{Ar}$  than the cut-off value ( $\sim 0.00006$ ) and are altered. (b). Average and SEM are shown on a *linear* scale for the plateau steps of  $\text{HNO}_3$  leached samples (Verati et al. 2005). A.I. values are  $\sim 3 - 5$  times higher than the recommended cut-off value; these samples yield plateau ages  $\sim 3 - 5$  m.y. older than those of Deckart et al. (1997). See text.

**K-feldspar.** This mineral is resistant to chemical weathering and in its high temperature forms - sanidine and anorthoclase - serve as good material for dating volcanic rocks. It is anhydrous and shows low amounts of atmospheric argon (Fig. 2a). Acid washing of mineral grains serves to remove (surface) alteration, with dilute HF being the reagent of choice (Dalrymple and Lanphere, 1969).

I begin with the study of Min et al. (2000), attempting cross calibration of the K-Ar and U-Pb dating schemes, utilizing minerals from the  $\sim 1.1$  Ga Palisade rhyolite. A number of single, clear grains of K-feldspar yield good  $^{40}\text{Ar}/^{39}\text{Ar}$  plateaux, averaging 1088 Ma (Fig. 9a). Other multi grain (cloudy) samples yield *statistically acceptable plateau* but are measurably younger (Fig. 9b). There is no reason for rejecting the latter as crystallization ages, beyond the qualitative (optical) observation they may be altered. (It is noted that the Ca/K ratio of the cloudy grains is  $\sim 5$  times

those of the clear grains). Figure 10a looks to the A.I. by observing the  $^{36}\text{Ar}/^{39}\text{Ar}$  ratios for all steps, normalized to  $J = 0.0100$ . For the (cloudy) grains, yielding younger ages of  $\sim 1068\text{-}1077$  Ma, the non-plateau steps show significantly higher quantities of  $^{36}\text{Ar}$ . For the plateau steps, the argon was drawn from the freshest sites within the cloudy grains. The average value of the A.I. is shown in Figure 10b, for the plateau steps, of both the clear (1088 Ma) and cloudy (1068-1077 Ma) grains. Alteration of the latter, shown by a  $\sim 20$  fold increase in the A.I., led to an associated  $\sim 2\%$  loss of  $^{40}\text{Ar}^*$ . In evaluating high temperature K-feldspar ages for possible alteration, the A.I. must be normalized to a single value - chosen to be 0.0100. K-feldspars used for argon dating may have K values varying from  $\sim 3\text{-}15\%$ . Whenever possible, the A.I. should be adjusted to a single value (chosen to be 10.0%). For K-feldspars from different geological environments, K contents may not be reported, and could vary by a factor of  $\sim 2$ , having an equivalent effect on the A.I. This amount is small compared to the changes we seek in detecting alteration, where the  $^{36}\text{Ar}$  content (and hence A.I.) will be raised 10 - 100 fold.

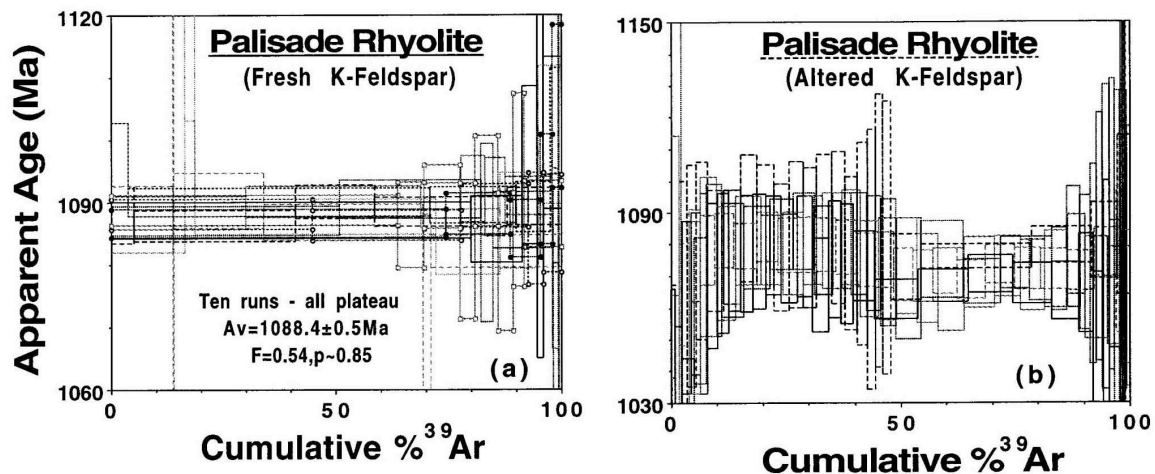


Figure 9.  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra for K-feldspar from the Palisade rhyolite (after Min et al., 2000). (a) Results for ten runs on clear grains. All yield excellent plateau, with an average age of 1088 Ma. (b) Results for five sets of “cloudy” grains. These yield plateaux that are statistically acceptable (probability  $> 0.05$ ), but are measurably younger at 1068-1077 Ma, each with errors of  $\pm 2 - 3$  m.y..

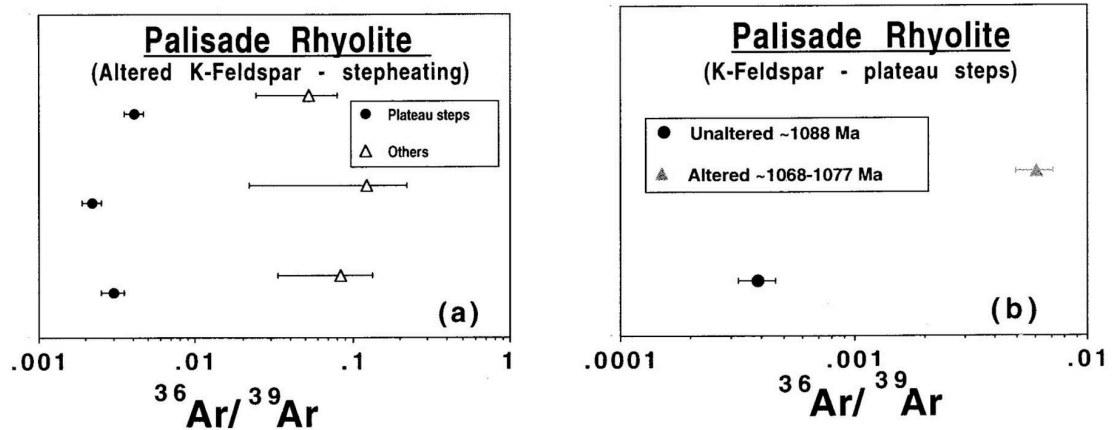


Figure 10. Assessing the alteration of the K-feldspar grains of the Palisade rhyolite (Min et al., 2000) using the A.I technique. Average values are shown with associated SEM on *log* scales. (a) For the cloudy grains, non-plateau steps show significantly higher amounts of  $^{36}\text{Ar}$  than the plateau steps. (b) Values for the *plateau steps only* on the clear (1088 Ma) and cloudy (1068-1077 Ma) grains. The latter show  $\sim 20$  times more  $^{36}\text{Ar}$  than the clear grains, reflecting alteration.

The  $^{36}\text{Ar}$  content of the fresh, 1.2 Ma (Alder Creek rhyolite) sanidine (Renne et al., 1998; Nomade et al., 2005), is  $\sim 1 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$ , lower than all the values noted in K-Ar dating (see Fig. 2a).

The clear K-feldspar grains (1088 Ma) from the Palisade rhyolite (Min et al., 2000) yield values of  $\sim 20 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$ , at the high end of that observed in K-Ar dating (Fig. 2a). This indicates that fixing a single sharp (A.I.) cut-off for freshness may not be possible, as  $^{36}\text{Ar}$  contents appear to be dependant on the age of the sample. This is investigated further below.

**Biotite.** This mineral finds wide use for argon dating purposes. A common alteration product is chlorite, which lowers the K and increases the Ca content of the mineral.  $^{36}\text{Ar}$  contents of this mineral are high in K-Ar dating work (see Fig. 2b); the average value ( $\sim 60 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$ ) is biased to the high side by many samples showing very high values (see McDougall and Harrison, 1999, Fig. 2-6). The latter apparently resulted from the analyses of samples with measurable chloritization. This alteration product contains significantly more water ( $\sim 10\%$  by wt) than fresh biotite ( $\sim 4\%$  by wt).

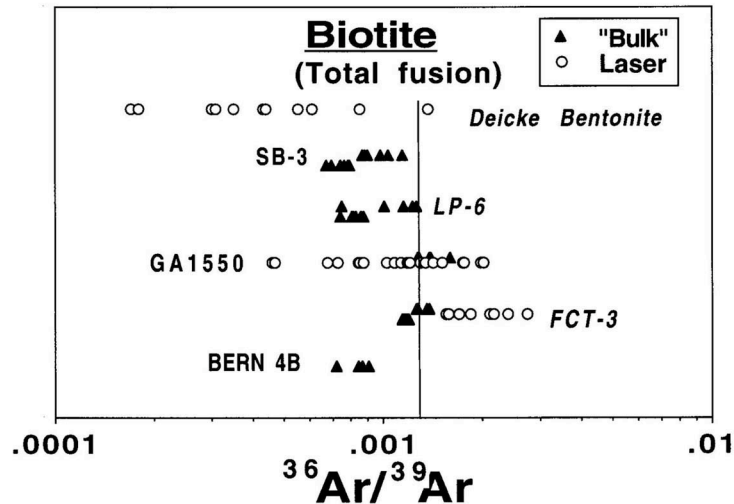


Figure 11. A.I. values for biotite,  $^{36}\text{Ar}$  values normalized to  $^{39}\text{Ar}$ ,  $J = 0.0100$ ,  $K = 8.0\%$ , shown on a *log* scale. Results shown for total fusion on  $\sim 10$  mg splits (“bulk” – blank corrected) and few flakes (laser) on standards. Tentative cut off for *total fusion* analyses on fresh material is set at 0.00130 (see text). Source of data: Baksi et al. (1996), Renne et al. (1998), Daze et al. (2003), Min et al. (2001).

Biotites used as standards (with low Ca/K values, hence unaltered) have been carefully analyzed. I utilize blank corrected values from work on tens of milligram splits (Baksi et al., 1996) and laser work on a few flakes (Renne et al., 1998; Daze et al., 2003). These show  $^{36}\text{Ar}$  values (in units of  $10^{-10}\text{cm}^3\text{STPg}^{-1}$ ), of  $\sim 35 - 60$  (see Fig. 11), in the range expected for fresh biotite. For unaltered material from Ordovician K-bentonites (Min et al., 2001),  $^{36}\text{Ar}$  levels are  $10 - 20 \times 10^{-10}\text{cm}^3\text{STPg}^{-1}$ , comparable to the lowest 5% listed for K-Ar dating by McDougall and Harrison (1999). Two tools may be used to detect alteration in biotite. The first is to look to  $^{37}\text{Ar}/^{39}\text{Ar}$  ratios in analyses. Elevated values ( $> 0.02$  – i.e.  $\text{Ca} > 0.3\%$  by wt) indicate alteration to chlorite. The second is to use the A.I. method. However, pinpointing a cutoff value for freshness is more difficult for this hydrous mineral (as well as for hornblende – see below), due to much higher levels of  $^{36}\text{Ar}$  than in anhydrous minerals. For biotite, the parameter would be the same as for K-feldspar, namely  $^{36}\text{Ar}/^{39}\text{Ar}$ ; the normalization should be to  $J = 0.0100$  and  $K = 8.0\%$ . A.I. values for standards fall in the range 0.0006 – 0.0013, and somewhat lower for the Ordovician K-bentonite (see Fig. 11). . This is a relatively large range of values; I shall use 0.00130 as the upper cut off value for fresh biotite specimens for *total fusion*

studies. For step-heating work, a lower cut off of  $\sim 0.0005$  seems appropriate for argon derived from the best (plateau) steps.

**Hornblende.** This mineral is commonly used for argon dating. I evaluate the homogeneity of samples, looking to (total fusion) age and to chemical composition (Ca/K ratios). Comprehensive data sets are available for laser  $^{40}\text{Ar}/^{39}\text{Ar}$  work on 1 - 3 grain splits of standards MMhb-1, PP-20 and NL-25 (Renne et al., 1998; Renne, 2000). For MMhb-1, ages differ by  $> 10$  m.y., (precision of ages  $\pm 1$  m.y) and grains differ in Ca/K content by  $\sim 30\%$ . Splits of PP-20 (a re-preparation of standard Hb3Gr) differ by 20 m.y. (precision of ages  $\pm 3$  m.y.) and Ca/K values differ in value by a factor of  $\sim 2$ . NL-25, shows Ca/K values differing by a factor of  $\sim 3$ ; individual ages differ by  $\sim 100$  m.y. (precision of ages  $\pm 15$  m.y.). These observations on the best specimens (standards), raise questions about the homogeneity of hornblende samples in general.

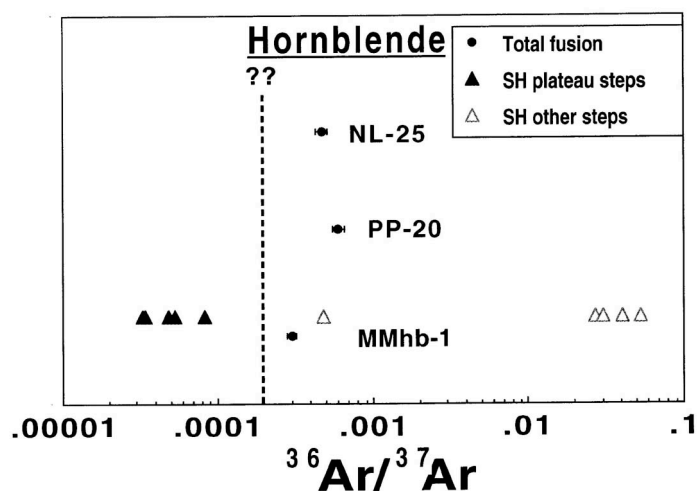


Figure 12. The A.I. for hornblende samples;  $^{36}\text{Ar}$  normalized to  $^{37}\text{Ar}$ . Results for total fusion (average and SEM) and stepheating on standards, shown on a *log* scale. For MMhb-1, values  $> 0.0005$  represent non-plateau steps, plateau steps show values  $< 0.0002$ . A tentative cut off for fresh material is set at 0.0002 for *plateau steps* (see text). Data from Renne et al. (1998), Renne (2000), and Harrison (1981).

$^{36}\text{Ar}$  contents, based on K-Ar dating (Fig. 2a), are intermediate between those of anhydrous minerals (feldspars) and hydrous minerals (micas), in line with its structural water content. The standards listed above have  $^{36}\text{Ar}$  contents (units of  $10^{-10}\text{cm}^3\text{STPg}^{-1}$ ) of  $\sim 10$  for MMhb-1,  $\sim 15 - 20$  for PP-20 and NL-25. The A.I. for this mineral could be tied to its K or Ca content. The latter is the

better choice, for K contents may vary by a factor of ~5. Thus,  $^{36}\text{Ar}/^{39}\text{Ar}$  values are ~ 0.0010 (MMhb-1), ~ 0.0020 (PP-20) and ~ 0.0095 (NL-25).  $^{36}\text{Ar}/^{37}\text{Ar}$  values (Fig. 12) are less scattered; MMhb-1 show slightly lower values (~0.00030), than the older PP-20 and NL-25 (~0.00045 - 0.00060). Stepheating work on MMhb-1 (Harrison, 1981), reveals  $^{36}\text{Ar}/^{37}\text{Ar}$  (ratio) variation (Fig. 12). Non-plateau steps carrying a very small percent of the total gas, show low ages high A.I. values (> 0.001); the plateau (least altered) steps show <0.0002. My tentative cutoff A.I. ( $^{36}\text{Ar}/^{37}\text{Ar}$ ) value in looking for unaltered samples will be 0.0002, for the *plateau* steps.

## DISCUSSION

The techniques outlined above have been utilized to critically evaluate published results for rocks linked to hotspot activity (Baksi, 2006). The focus therein is to (1) verify plateau sections meet proper statistical requirements and (2) detect alteration by the A.I. technique. For material showing substantial alteration, plateau ages are liable to be underestimates of the time of crystallization. Herein, after relating the A.I. method to previous work, I look to (a) important failures to evaluate isotopic results by statistical methods, (b) the mode of applying the atmospheric argon correction and the relationship of the argon isotopes added to silicate phases (c) the variation of chemical weathering through space and time and (d) the importance of subduction in cycling atmospheric argon (back) into the mantle.

### *Extending previous work*

Over thirty years ago, it was observed that altered whole-rock basalts from the ~16 Ma Columbia River Basalts, USA, contain significantly more atmospheric argon than fresh material (Baksi, 1974a). Even for very young (~ 70 ka) material, alteration raised the  $^{36}\text{Ar}$  content of the rock significantly (Baksi, 1974b). Roddick (1978) looked to the sources of atmospheric argon in argon dating studies. He emphasized the role of variable blanks in smearing isochron plots (see also Baksi, 1973; Hayatsu and Carmichael, 1977). Roddick (1978) examined the results on whole-rocks from the Ferrar Magmatic Province, Antarctica (Fleck et al., 1977). It was noted specimen 64.01 contained

much less  $^{36}\text{Ar}$  than 27.17; the former apparently gave the proper crystallization age, whereas the latter did not. There was no attempt to *quantify* the  $^{36}\text{Ar}$  content of these samples, rather to look at the atmospheric argon content of the various steps; the latter is determined, in part, by the K content and age of the sample. The A.I. measures the  $^{36}\text{Ar}$  content *quantitatively* or makes use of a *non-dimensional parameter*, for  $^{40}\text{Ar}/^{39}\text{Ar}$  dating results. Thus, it is noted that though 64.01 and 27.17 give acceptable plateaus (see Fig. 13a), neither correctly reflects the age of crystallization ( $\sim 180$  Ma). The A.I. of these samples explains the different ages - *both* samples are altered (Fig. 13b). The plateau ages of 64.01 and 27.17 underestimate the crystallization age by  $\sim 3\%$  and  $\sim 15\%$ , respectively.  $^{36}\text{Ar}$  contents (in units of  $10^{-10}\text{cm}^3\text{STPg}^{-1}$ ) are  $\sim 29$  (overall) and  $\sim 23$  (plateau steps) for 64.01. For 27.17, the corresponding values are 220 and 160, respectively. These values should be compared to the cutoff for fresh samples of  $< 6$ . The stepheating procedure shows that both samples are altered pervasively. A third specimen (27.46) gave a (statistically) acceptable plateau age of  $\sim 132$  Ma, which underestimates the crystallization value by  $\sim 30\%$ . The A.I. value of its “plateau” steps is 0.062, slightly higher than that of the very altered 27.17 (0.042), but not sufficiently high to explain the (further) lowering of the age by  $\sim 30$  m.y.. Not all cases of lowered ages for undisturbed igneous rocks result from alteration. Thin section examination (Fleck et al., 1977) shows that the matrix of 27.46 is made up largely of devitrified glass. Careful petrographic examination of samples prior to dating, must remain standard practice.

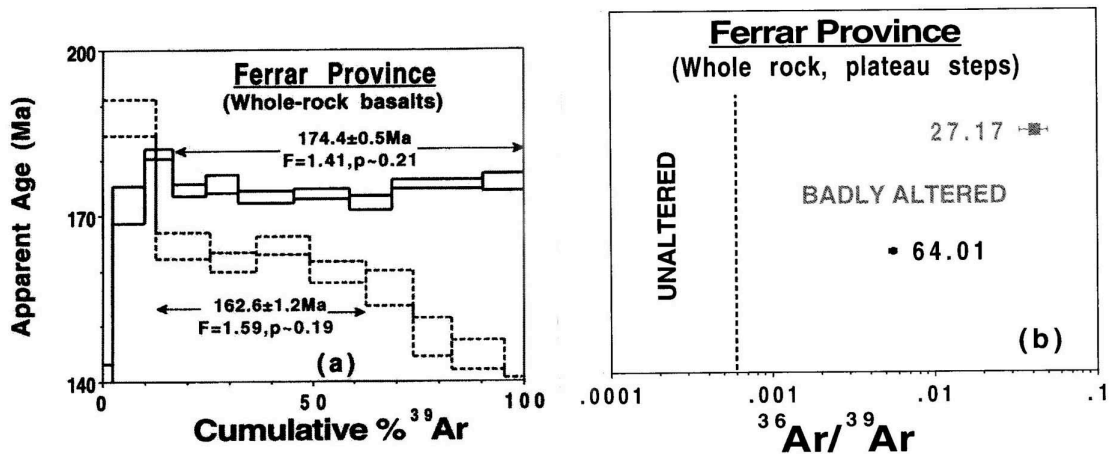


Figure 13. Assessment of the  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating work of Fleck et al. (1977) on whole-rock basalts from the Ferrar Magmatic Province. (a) Age spectra for two samples yielding statistically acceptable plateau ages. Symbols and notations are as in Figure 3a. (b) A.I. for the plateau steps, average and SEM shown on a  $\log$  scale. Both samples are altered and yield incorrect low (plateau) ages (see text).

#### *Further statistical observations.*

Proper utilization of the goodness of fit parameter to plateau/isochrons is often overlooked. The fundamental assumptions underlying the use of the method (e.g. Faure, 1986) are all samples (a) must be of the same age (b) should be “comagmatic” – show the same initial isotopic ratio and (c) must have remained closed to gain/loss of parent/daughter since the time of the event being dated. Three cases are examined.

The first is the dating of a “Permo-Triassic boundary crater” (Becker et al., 2004), which has been questioned (Renne et al., 2004). The age spectrum (Fig. 14a) shows excess (statistical) scatter; the system is “disturbed”(gain/loss of parent/daughter isotopes). The A.I. plot (Fig. 14b) shows the plagioclase is badly altered, containing  $\sim 100$  times too much  $^{36}\text{Ar}$ , and cannot yield a valid age. The purported age of  $250.1 \pm 4.5$  Ma (Becker et al. (2004)) is arithmetically and statistically invalid, does not take into account the “disturbed” nature of the sample, and does not accurately elucidate the age of the Bedout Crater.



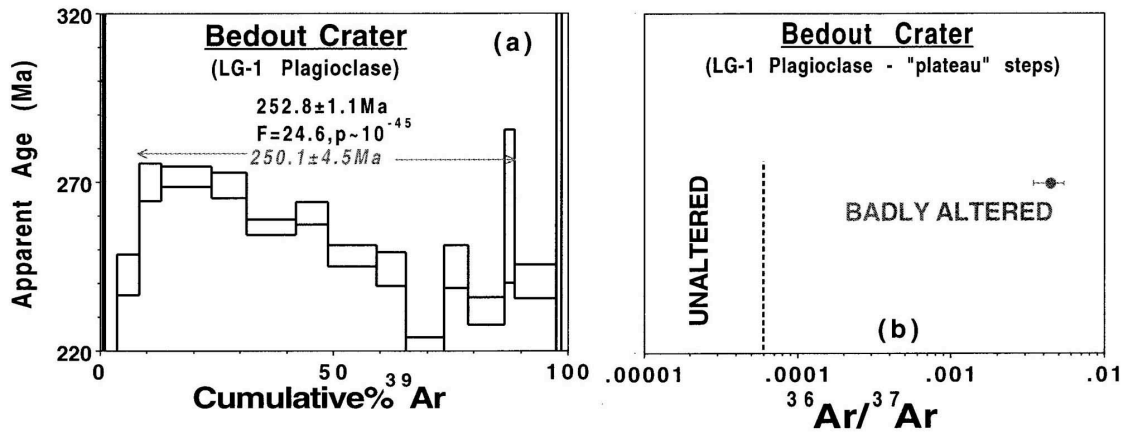


Figure 14. Critical examination of  $^{40}\text{Ar}/^{39}\text{Ar}$  dating results on the Bedout Crater (Becker et al. 2004). (a) Age spectrum plot for a plagioclase separate, with the authors' plateau section delineated by arrows and listed in italics. Symbols and legends as in Fig. 3a. Statistical evaluation yields values listed in bold letters. Excess scatter is present and no accurate age was recovered. (b) The average A.I. and SEM of plateau steps shown on a *log* scale. The specimen is grossly altered, showing  $\sim 100$  times more  $^{36}\text{Ar}$  than fresh material, and cannot be expected to give an accurate crystallization age (see text).

Incorrect use of statistical parameters in other types of isotopic dating is not uncommon. In a samarium-neodymium study, Basu et al. (1981) presented a  $\sim 3,800$  Ma isochron for rocks from the Singhbhum craton, eastern India. Moorbath et al. (1986) questioned this age.  $^{40}\text{Ar}/^{39}\text{Ar}$  dating (Baksi et al., 1987) indicated the batholithic complex was  $\sim 3300$  Ma in age. Subsequently, Sharma et al. (1994) revised the Sm-Nd age to  $3292 \pm 26$  Ma. The isochron analysis of the Basu et al. (1981) (Fig. 15a), shows excess scatter ( $p < 0.05$ ). Considerable geological error is present; rocks collected  $\sim 50$  km distant from one another, are unlikely to be coeval and/or comagmatic – i.e. show the same age and identical initial neodymium isotopic ratios at time  $t = 0$ . Allegre et al. (1999) presented a rhenium-osmium isochron age of  $65.60 \pm 0.15$  Ma for rocks from the Deccan Traps. Samples were collected from locations separated by  $\sim 700$  km (see Allegre et al., 1999, Fig. 1); such distant rocks are unlikely to be coeval and/or comagmatic. Figure 15b shows the resulting isochron; excess scatter of data is revealed and the age must be rejected as an accurate estimate of the time of extrusion of the Deccan Traps. Gross scatter results from breakdown of all three conditions for isochron plots. Two sets of replicate analysis on a sample (see Fig 15b, inset), do not define a

single “point” on the isochron and the tie-line between the replicate analysis of AP1030, runs oblique to the isochron. The sample in question has suffered gain/loss of Re/Os since ~65 Ma.

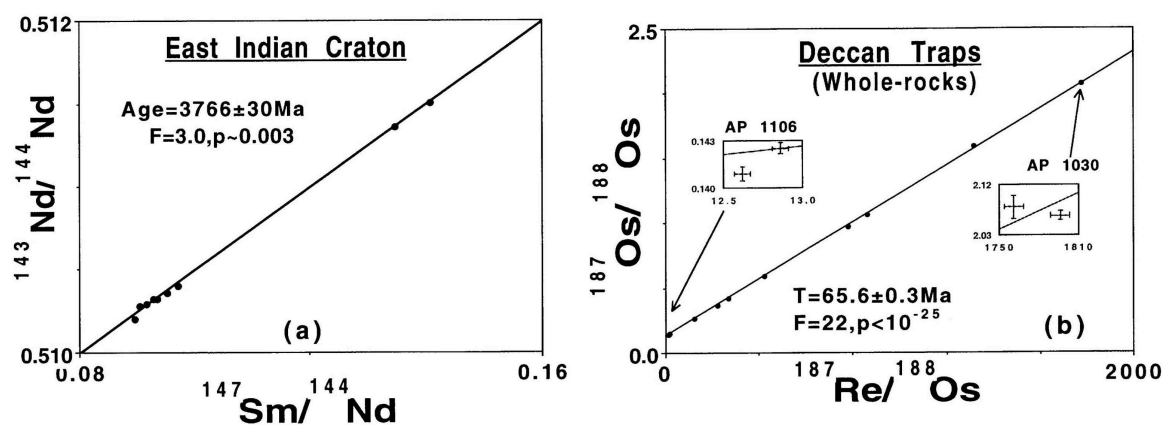


Figure 15. (a) Sm-Nd whole-rock isochron for the Singbhum Craton, eastern India (Basu et al., 1981). Symbols as in Fig. 3a. The goodness of fit parameter and associated probability value indicate geological error is present. The ~3800 Ma age was subsequently corrected to ~3300 Ma – see text. (b) Re-Os whole-rock isochron for the Deccan Traps, India (after Allegre et al., 1999). Symbols as in Fig. 3a. The goodness of fit parameter shows gross geological error and negates the high precision “age” as an accurate value for the time of formation of the Deccan Traps. Replicate analyses of individual samples (see insets), shows excess scatter, and suggest post-crystallization movement of Re and/or Os (see text).

The mathematics underlying probability theory (and hence statistics), was placed on a firm footing by the work of Pierre Fermat and Blaise Pascal about 350 years ago. In a letter dated July 29, 1654, Pascal wrote to Fermat, “I can no longer doubt the truth of my results after finding myself in such wonderful agreement with you”. Also, “I see indeed that truth is the same at Toulouse and at Paris”. Statistical “truths” are universal, and we disregard them at our peril.

### ***Weathering profiles – cryptomelane.***

The search for datable minerals in weathering profiles has drawn considerable attention, with cryptomelane being the material of choice. I examine some aspects of one such effort (Feng and Vasconcelos, 2001);  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating experiments were carried out on < 1 Ma samples from Queensland, Australia. The method is, at best, a semi-quantitative tool for arriving at soil formation rates. Eighteen age spectra were used to arrive at plateau ages by Feng and Vasconcelos (2001) – see their Figure 2. Six of these involve two steps (each) and, by definition, cannot yield plateau ages.

Another ten fail the statistical (F value) test to be used as accurate estimates of the time of formation. Cryptomelane's chemical composition,  $\text{KMn}_8\text{O}_{16}\cdot n\text{H}_2\text{O}$ , suggests it should display high A.I. values.  $^{36}\text{Ar}/^{39}\text{Ar}$  ratios for the plateau steps fall in the range 0.0004 – 0.0010, about the same as unaltered whole-rock material ( $< 0.0006$ ). Cryptomelane does not contain *structural* water; during overnight bakeout at  $\sim 200^\circ\text{C}$  under high vacuum conditions, the water is lost, and  $^{36}\text{Ar}$  levels (and hence A.I. values) fall to low levels.

### ***Weathering and the paleoatmosphere.***

One of the most interesting problems addressed by argon workers is to recover points on the “von Weiszacker” trajectory. This is the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the Earth's atmosphere from  $\sim 4.5$  Ga to today, as it has increased from  $< 1$  (cf. Renne, 2000) to 295.5 (Nier, 1950). In 1937, Carl von Weiszacker, noted the presence of “excess”  $^{40}\text{Ar}$  in the Earth's atmosphere, which he suggested resulted from the escape of this isotope from rocks and minerals, wherein it was produced by the (then unknown) decay of  $^{40}\text{K}$  (Dalrymple and Lanphere, 1969). The search for ancient atmospheric argon in rocks and minerals has been directed at material that has interacted substantially with the atmosphere at the Earth's surface. I look to the dating of pyroxene separates from the cumulate zone of a layered tholeiitic sill in the Canadian Shield (Hanes et al., 1985). A section of their stepheating results gave an isochron age of 2.7 Ga and an initial argon isotopic ratio of  $258 \pm 3$  (Fig. 16a). Hanes et al. (1985) argued for deuteritic amphibole in these mantle derived rocks formed by “interaction of circulating seawater readily available in the submarine volcanic environment”. Further, “this seawater would carry argon equilibrated with the atmosphere, and thus the trapped initial argon in the amphibole .... provide(s) information on the atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio at ... 2.7 Ga” (Hanes et al., 1985, p. 956). I examine the A.I. of their deuteritic amphibole normalized to  $^{39}\text{Ar}$  (Fig. 16b). It shows the degree of alteration (hydration) of anhydrous phases, with a  $\sim 20$  fold increase in  $^{36}\text{Ar}$  levels, resulting from interaction of the preexisting silicate phases with

seawater. The work of Hanes et al. (1985) yields an important point on the “von Weiszacker” trajectory.

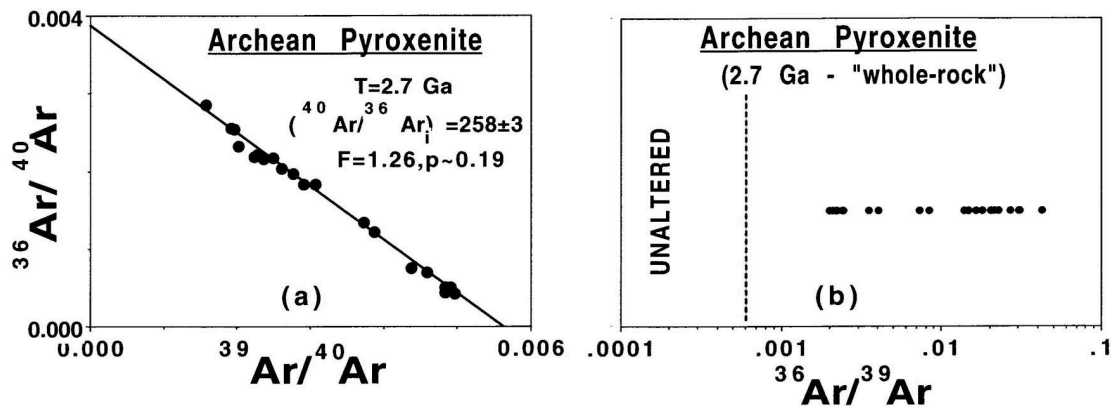


Figure 16. Sampling the paleoatmosphere at 2.7 Ga. Analysis of a pyroxenite (whole-rock) by Hanes et al. (1985). (a) 22 steps from stepheating experiments lie on an isochron (acceptable statistics) with an age of 2.7 Ga, initial argon ratio of 258. Symbols and legends as in Fig. 3a. Argon was derived from deuteric amphibole formed by the rock’s interaction with seawater at 2.7 Ga (Hanes et al., 1985). (b) A.I. normalized to  $^{39}\text{Ar}$  for the isochron steps, shown on a log scale. The pyroxenite has been grossly “altered” (see text).

### ***Chemical weathering (alteration) through space and time.***

The intensity of chemical weathering is dependant on climate (geographic location). Foland et al. (1993) presented results on the Kirkpatrick Basalt, Antarctica. A plagioclase separate and a glass concentrate yield plateau ages of  $179.4 \pm 0.4$  and  $179.2 \pm 0.2$  Ma (Fig. 17). Both show substantial loss of  $^{40}\text{Ar}^*$ . Their results are evaluated for freshness of the material dated using the A.I. method (Fig. 17). The plagioclase sample shows A.I. values falling by three orders of magnitude, as the laboratory extraction temperature is raised. The high temperature steps, drawing gas from unaltered section, yield a plateau age. The glass concentrate shows similar drop in A.I. during the step heating. Stepheating work on (acid) untreated samples can recover crystallization ages for samples from the interior (chemically unaltered) sections of the crystals on high latitude samples. Further  $^{40}\text{Ar}/^{39}\text{Ar}$  work on Antarctic samples should confirm low levels of alteration. Knight and Renne (2005) report  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages spanning ~180-174 Ma for the Ferrar

Dolerite; these could represent emplacement ages and/or cooling ages for plagioclase. Alternately, magmatism may have been narrowly focused at ~180 Ma; if so, the A.I. of ~180 Ma samples should be markedly lower than those yielding the younger ages.

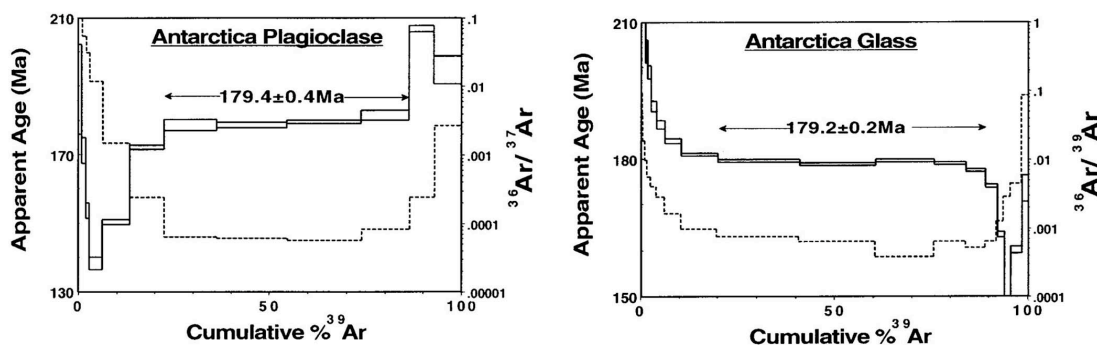


Figure 17. (a) and (b) Age spectra (solid lines) and A.I. plots (dotted lines on a *log* scale)) for a plagioclase separate and a glass concentrate sample from Antarctica (data from Foland et al., 1993). Each yields a good plateau age of ~180 Ma. Altered low temperature sites show high A.I.. The plateau steps, drawn from fresh sites show ~1000 times less  $^{36}\text{Ar}$  (see text).

High temperature K-feldspars are resistant to chemical weathering. The A.I. of material of differing ages, from ~ 2 ka to 1.1 Ga, are normalized for (a) the level of neutron irradiation ( $J = 0.0100$ ) and (b)  $K = 10.0\%$  (see Fig. 18). A clear pattern emerges - alteration appears to increase with the time of exposure. An interesting test would be to carry out  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating work on > 200 Ma K-feldspar, varying the intensity of the HF leaching procedure.

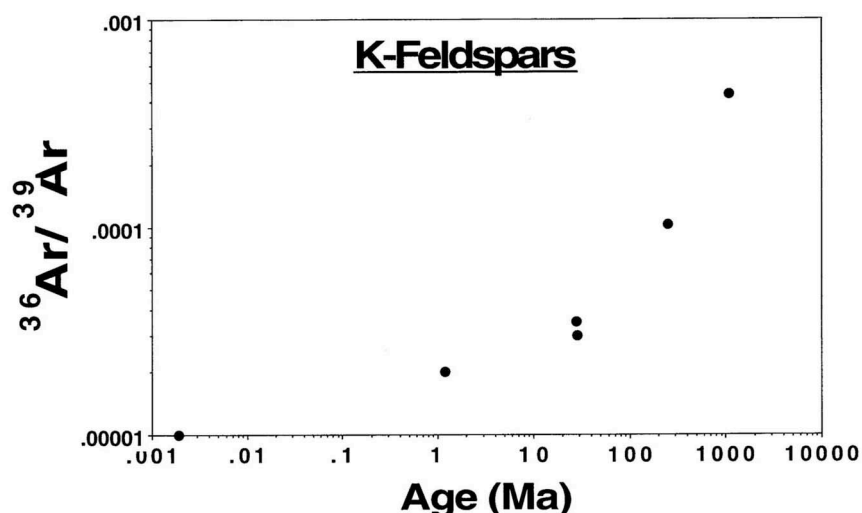


Figure 18. The A.I. of K-feldspars giving plateau ages from different localities shown on a *log-log* scale. An increase in A.I. with age is noted. Data points used: 1.9 ka – 79 AD Vesuvius eruption

(Renne et al. 1997): 1.2 Ma – Alder Creek Rhyolite (Nomade et al., 2004); 28.0 and 28.3 Ma – Fish Canyon Tuff and Taylor Creek Rhyolite (Renne et al., 1998); 250 Ma – Permo-Triassic boundary ash (Renne et al., 1995); 1088 Ma – Palisade Rhyolite (clear grains) – (Min et al., 2000). See text.

The reasons underlying the ~ 50 fold increase in  $^{36}\text{Ar}$  content of ~1.1 Ga old K-feldspar, compared to the ~2 ka one (Fig. 18), will be considered in detail elsewhere. It may result from chemical weathering (alteration), either in episodic manner, or slowly over the life of the mineral. In either case, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio used to apply the atmospheric argon correction should be  $< 295.5$ . This would lower the amount of atmospheric  $^{40}\text{Ar}$  in such material, raising its age correspondingly. The latter amounts to ~1 – 2 Ma for the ~1.1 Ga K-feldspar, not sufficient to explain the difference between the U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  ages noted by Min et al. (2000). A critical, though unresolved, problem is whether chemical weathering of samples over tens of millions of years, causes partial loss of  $^{40}\text{Ar}^*$ . Thus, the ~1.1 Ga and ~250 Ma K-feldspars shown in Fig. 18, are ~1% younger than U-Pb ages on these same rocks/ash bed (Min et al., 2000; Renne et al., 1995). These  $^{40}\text{Ar}/^{39}\text{Ar}$  ages are reported relative to the calibrations of Renne et al. (1998), which yield ages that are *older* than other intercalibration studies (Roddick, 1983; Lanphere et al., 1990; Baksi et al., 1996). Further, the age of GA1550 Biotite, the primary standard used by Renne et al. (1998), has a K determination made by isotope dilution technique, but the absolute argon calibration has been questioned (Lanphere and Baadsgaard, 2004). Efforts to revise the decay constants used for argon dating (e.g. Min et al., 2000; Kwon et al., 2002), need to be augmented by other considerations. Firstly, the possible lowering of argon ages by alteration for samples  $>200$  Ma in age. The absolute age(s) of standards used for K-Ar dating need to be worked out more fully (cf. Lanphere and Baadsgaard, 2004). Finally, the possibility of  $^{39}\text{Ar}$  recoil loss from standards – thereby making the ages used for K-Ar work and  $^{40}\text{Ar}/^{39}\text{Ar}$  dating unequal (Baksi et al., 1996) - needs to be examined.

***The role of argon in subduction zone related studies.***

Large amounts of argon dissolved in ocean water are recycled into the Earth's interior at subduction zones (e.g. Sumino et al., 2005). Order of magnitude calculations suggest that plate tectonics of the current style over  $\sim 4$  Ga, would recycle a volume subequal to that in the Earth's atmosphere today. Large amounts of atmospheric argon are added to silicates in the mantle wedge by the dehydration process. This will raise the level of  $^{36}\text{Ar}$  seen in magmas so generated, and in the mafic and intermediate rocks formed.

Over three decades ago, attempts were made to look for rocks showing  $(^{40}\text{Ar}/^{36}\text{Ar})_i$  differing from the atmospheric value (Dalrymple, 1969; Krummenacher, 1970; Baksi, 1974a, b). The Mt. Sakurajima (Japan) lavas of 1951 (subduction zone area) showed  $(^{40}\text{Ar}/^{36}\text{Ar})_i \sim 292$  (Dalrymple, 1969); this value is measurably lower than the atmospheric value of 295.5 (Nier, 1950). Cherdyntsev and Shitov (1967) noted that gases released from volcanoes in the Kamchatka area show  $^{36}\text{Ar}$  in excess of that in the atmosphere by 1-6%. They suggested that argon from Earth's ancient atmosphere was stored in the upper mantle in rocks and released when the rocks are melted. Both rocks and volcanic gases from areas close to subduction zones may then show "excess"  $^{36}\text{Ar}$ . Water recycled into the mantle in such areas carries  $\sim 1 \times 10^{-6} \text{cm}^3 \text{STPg}^{-1}$  of  $^{36}\text{Ar}$  ( $\sim 3-4$  km depth,  $4^\circ\text{C}$  – Bieri et al., 1968). As the subducted slab heats up to  $\sim 50^\circ\text{C}$ , loss of  $\sim 50\%$  of the dissolved argon may be expected based on the temperature alone (Bieri et al., 1968; Hamme and Emerson, 2004). Increased (pore) pressure may hold the argon loss down to lower levels. As the subducted slab dehydrates, substantial quantities of  $^{36}\text{Ar}$  ( $> 10^{-7} \text{cm}^3 \text{STPg}^{-1}$ ?) are carried into the overlying mantle wedge. Some of this gas will escape as volcanic emanations possibly showing  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio  $< 295.5$ , as noted in the Kamchatka area (Cherdyntsev and Shitov, 1967). As magmatism is induced in these areas, kinetic effects in the rock-water interaction (see Behrens and Zhang, 2001, and references therein), could result in isotopic fractionation favoring the lighter isotopes. Lavas (mafic and more notably those of intermediate composition) should show high levels of  $^{36}\text{Ar}$  and possibly  $(^{40}\text{Ar}/^{36}\text{Ar})_i < 295.5$ .

Argon studies should be carried out on lavas from some key areas (Japan?, Central America?) where a wealth of (trace element) geochemical analyses are available. Low levels of  $^{36}\text{Ar}$  ( $< 10^{-9}\text{cm}^3\text{STPg}^{-1}$ ) should be seen for rocks (basalts?) showing no Nb-Ta anomalies on spidergram plots. By contrast (intermediate?) rocks with spidergrams displaying troughs at Nb-Ta, should show higher amounts of  $^{36}\text{Ar}$ . A useful parameter to monitor is the  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio of these rocks. Andesites incorporating material from the subducted slab, may show argon isotopic fractionation effects (i.e.  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio  $> 5.35$ , the atmospheric argon value – Nier, 1950).

## CONCLUSIONS

Incorrect low argon ages for undisturbed igneous rocks commonly result from alteration (chemical weathering) of the phases used for dating, not evident by the methods routinely used for such purposes. Optical methods are qualitative and subjective in nature. A *quantitative* method for assessing the alteration of material utilized for argon dating has been developed, making use of the data routinely gathered during mass spectrometry. This looks to the critical role water plays in chemical weathering processes. Large amounts of dissolved atmospheric argon in the water interact with the low levels seen in rocks, resulting in the  $^{36}\text{Ar}$  levels in the silicate phases being raised by factors of 10 – 1000; all altered phases are hydrous and consequently exhibit high levels of  $^{36}\text{Ar}$ . The method has been applied with success to K-Ar dating results (Baksi, 1987, 1989; Baksi and Hoffman, 2000). Herein, it is extended to  $^{40}\text{Ar}/^{39}\text{Ar}$  dating studies, using non-dimensional parameters. The alteration index (A.I.) involves looking to the  $^{36}\text{Ar}/^{39}\text{Ar}$  ratio for relatively K-rich material (K-feldspar, whole-rock basalt and micas) and to the  $^{36}\text{Ar}/^{37}\text{Ar}$  ratio for Ca-rich material (plagioclase feldspar and hornblende). These parameters must be normalized for the total production of  $^{39}\text{Ar}$  and  $^{37}\text{Ar}$ , using a single value for the irradiation parameter ( $J = 0.0100$ , herein) and to a single K value for a given mineral/whole-rock work. The use of this technique may be problematical where substantial amounts of atmospheric argon are added to the samples during the neutron irradiation procedure (e.g. Roddick, 1983).



Chemical weathering (alteration) is strongly dependent on both location and the age of the sample. Water is known to be pervasive through much of the crust, and most material regardless of age, will show alteration. Selected ~ 200 Ma rocks from Antarctica show low degrees of alteration.  $^{36}\text{Ar}$  contents for K-feldspar appears to be time dependant. It is critical that all argon data be reviewed for alteration using the A.I. test. As shown herein, *it is possible to obtain statistically valid plateau ages that underestimate crystallization ages by ~2-15%*. (“Not all  $^{40}\text{Ar}/^{39}\text{Ar}$  ages are equal(ly valid); some are more equal than others”). Results on seafloor rocks are considered in the companion article (Baksi, 2006). For whole-rock basalts and plagioclase feldspar, raising the A.I. to > 5 times the cutoff value for freshness, lowers the argon age by a few percent; greater amounts of alteration can lower argon ages by ~10%, though still yielding *statistically acceptable* plateau sections in  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating studies.

Large amounts of argon dissolved in seawater, are recycled back into the Earth’s interior at subduction zones. These areas serve to transfer  $^{36}\text{Ar}$  from the atmosphere back into the mantle. Dehydration of the subducted slab and subsequent melting of rocks in the mantle wedge plays a critical role in magmatism in such areas. Careful measurement of the level of  $^{36}\text{Ar}$  in island arc magmatic material should provide a sensitive tool in elucidating the nature and role of the fluids driven off during the subduction process. Rocks formed by incorporation of material from the subducted slab, should show relatively high  $^{36}\text{Ar}$  levels and perhaps  $^{36}\text{Ar}/^{38}\text{Ar}$  ratios > 5.35. Andesites formed by Bowen type fractional crystallization of mafic magmas, should show lower amounts of  $^{36}\text{Ar}$  and  $^{36}\text{Ar}/^{38}\text{Ar}$  ratios of ~5.35.

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## APPENDIX

I illustrate the mode of calculating the alteration index for anhydrous silicate phases in  $^{40}\text{Ar}/^{39}\text{Ar}$  dating studies.

### For whole-rock basalt and K-feldspar.

$$\mathbf{A.I.} = [({}^{36}\text{Ar}/{}^{39}\text{Ar})_{\text{M}} - ({}^{36}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}} \times ({}^{37}\text{Ar}/{}^{39}\text{Ar})_{\text{C}}] \times (\mathbf{J}/\mathbf{0.01}) \times (\mathbf{B}/\mathbf{D}).$$

The term in square brackets, corrects for  $^{36}\text{Ar}$  derived from Ca isotopes during neutron irradiation;  $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}}$  is a reactor constant,  $\sim 0.00025 - 0.00028$ .  $({}^{36}\text{Ar}/{}^{39}\text{Ar})_{\text{M}}$  = measured isotope ratio,  $({}^{37}\text{Ar}/{}^{39}\text{Ar})_{\text{C}}$  = (measured) isotope ratio, corrected for decay of  $^{37}\text{Ar}$ , B = K content (%) of specimen and D = K content for normalization purposes, 0.65% for whole-rock material and 10.0% for K-feldspar.

### Whole-rock basalt.

**The cutoff value for fresh material is A.I. < 0.0006 (see Fig. 4).**

(i) *Unaltered*. Andesitic basalt RM82-11 (Mahoney et al., 1983). Specimen VI, see Fig. 4. Dated at Queen's University (Baksi, unpubl. data).  $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}} = 0.000254$ , J = 0.00686, K = 0.75%. (Plateau) step 6, Age  $\sim 116$  Ma.  $({}^{36}\text{Ar}/{}^{39}\text{Ar})_{\text{M}} = 0.00077$ ,  $({}^{37}\text{Ar}/{}^{39}\text{Ar})_{\text{C}} = 1.515$ .

$$\mathbf{A.I.} = [0.00077 - 0.000254 \times 1.515] \times (0.00686/0.01) \times (0.75/0.65) = \mathbf{0.00030}.$$

(ii) *Altered*. Whole-rock basalt 64.01 of Fleck et al. (1977). See Fig. 13.  $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}} = 0.000265$ , J = 0.00775, K = 1.45%. 780°C (plateau) step, Age  $\sim 174$  Ma.  $({}^{36}\text{Ar}/{}^{39}\text{Ar})_{\text{M}} = 0.0025$ ,  $({}^{37}\text{Ar}/{}^{39}\text{Ar})_{\text{C}} = 1.372$ .

$$\mathbf{A.I.} = [0.0025 - 0.000265 \times 1.372] \times (0.00775/0.01) \times (1.75/0.65) = \mathbf{0.0037}.$$

*Note the  $\sim 10$  fold increase in A.I. for the altered sample, compared to unaltered RM82-11.*

### K-feldspar.

**A single cutoff value for this mineral is not proposed, as  $^{36}\text{Ar}$  contents appear to be age dependant (see text).**

Samples from the Palisade Rhyolite (Min et al., 2000); *see Fig.10*.  $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} \sim 0.00027$ ,  $J = 0.01518$ ,  $K \sim 7\%$ .

(iii) *Unaltered (clear grain)*, age 1088 Ma. (Plateau) step 30692-201C.  $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{M}} = 0.00050$ ,  $(^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}} = 0.0000$ .

$$\mathbf{A.I.} = [(0.00050 - 0.00027 \times 0.0)] \times (0.01518/0.01) \times (7/10) = \mathbf{0.00053}.$$

(iv) *Altered (cloudy grains)*, age  $\sim 1068$  Ma. (Plateau) step 30392-23J.  $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{M}} = 0.00399$ ,  $(^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}} = 0.023$ .

$$\mathbf{A.I.} = [0.00399 - 0.00027 \times 0.023] \times (0.01518/0.01) \times (7/10) = \mathbf{0.00424}.$$

*Note the eight fold increase in A.I. and rise in Ca/K  $(^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}}$  ratio, for the altered material.*

### **Plagioclase feldspar.**

**A cutoff value for fresh material is set at  $\mathbf{A.I.} < 0.00006$  (see Fig. 7a).**

$$\mathbf{A.I.} = [(^{36}\text{Ar}/^{39}\text{Ar})_{\text{M}} - (^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} \times (^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}}] \times (J/0.01) / (^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}}$$

Note:  $\text{Ca}/\text{K} \sim 2 \times (^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}}$  for all reactor facilities.

(v) *Unaltered* CAMP plagioclase (Hames et al., 2000), specimen SCD-2C, *see Fig. 7*.

$(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 0.00027$ ,  $J = 0.001734$ .  $680^\circ\text{C}$  (plateau) step, age  $\sim 200$  Ma.  $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{M}} = 0.0102$ ,  $(^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}} = 22.43$ .

$$\mathbf{A.I.} = [0.0102 - 0.00027 \times 22.43] \times (0.001734/0.01) / (22.43) = \mathbf{0.000032}$$

(vi) *Altered*. CAMP plagioclase (Deckart et al., 1997), GUI35 – *see Fig. 9*

$(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 0.00027$ ,  $J = 0.0307$ .  $830^\circ\text{C}$  (plateau) step, age  $\sim 194$  Ma.  $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{M}} = 0.00756$ ,  $(^{37}\text{Ar}/^{39}\text{Ar})_{\text{C}} = 10.65$ .

$$\mathbf{A.I.} = [0.00756 - 0.00027 \times 10.65] \times (0.0307/0.01) / (10.65) = \mathbf{0.00135}.$$

*Note the  $\sim 30$  fold increase in A.I. for the altered sample. SDC-2C was leached with HF prior to dating, whereas GUI35 was not treated with acid.*

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