

**A quantitative tool for detecting alteration in undisturbed rocks
and minerals – II: application to argon ages related to hotspots.**

Ajoy K. Baksi

Department of Geology & Geophysics, Louisiana State University,

Baton Rouge, LA 70803, USA

(email: akbaksi@yahoo.com)

ABSTRACT

Alteration of undisturbed igneous material used for argon dating work, often results in inaccurate estimates of the crystallization age. A new *quantitative* technique to detect alteration has been developed (see previous article), utilizing the ^{36}Ar levels observed in rocks and minerals. The method is applied to data in the literature for rocks linked to hotspot activity.

For subaerial rocks, argon dating results are critically examined for the Deccan Traps, India. The duration of volcanic activity and its coincidence in time with the K-T boundary, are shown to be uncertain. The bulk of dated sea-floor material (recovered from the Atlantic, Indian and Pacific Oceans) proves to be altered. Ages determined using large (hundreds of milligram) samples are generally unreliable, due to inclusion of altered phases. This includes studies suggesting an age of ~ 43 Ma for the bend in the Hawaiian-Emperor Chain. More recent attempts, using much smaller subsamples (~ 10 milligrams) that have been acid leached to remove alteration products, are generally of higher reliability. Plagioclase separates sometimes yield reliable results. However, many whole-rock basalts from the ocean floor yield ages that are, at best, minimum estimates of the time of crystallization. Most “rates of motions”, calculated from hotspot track ages, are shown to be invalid.

Sea floor rocks are recovered at considerable expense, but often are not suitable for dating by the argon methods. Most are severely altered by prolonged contact with seawater. A method is recommended for testing silicate phases prior to attempts at argon dating. This involves a quantitative determination of the ^{36}Ar content of the material at hand; dating phases without pretreatment – leaching with HNO_3 for material containing ferromagnesian phases, and HF for feldspars – is strongly discouraged.

“Truth alone was the daughter of time” (Leonardo da Vinci, ca. 1500)

INTRODUCTION

The $^{40}\text{Ar}/^{39}\text{Ar}$ dating stepheating technique (Merrihue and Turner, 1966), is the most widely applied radiometric tool in earth sciences. For mafic rocks it may be the only tool to yield precise and accurate age information. Reproducibility of the step ages, permits evaluation of the accuracy and precision of resulting estimates of the crystallization age of igneous rocks and minerals. Such ages must be listed with associated errors. For $^{40}\text{Ar}/^{39}\text{Ar}$ dating, the formula of Dalrymple et al. (1981) is used to calculate the (random) errors in ages. Systematic and random errors must not be associated with one another. Alteration causes partial loss of $^{40}\text{Ar}^*$ and leads to “ages” that are *systematically* too young.

Numerous $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating ages in the literature do not meet the basic “mathematical” requirements as precise and accurate estimates of time of crystallization. Many “ages” related to hotspot generated rocks, have been shown to be statistically invalid (see Baksi, 1999, 2005). The availability of such unreliable “numbers” in the literature, has led to problems. The field geologists’ adage “I wouldn’t have believed it, if I hadn’t seen it”, has been turned into “I wouldn’t have seen it, if I hadn’t believed it”. About fifty years ago, Irving Langmuir foresaw the extreme situation in this regard, and termed it “pathological science”. As elaborated therein (see Langmuir, 1989), “people are tricked into false results by wishful thinking”.

I shall investigate the effects of alteration, with applications to rocks recovered from submarine environments linked to hotspot activity. McDougall and Harrison (1999, p. 33) observe, “Very few igneous rocks from the deep-sea environment meet the criteria of freshness and crystallinity for K-Ar dating, as hydrothermal alteration and submarine weathering result in development of chlorite, smectite and other clay minerals, as well as calcite, at the expense of primary high-temperature minerals”.

METHODOLOGY

Radiometric ages play a critical role in earth sciences in elucidating the timing, duration (rates) of various processes. For such calculations, the ages should be accurate and precise. For post-Paleozoic rocks, I suggest a (1σ) precision of $\pm 1.0\%$ of the age is a prerequisite. In cases where the (random) error is estimated to be $>2\%$, “ages” should *not* be used for calculation of (absolute) plate velocities.

Argon ages available in the literature on undisturbed rocks, will be evaluated as valid estimates of the time of crystallization. Firstly, they will be tested for statistical robustness as outlined in earlier efforts (Baksi, 1999, 2005). Next, the state of chemical alteration of the material dated will be evaluated by the alteration index (A.I.) technique; *silicate phases that have suffered detectable alteration, can yield statistically valid plateau sections that underestimate the time of crystallization by $\sim 2-10\%$* (Baksi, 2006). Statistical tests are often disregarded (see Baksi, 2006). Sometimes, the the statistics appear to be “too good” i.e. probability values are well in excess of > 0.95 . Isolated cases may be due to chance, but generally critical examination is called for. The case of the Gettysburg sill, northeastern USA, has been examined elsewhere (Baksi, 1991, 2006). The study of Turrin et al. (1994) on the Alder Creek rhyolite sanidine is examined. Both the age spectrum and isochron plots (Fig. 1), yield probability values that are very high. (The original statistics of Turrin et al. (1994) for the isochron plot are in error). Reducing the step age errors to $\sim 30\%$, lowers the probability values to ~ 0.5 . The error associated with the final age is reduced proportionately.

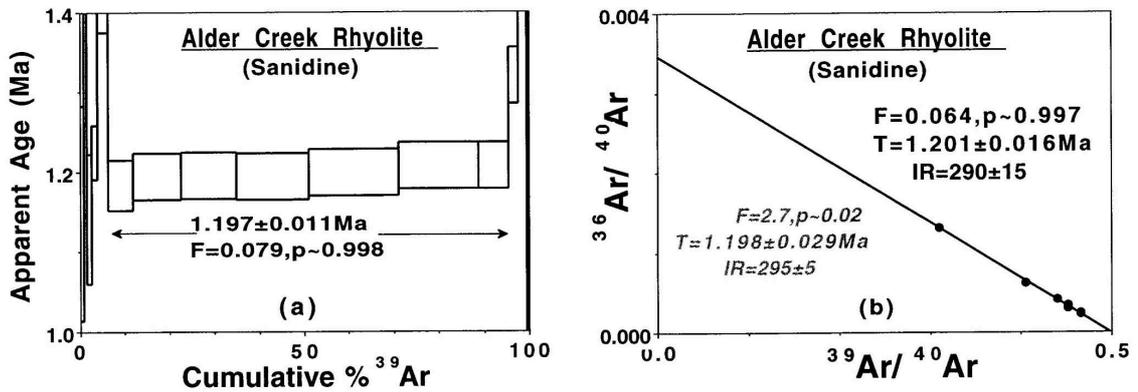


Figure 1. $^{40}\text{Ar}/^{39}\text{Ar}$ dating results on the Alder Creek (rhyolite) sanidine (after Turrin et al., 1994). (a) Age spectrum with the plateau section delineated; age listed with 1 sigma error, the goodness of fit parameter (F) and the probability of occurrence (p) - see text. The plateau is “too good” with $p \sim 0.998$. (b) The isochron plot for the same data set. T = age, IR = initial ($^{40}\text{Ar}/^{36}\text{Ar}$) ratio, F and p as above. This age overlaps the plateau value. The points fit the line too well, $p \sim 0.997$. The isochron listings of Turrin et al. (1994) are in error.

The bulk of this effort is directed towards $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating data. Guidelines for statistical evaluation of plateau sections and isochron figures have been outlined elsewhere (Baksi, 1999, 2005). These techniques will be utilized herein to test for statistical robustness of the data. In particular, the goodness of fit parameter (hereinafter F), will be used along with the number of “steps” involved, to arrive at a probability figure (p) making use of Chi Square Tables. Where $p < 0.05$ (95% confidence level test), excess scatter, beyond estimated analytical errors, is indicated. Geological error is present, and the calculated “age” is not an accurate estimate of the time of crystallization. The second set of tests examines the alteration index (A.I.) of the plateau (least altered) steps and looks to the ^{36}Ar content of the sample. A parameter, normalized to the K content of certain phases (whole-rocks, K-feldspar and mica) and to the Ca content of others (plagioclase feldspar and hornblende), is used. The methodology, rationale and efficacy of the method has been outlined elsewhere (Baksi, 2006).

$^{40}\text{Ar}/^{39}\text{Ar}$ ages will be reported relative to those of standards preferred by Renne et al. (1998).

Errors are quoted and shown in figures at the 1σ level. Where necessary, ages have been

recalculated to the decay constants, abundances suggested by Steiger and Jager (1977). The A.I. cut-off for fresh whole-rock basalt is $^{36}\text{Ar}/^{39}\text{Ar} < 0.0006$ and that for plagioclase is $^{36}\text{Ar}/^{37}\text{Ar} < 0.00006$; ^{36}Ar content for fresh whole-rock basalt is $< 6 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$ (Baksi, 2006).

RESULTS

For proper statistical evaluation of “ages”, as well as A.I. calculation, full data sets (isotopic ratios) are required. These are often not available in the literature; in many instances, such data sets were *not* made available even after repeated requests made to the editors of journals and to the concerned authors.

Subaerial material – continental flood basalts.

These provinces have been genetically linked to hotspot activity. Further, they are said to be responsible for global faunal extinction events. Critical examination of these the timing and duration of flood basalt volcanism in numerous cases is hampered by lack of access to the detailed data sets. A large body of data is available for the Deccan Traps, India, and these will be considered in detail.

Deccan Traps, India. Results generated at different laboratories are reduced to a single base, the calibrations preferred by Renne et al. (1998). The Deccan Province has been linked to the K-T boundary extinction event (Courtillet et al., 1988; Duncan and Pyle, 1988; Hofmann et al., 2000). The age of the K-T boundary, relative to the monitor ages used herein, is placed at 65.58 Ma (see Knight et al., 2003). $^{40}\text{Ar}/^{39}\text{Ar}$ “plateau” ages that pass the relevant statistical test for validity must also be unaltered as based on A.I. tests (Baksi, 2006).

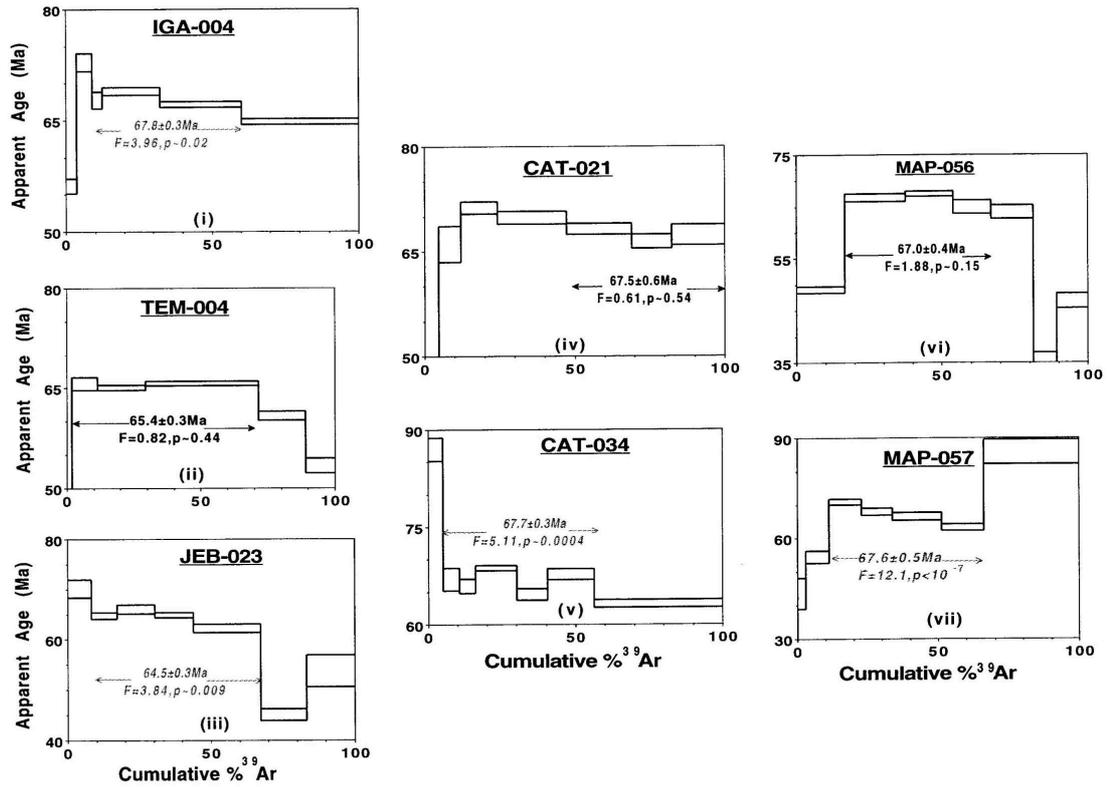


Figure 2. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra on whole-rock basalts from the Deccan Traps, India (Duncan and Pyle, 1988). Symbols and numbering as in Figure 1a. Specimens (i) through (vii) are in stratigraphic succession. Ages shown in italics rejected on statistical grounds. Acceptable ages for three specimens (TEM-004, CAT-021, MAP-056) are out of stratigraphic order (see text).

Isotopic data for the results of Duncan and Pyle (1988), were obtained (R.A. Duncan, pers. comm., 1989). Numerous step ages and plateau values (Fig. 2) differ from those listed in Duncan and Pyle (1988). Most of the “plateau ages” fail the relevant statistical tests. Only three pass this test – 65.4 ± 0.5 (TEM-004), 67.5 ± 0.5 (CAT-021) and 67.0 ± 0.4 Ma (MAP-056). The latter two are significantly older than the K-T boundary. TEM-004 lies ~1.2 km *below* CAT-021 (Duncan and Pyle, 1988, Fig. 2), but yields a measurably *younger* age (2.1 m.y., whereas the 95% confidence interval is ± 1.3 m.y). Also, TEM-004 lies ~1.6 km *below* MAP-056 (Duncan and Pyle, 1988, Fig. 2), but yields a measurably *younger* age (1.6 m.y., whereas the 95% confidence interval is ± 1.0 m.y). These “ages” violate the principle of superposition, and must be rejected. Based on the A.I. of their

plateau (least altered) steps (Fig. 3a), all rocks are significantly altered and no accurate ages were recovered.

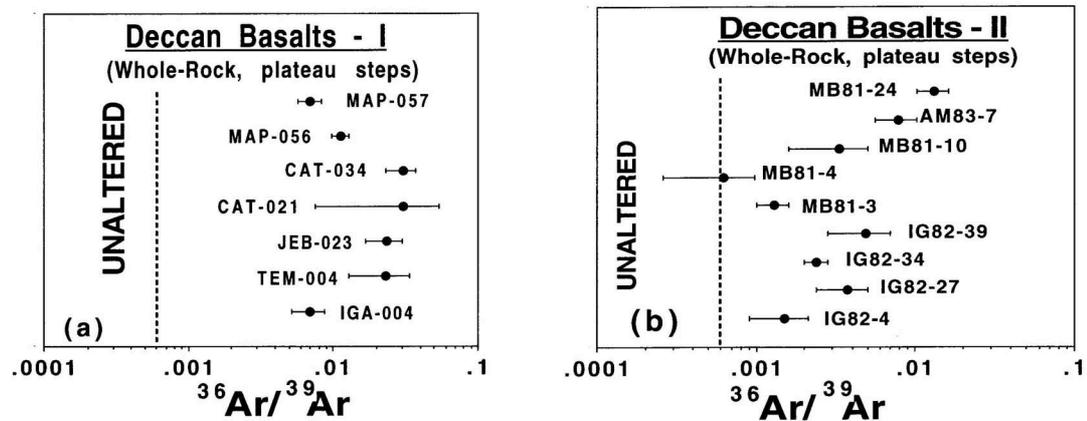


Figure 3. Assessing the alteration state of whole-rock basalts from the Western Ghats section. Average A.I. values and the standard error on the mean (SEM) are shown for plateau steps (best sites) on *log* scales. (a) Rocks of Duncan and Pyle (1988) – see Fig. 2. All rocks are altered and plateau ages are rejected. (b) Rocks of Venkatesan et al. (1993) – see Fig. 4. With a few exceptions, samples are altered and plateau ages are rejected (see text).

The results of Venkatesan et al. (1993) are examined in age spectrum form (Fig. 4), using the relevant data sets (K. Pande, pers. comm., 1996). Only two (of eight) ages pass the statistical test, i.e. for IG82-39 and MB81-24. The A.I. test (Figure 3b) shows the rocks are somewhat fresher than those of Duncan and Pyle (1988). The two rocks that pass the statistical test for plateau ages are quite altered; the resulting ages can only be used as minimum values. No proper crystallization ages were recovered from the study of Venkatesan et al. (1993).

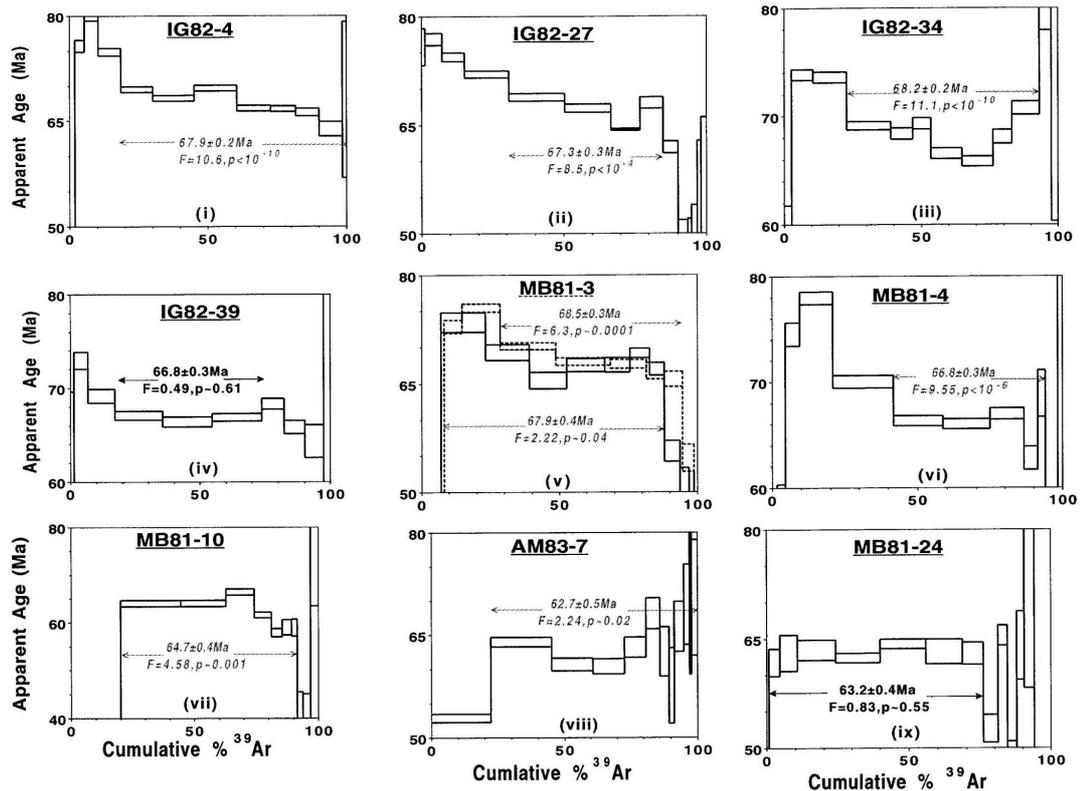


Figure 4. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra on whole-rock basalts from the Deccan Traps, India (Venkatesan et al, 1993). Symbols and numbering as in Figure 1a. Samples (i) through (ix) are in stratigraphic succession. Ages shown in italics rejected on statistical grounds. Only two specimens (IG82-39 and MB81-24) give acceptable plateau ages (see text).

Courtillet et al. (1988) presented ages from the eastern sections of the Deccan. Detailed isotopic results were obtained (G. Feraud, pers. comm., 1998). All five specimens pass the relevant statistical tests (Fig. 5). The whole-rock shows loss of $^{40}\text{Ar}^*$ and fails the A.I. test for freshness (0.0034 ± 0.0004 , compared to < 0.0006 for fresh material); its age is significantly younger than the K-T boundary, although it is from one of the *lowermost* flows in the area. Plagioclase ages are: DK0103 - 66.6 ± 0.4 Ma, and for the Narmada section (moving up stratigraphic sequence): NA16 – 67.6 ± 0.9 , NA17 – 64.9 ± 0.3 and NA18 – 63.6 ± 0.3 Ma. The last (a dyke) is clearly altered (Fig. 6) and its age is rejected. Specimens NA16/17 are slightly altered and suggest volcanism in this area continued for $\sim 2 - 3$ m.y.. The DK specimen is least altered; its age, and that of NA16, suggest the

oldest parts of the Deccan Traps (overlying the Lameta and Bagh beds) are > 1 m.y. older than the K-T boundary.

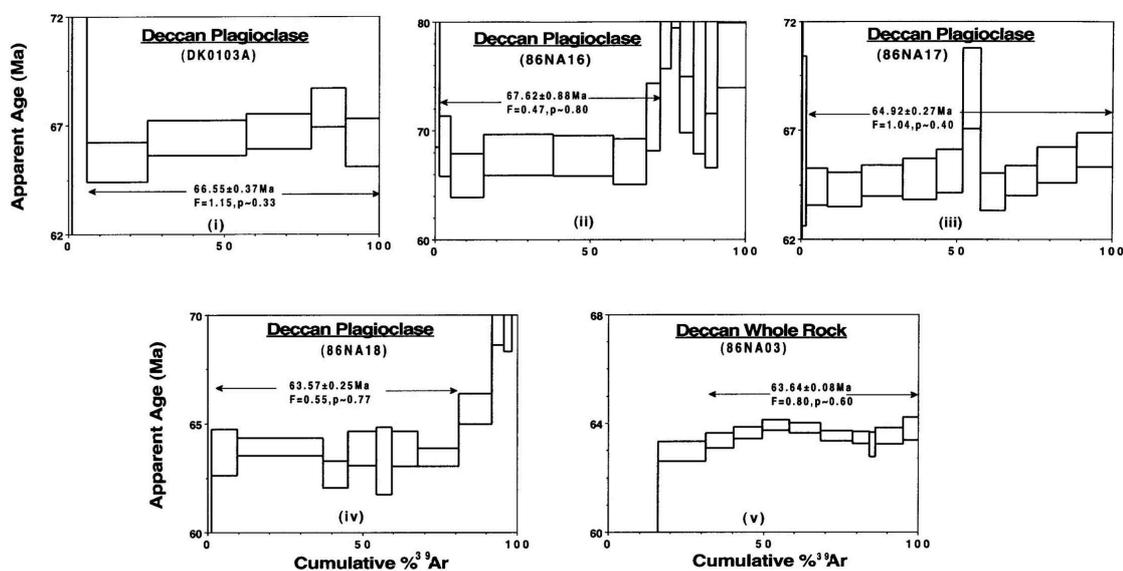


Figure 5. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra on four plagioclase separates and a whole-rock basalt from the Deccan Traps, India (Courtilot et al, 1988). Symbols and numbering as in Figure 1a. All give statistically acceptable plateau ages.

Hofmann et al. (2000) presented $^{40}\text{Ar}/^{39}\text{Ar}$ ages on rocks from Western Ghats section. Plagioclase separates gave statistically acceptable plateaus, but are “too good”, with probability values > 0.99 in many cases (see Fig. 7). Errors in step ages have been overestimated by factors of ~3. If so, JW5 (64.86 ± 0.24 Ma) is *measurably younger* than the overlying JW7 (65.77 ± 0.29 Ma). The A.I. plot (Fig. 6b), indicates that most samples have suffered minor alteration and ages should approximate crystallization values. Further discussion is not attempted herein. It is unclear how their ages (obtained relative to Hb3Gr at 1072 Ma) should be converted to those preferred by Renne et al. (1998). The work of Roddick (1983) suggests ages should be *increased* by ~1.0%, whereas that of Renne (2000) indicates ages need to be *decreased* by ~0.6%. (The analyses of Renne (2000) on PP-20, yields an age of 1067 Ma and *not* 1073-1074 Ma, relative to Fish Canyon sanidine at 28.02 Ma).

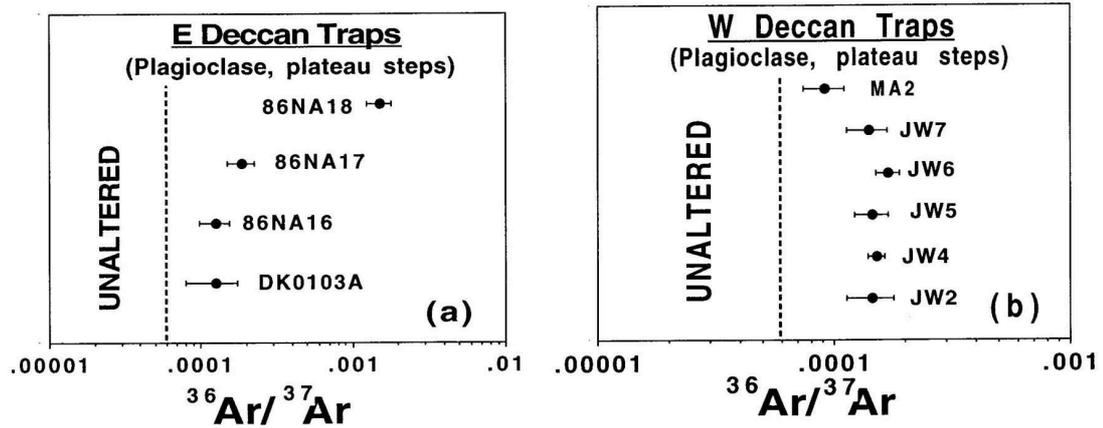


Figure 6. Assessing the state of alteration of Deccan plagioclase samples of (a) Courtillot et al (1988) – see Fig. 5 and (b) Hofmann et al. (2000) – see Figure 7. Average A.I. and SEM of plateau steps shown on \log scales. Most samples show minor alteration and plateau ages should be close to crystallization values (see text).

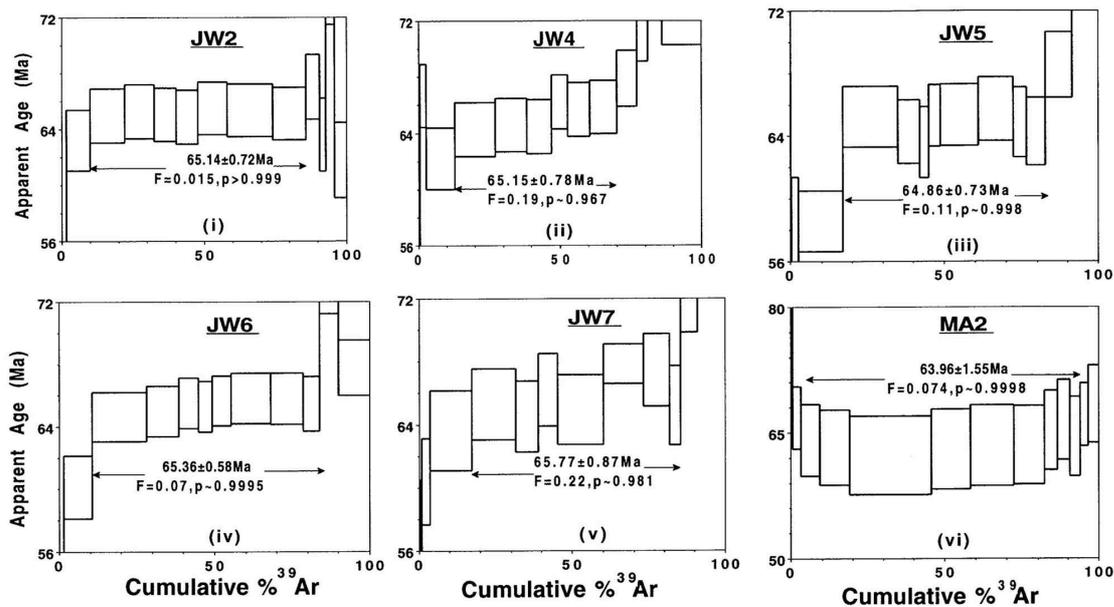


Figure 7. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra on six plagioclase separates from the Deccan Traps, India (after Hofmann et al, 2000). Ages reported relative to 1072 Ma for Hb3Gr (see text). Symbols and numbering as in Figure 1a. Specimens (i) through (vi) are in stratigraphic succession. The statistics are too good ($p > 0.96$); step age errors have been overestimated (see text).

Allegre et al. (1999) presented a whole-rock Re-Os isochron age of 65.60 ± 0.15 Ma. This is not acceptable as a crystallization value as the results appear to violate all three assumptions necessary for isochron ages (Baksi, 2006). The thickest sections of the Deccan Traps (e.g. the Western Ghats composite section) primarily show reversed magnetic polarity, and are hypothesized to have formed

during chron 29r (see Baksi, 1994). Critical examination of all ages, leaves (only) a few accurate measures of the time of crystallization. Some are measurably older than chron 29r (66.17 – 65.33 Ma) and sections of the eastern Deccan appear to be > 1 m.y. older than the K-T boundary (65.58 Ma). There is no unequivocal evidence that the most voluminous sections were formed during chron 29r, or that the extrusion of the Deccan Traps is coincident in time with, and was responsible for, the K-T boundary faunal extinctions.

The oceanic realm

The main emphasis will be on rocks from “hotspot tracks” and purported connections to plume activity. I look to results generated with “old-fashioned” set ups first, where large samples, (hundreds of milligrams), generally not acid leached, were used, and yielded poor results. With the advent of modern instrumentation (York et al., 1984), sample sizes were reduced to tens of milligram; many were hand picked under binocular microscope and/or subjected to acid leaching. These contain fresh(er) material, display lower A.I. values, and yield better ages.

$^{40}\text{Ar}/^{39}\text{Ar}$ stepheating work on (terrestrial) whole-rock basalts (or purified groundmass) should be carried out on powdered material. Use of “chunks” permits altered material within the sample to remain undegassed, leads to very high amounts of atmospheric argon in the analyses, and incorrect ages (cf. Baksi, 1974a). The material should be dated in fairly coarse fractions (~10 to 60 mesh size), since fine grinding introduces ^{36}Ar into the sample (Baksi, 1974a). For *fresh* whole-rock material, single pieces of >20 g have been dated successfully by the K-Ar method (Baksi, 1974b).

Evaluation of some early work. K-Ar dates are almost invariably minimum estimates of crystallization ages, based on high ^{36}Ar contents. Attention is directed to $^{40}\text{Ar}/^{39}\text{Ar}$ studies. Seidemann (1978) analyzed near-ridge pillow basalts containing excess ^{40}Ar . Figure 8 looks to the A.I. on two splits of T3-71-D-148, identified as being more and less altered (Seidemann, 1978, Table 2). Both are clearly altered, with the “fresher” sample showing an order of magnitude less ^{36}Ar than the more altered one. Walker and McDougall (1982) carried out K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ study of pillow

basalt material from the Dabi Volcanics of Papua New Guinea. (^{36}Ar values are listed in units of $10^{-10}\text{cm}^3\text{STPg}^{-1}$). The boninites showing $^{36}\text{Ar} \sim 2 - 6$, are less altered than the tholeiites ($^{36}\text{Ar} \sim 10 - 90$). Boninite 38.2B (Fig. 9a) shows partial loss of $^{40}\text{Ar}^*$, and a marginal (<50% of the total gas) plateau age of ~ 50 Ma (*not* ~ 54 Ma as listed by Walker and McDougall (1982)). These steps exhibit high A.I. values (Fig. 9b). Tholeiite 28.3 does *not* yield a “meaningful plateau age of 58.9 ± 1.1 Ma” (Walker and McDougall, 1982, p. 2185) for the steps delineated by arrows in Fig. 9a. Initial steps show very high ^{36}Ar levels, introduced during the neutron irradiation procedure. The intermediate temperature steps from the relatively unaltered phases of the rock show no plateau age (see Fig. 9b). The conclusion that “the ages of the tholeiitic and boninitic volcanics are almost identical at 58.9 ± 1.1 Ma” (Walker and McDougall, 1982, p. 2188) is unfounded.

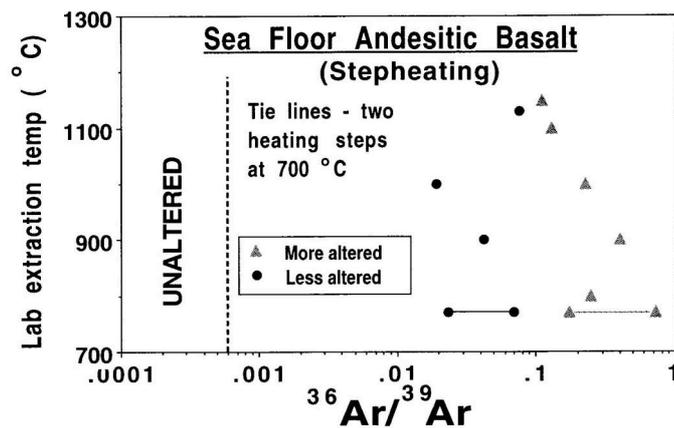


Figure 8. Assessment of the freshness of two altered sea-floor andesitic basalts used for $^{40}\text{Ar}/^{39}\text{Ar}$ study (Seidemann, 1978). A.I. (on a log scale) plotted versus laboratory extraction temperature. The results confirm the modality of using the $^{36}\text{Ar}/^{39}\text{Ar}$ ratio as an alteration index.

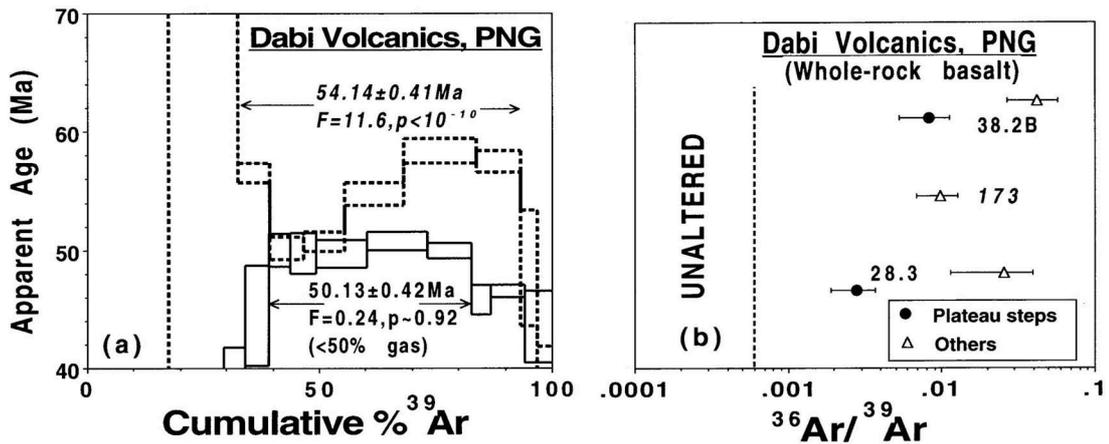


Figure 9. Evaluation of argon dating results of Walker and McDougall (1982) on the Dabi Volcanics, Papua New Guinea (a) $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for two whole-rock samples. Symbols and captions as in Fig. 1a. Neither sample yields a plateau age. (b) A.I. values shown with associated SEM on a *log* scale. High values for plateau steps indicate alteration (see text).

Oceanic plateaus. These formations are linked to hotspot activity and it is critical to obtain accurate radiometric information. Sinton et al. (1998) attempted $^{40}\text{Ar}/^{39}\text{Ar}$ dating of samples from the Caribbean area, and presented plateau ages of $\sim 75\text{-}95$ Ma. The Gorgona and Curacao samples (92-97, 79BE-73 and 79KV-9) gave isochrons with initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios < 295.5 , caused by disturbed (K-Ar) systems (cf. Lanphere and Dalrymple, 1978) and their ages are rejected. Sinton et al.'s (1998) isochron plots permit assessment of the freshness of the rocks (Fig. 10). All rocks show alteration, and their "ages" can, at best, serve as minimum estimates. Rocks from the DSDP Leg 150 and Gorgona Island (150-11-2 and 92-27) are severely altered. There is no accurate radiometric evidence of two stages of magmatism at ~ 90 and ~ 76 Ma (Sinton et al., 1998), nor of volcanics in the Dominican Republic and Costa Rica formed over the Galapagos hotspot.

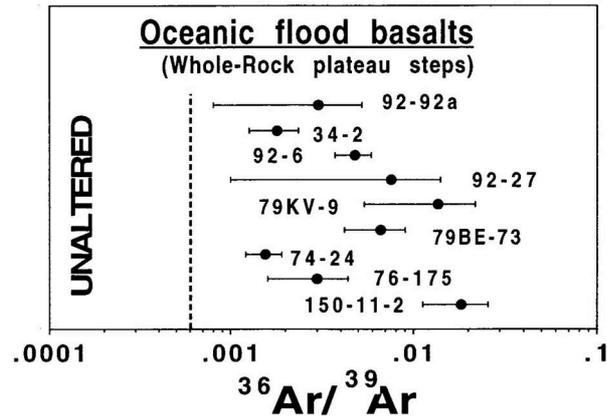


Figure 10. Assessing the alteration of whole-rock basalts from the Caribbean area, dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Sinton et al. 1998). A.I. and SEM for plateau steps are shown on a *log* scale. All rocks are altered, and no reliable crystallization ages were obtained (see text).

Mahoney et al. (1993) listed ages for the Ontong Java Plateau, suggesting it was formed at 122 – 123 Ma in a short interval of time. The isotopic data for this very important work are *not* available for inspection. The isochron plot for 130-807C-84R-6 (0-3) (Mahoney et al., 1993, Fig. 2), permits A.I. calculation. The results are compared to a similar rock (RM82-5, Mahoney et al., 1983) from the Rajmahal Traps, India (Fig. 11). The latter yields step ages of higher precision (Fig. 11a) and is substantially fresher than the Ontong Java Plateau rock (Fig. 11b). The Mahoney et al. (1993) age is a *minimum* estimate; the Ontong Java Plateau was formed at > 123 Ma; the duration of this event, remains unknown.

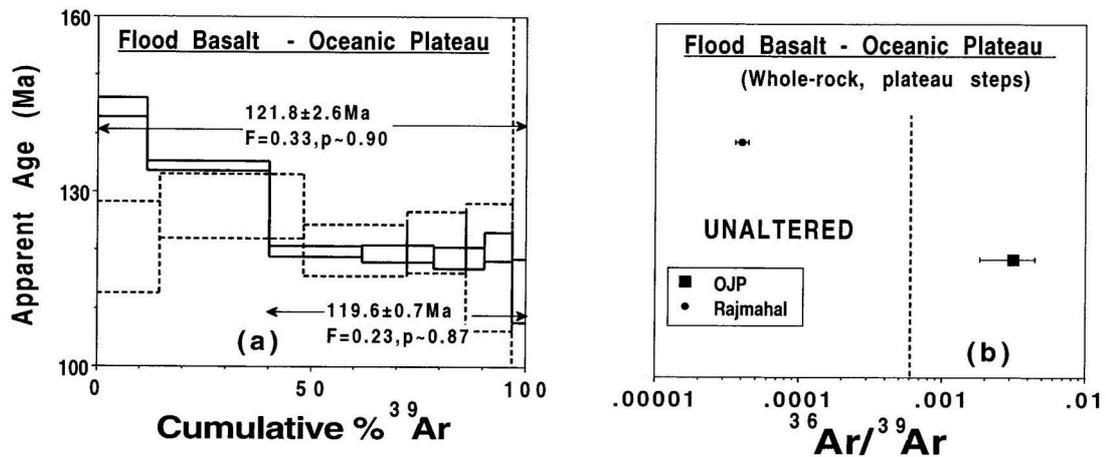


Figure 11. Evaluation of $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Ontong Java Plateau (Mahoney et al., 1993); results compared to a similar basalt from India (Baksi, unpubl. data). (a) Age spectra OJP (dotted lines) and RM82-5 (solid lines). Symbols and captions as in Fig. 1a. RM82-5 yields step ages with smaller errors and a more precise plateau age. (b) The A.I. for plateau steps, average and SEM values shown on a *log* scale. The OJP rock is altered, and yields a *minimum age* for the time of formation (see text).

Sinton et al. (1997) looked to a suite of rocks on Nicoya Peninsula, Costa Rica. Using geochemical, isotopic and radiometric data, they linked these rocks to the Galapagos plume and argued for their formation mostly in the time frame ~90 - 84 Ma. A full table of isotopic data is *not* available; their Figure 2 (isochron plots) permits evaluation of their ages and freshness of the material dated (Fig. 12). None of these rocks should yield true estimates of the crystallization age, since even the (best) plateau steps are derived from altered sites. Both plagioclase samples show alteration, and cannot be expected to give accurate crystallization ages. There are no (accurate) ages of ~88, ~83 and ~64 Ma (Sinton et al., 1997), and genetic connections to the Galapagos plume are questioned.

All three cases examined above involved dating small quantities of material using ultra-sensitive mass spectrometers and low-blank extraction apparatus. Modern instrumentation, per se, does *not* guarantee better (correct) age results. The samples in these studies were dated without acid

leaching to remove alteration products. It is unsurprising that such submarine rocks did not yield accurate estimates of crystallization age.

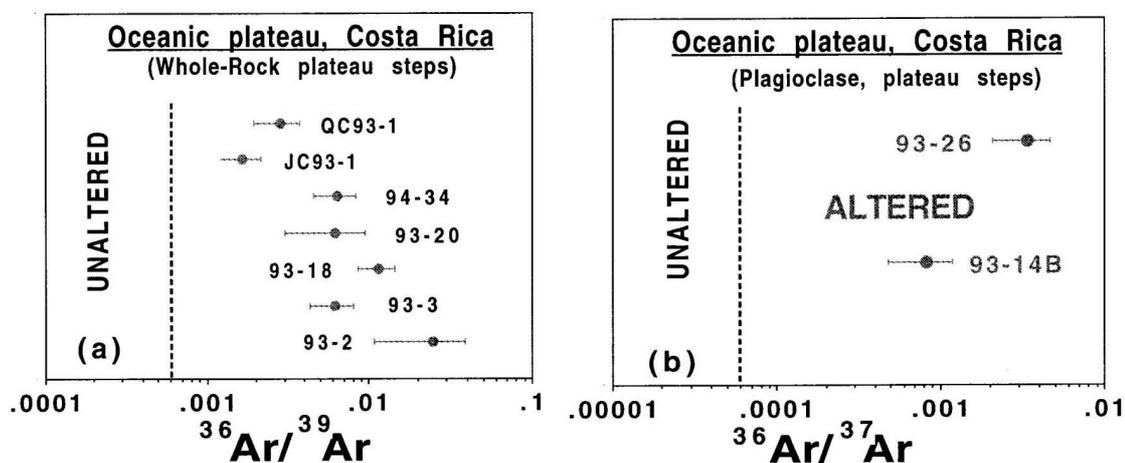


Figure 12. Evaluating the $^{40}\text{Ar}/^{39}\text{Ar}$ work of Sinton et al. (1997) on rocks from the Nicoya Peninsula, Costa Rica. Average A.I. and SEM for plateau steps are shown on a \log scale. (a) Whole-rock samples are altered showing 3 - 100 times more ^{36}Ar than fresh material. Plateau ages for these samples are rejected. (b) Two plagioclase separates; both are altered and the plateau ages of Sinton et al. (1997) are rejected as accurate estimates of the time of crystallization (see text).

Rocks from the Indian Ocean. Basalts from the Ninetyeast Ridge were subjected to argon dating (Duncan, 1978, 1991). The purported plateau ages have been demonstrated to show gross excess scatter (Baksi, 1999, 2005). K-Ar dates (Duncan, 1978), show high amounts of ^{36}Ar , unsurprising since Duncan (1978), reports observation of smectite and chlorite in thin sections. Such rocks cannot yield accurate crystallization ages. The A.I. of the best $^{40}\text{Ar}/^{39}\text{Ar}$ (plateau) steps (Fig. 13a) confirms that all rocks are altered. A later study (Duncan, 1991), used even more altered rocks (see Fig. 13a). All of the site 756-758 rocks are severely altered, with ^{36}Ar contents 30 - 200 times higher than for fresh basalts. Further, the ages of Duncan (1991) have been shown to be invalid on statistical grounds (Baksi, 1999, 2005). The oft cited age progression for the Ninetyeast Ridge and its connection to the Kerguelen Hotspot as based on the work of Duncan (1978) and Duncan (1991) is rejected, since no reliable crystallization ages were recovered.

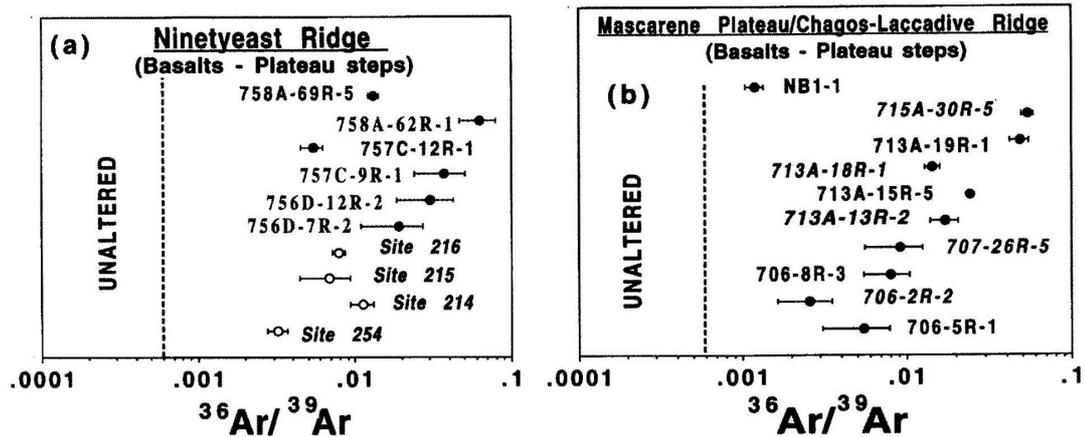


Figure 13. Testing the alteration state of whole-rock basalts from the Indian Ocean linked to hotspots. The A.I. (average and SEM) for plateau steps shown on *log* scales. (a) Samples from the Ninetyeast Ridge analyzed by Duncan (1978) and Duncan (1991). Both sets of rocks are altered. All “plateau” ages listed by the authors are rejected (see text) (b) Rocks from the Chagos-Laccadive Ridge analyzed by Duncan and Hargraves (1990). Samples are badly altered and the plateau ages are rejected. Only NB1-1 appears relatively fresh (see text).

Duncan and Hargraves (1990) carried out whole-rock dating of basalts from the Chagos-Laccadive Ridge and the Mascarene Plateau. Their “ages” show excess scatter in isochron plots and age spectra (Baksi, 1999, 2005). The A.I. plot (Fig. 13b) shows most of them are severely altered, and their “ages” must be rejected. NB1-1 appears to be mildly altered and its age serves as an estimate of its time of crystallization (cf. Baksi, 2005). The conclusions of Duncan and Hargraves (1990) regarding the temporal tracking of the Reunion Hotspot, are discounted.

Rocks from the Atlantic Ocean. The ages of Duncan (1984) for the New England Seamounts have been shown to be statistically invalid (Baksi, 1999, 2005). The A.I. shows the amphibole specimens are altered, except for the last two steps of the Nashville Seamount sample. Two steps cannot define a plateau, but it is likely the crystallization age is ~83 Ma. For the whole-rocks, the A.I. of the plateau steps are ~0.005 (Atlantis II) and ~0.0025 (Bear); the cutoff for fresh samples is < 0.0006 (Baksi, 2006). The conclusions of Duncan (1984) regarding age progression in the New England Seamounts, and its associated “hotspot”, are unfounded.

Statistical analysis of age spectra and isochrons (Baksi, 1999, 2005) shows the ages of O'Connor and Duncan (1990) for the track of the Tristan da Cunha hotspot in the South Atlantic Ocean are unfounded. The A.I. of the plateau steps is evaluated in Figure 14a. Only two rocks (93-11-8 and 93-14-1) are fresh, but these did not yield valid plateau/isochron ages (see Baksi, 2005). Other samples are badly altered (Fig. 14a) and cannot yield valid crystallization ages. The conclusions of O'Connor and Duncan (1990), tracing the Tristan da Cunha hotspot on the African and South American plates, are negated. O'Connor and Le Roex (1992) presented $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating ages for the St. Helena and Gough volcanic chains. Statistical examination of their age spectra (Fig. 15) shows that 6 out of ten results do not yield proper plateaus, and the ages are rejected. The A.I. of most of the rocks are high (Fig. 14b), indicating alteration; no accurate crystallization ages were obtained for these rocks. AG51-9-1 is minimally altered and its age should be ~19.1 Ma. For the other rocks, ages are not known accurately. Conclusions regarding the reconstruction and motion of the African plate over the hotspot-plume systems, and quantitative calculation of plate motions (O'Connor and Le Roex, 1992) are not justified.

Pacific Ocean and surroundings.

There are a large number of purported hot spot tracks in the Pacific Ocean. Many of these have been “dated” and the results are widely quoted and used in the literature. The list of Clouard and Bonneville (2005) of hotspot related papers, proved useful for locating the relevant data sets. A preliminary investigation based on statistical appraisal of “plateaus” (Baksi, 2004), showed that many of the ages reported are invalid as proper estimates of time of crystallization.

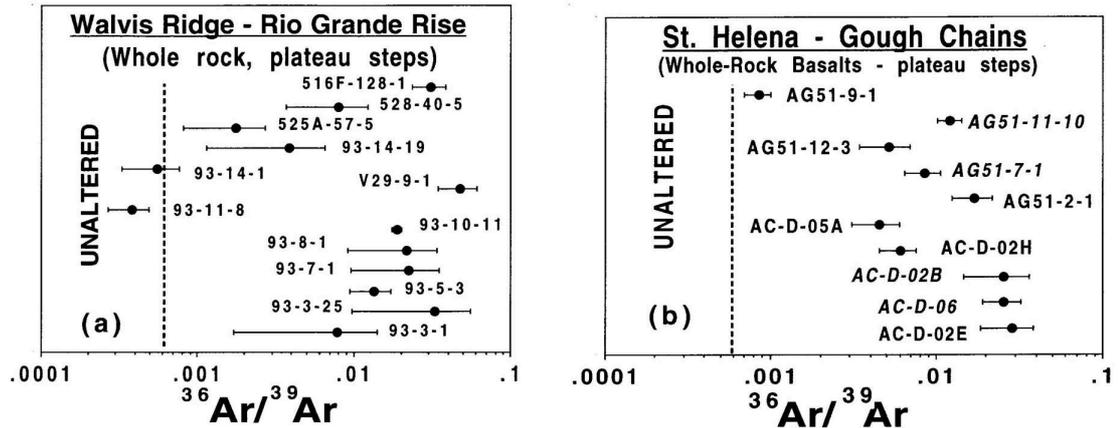


Figure 14. Assessing the alteration state of the volcanic rocks from hotspot tracks in the Atlantic Ocean. Average A.I. and SEM of the plateau steps shown on *log* scales. (a) Rocks from the Walvis Ridge – Rio Grande Rise (O’Connor and Duncan, 1990). Most samples are badly altered and cannot yield valid crystallization ages (see text) (b) Rocks from the St. Helena – Gough Chains (O’Connor and Le Roex, 1992). Most samples do not yield accurate estimates of the crystallization age (see Fig. 15 and text).

Pacific Northwest, USA. Duncan (1982) suggested that the Yellowstone Hotspot track could be traced to an island chain that collided with North America, forming the Coast Range of Oregon and Washington. Statistical examination of the relevant $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating data (Baksi, 2005) indicated that none of the ages were proper estimates of the time of formation of these rocks. For K-Ar dates (Duncan, 1982, Table 1) most rocks contain $> 20 \times 10^{-10} \text{cm}^3 \text{STPg}^{-1}$ of ^{36}Ar , and are altered. For $^{40}\text{Ar}/^{39}\text{Ar}$ work, A.I. values on D80-RB-31 and D80-CV-25 are ~ 0.015 , compared to < 0.0006 for fresh material. At low extraction temperatures, D78-SR-10 shows severe alteration; the two highest temperature sites tap into less altered sites (A.I. ~ 0.002). Sample D78-SR-1 is altered based on its very high ^{36}Ar content. The stepheating experiment shows high levels of ^{36}Ar in the low-intermediate temperature steps. The two highest temperature steps are drawn from sites that are somewhat fresher (A.I. ~ 0.001). Two steps cannot define a plateau age; the *minimum* age of these rocks is ~ 55 Ma. Accurate ages for these rocks in the Pacific Northwest are unknown; there is no (age) data for a hotspot track for this island chain or of a link to the Yellowstone Hotspot.

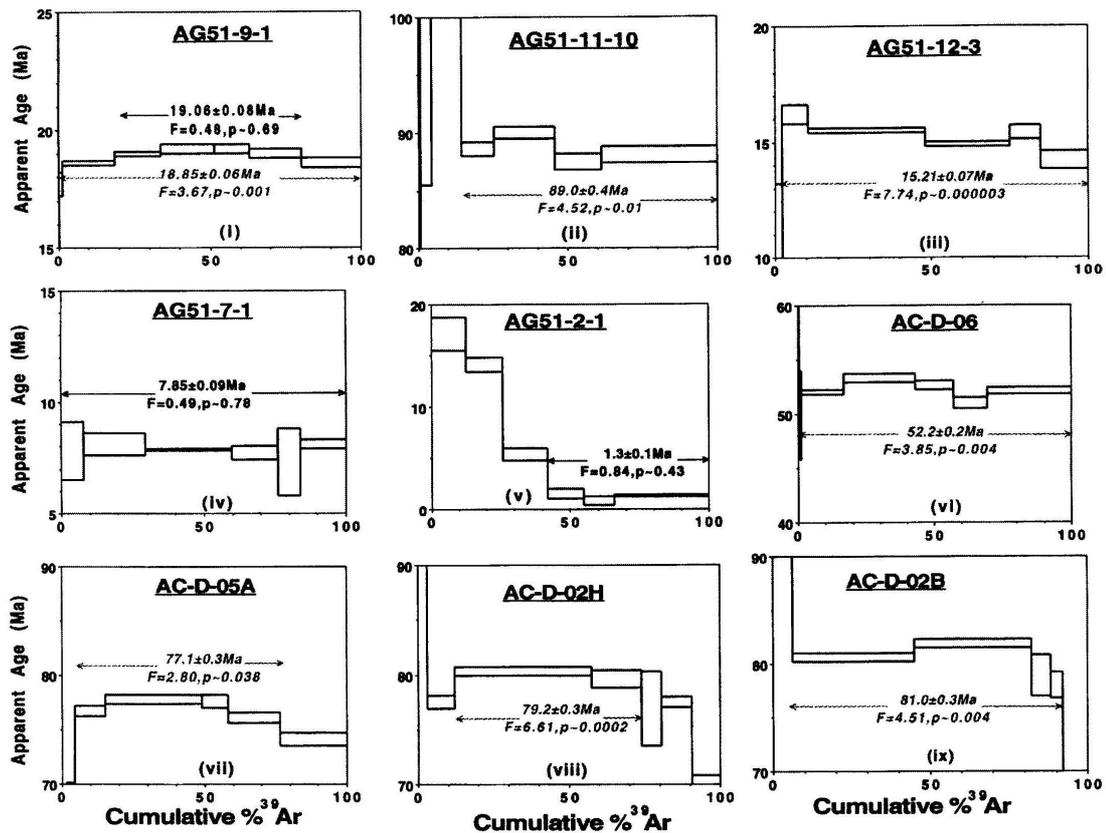


Figure 15. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for nine whole-rock samples from the St. Helena and Gough volcanic lines dated by O'Connor and Le Roex (1992). Symbols and legends as in Fig. 1a. Only three samples (51-9-1, 51-7-1, 51-2-1) pass the relevant statistical tests for validity - ages in italics are rejected on statistical grounds (see text).

Seamounts in the North Central Pacific. Pringle (1993) presented K-Ar, and $^{40}\text{Ar}/^{39}\text{Ar}$ data on rocks from the Musicians Seamounts. K-Ar data are assessed for freshness; with a few exceptions (plagioclase separates from Haydn and West Mendelssohn) all show ^{36}Ar values > 10 times that for fresh material. The A.I. values for $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion on the whole-rock samples, are 20 - 100 times higher than the cutoff value of 0.0006. All whole-rock samples are badly altered. The total fusion work on plagioclase separates show better results; A.I. values are 3 - 10 times higher than for fresh material (cutoff value < 0.00006). These samples were leached in warm 3 to 6 N HCl (Pringle, 1993); it has been shown that this procedure is not effective in *totally* removing all traces of alteration (Baksi, 2006). The stepheating work of Pringle (1993) reveals further details on A.I. plots

(Fig. 16). The plagioclase separates are altered (Fig. 16a). “Plateau” ages are, at best, minimum values for the time of crystallization. The whole-rock material (Fig. 16b), shows very high amounts of ^{36}Ar , as these altered rocks were dated in core (chunk) form. All ages are rejected as accurate estimates of the time of crystallization.

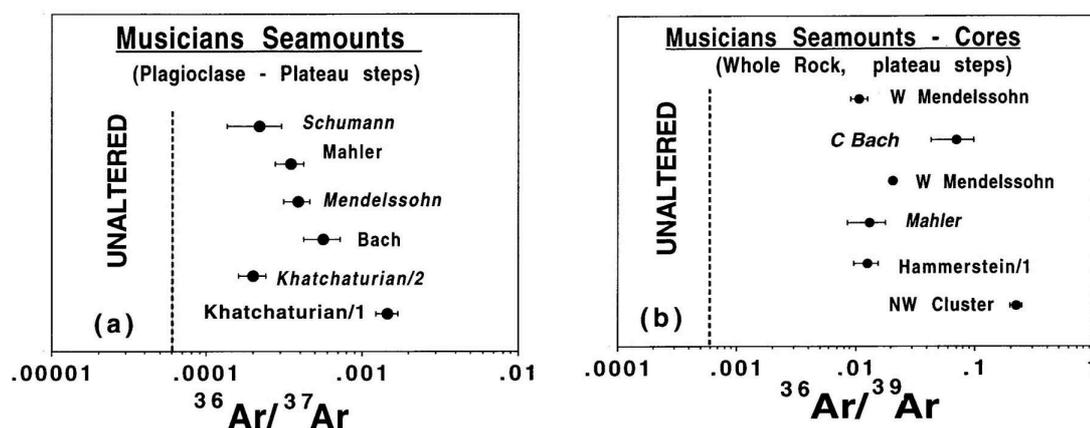


Figure 16. Assessing the alteration state of rocks from the Musicians Seamounts dated by Pringle (1993). The A.I. and SEM for plateau steps shown on *log* scales. (a) Results for plagioclase separates; all samples are altered. (b) Results for whole-rocks; very high A.I. values show samples are badly altered. No accurate ages were recovered (see text).

Western Pacific Seamounts. Ozima et al. (1977) presented $^{40}\text{Ar}/^{39}\text{Ar}$ dating results for six whole-rock samples dredged from Guyots. Numerous step ages are incorrectly reported (see Baksi, 2004). Further, F was put equal to $(\text{SUMS}/(N-2))^{1/2}$, (SUMS = sum of the residuals on the isochron fit (see York, 1969; Roddick, 1978)), whereas it should be = $\text{SUMS}/(N-2)$. This reduced many straight lines with excess scatter (errorchrons) into acceptable isochrons. A summary of their age spectra (calculated with the $(^{40}\text{Ar}/^{36}\text{Ar})_i$ values used by the authors), is listed in Table 1.

Only two samples yield statistically acceptable plateau ages. The Seiko Guyot sample shows an initial argon ratio below the atmospheric value. This is unacceptable, and results from dating of disturbed (altered) rocks (cf. Lanphere and Dalrymple, 1978). The results of Ozima et al (1977) are evaluated for alteration by the A.I. technique (Fig. 17a). All six rocks are severely altered,

TABLE 1. Results for $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating studies on whole-rock samples from the Western Pacific. Age spectra calculated using the $(^{40}\text{Ar}/^{36}\text{Ar})_i$ values of Ozima et al. (1977). F = goodness of fit parameter, p = corresponding probability value (see text). Errors listed at the 1σ level.

Sample (Guyot)	$(^{40}\text{Ar}/^{36}\text{Ar})_i$	Plateau Age (Ma)	F (p)
Wilde	296±7	96.1±0.7	0.68 (~0.61)
Lamont	334±9	88.3±3.0	0.26 (~0.77)
Scripps	312±4	100.1±0.4	6.0 (~0.0004)
Renard	327±6	98.0±0.8	10.4 (< 10^{-5})
Makarov	302±7	98.5±1.3	3.31 (0.02)
Seiko	256±19	No plateau	Not applicable

containing ~50 - 100 times more ^{36}Ar than fresh samples, and cannot yield proper crystallization ages. Ozima et al (1978) analyzed three DSDP rocks; these show ^{36}Ar values >200 times higher than for fresh basalts. The authors noted “Microscopic examination did not give any positive evidence for (such) K-bearing alteration products” and “preliminary electron microprobe analysis showed that K residues (sic) – essentially along the grain boundaries” (p. 702). The latter indicates alteration. The A.I. test (Fig. 17b) shows that the rocks are very badly altered (~200 times the cut-off value); such rocks should *not* be used for argon dating work.

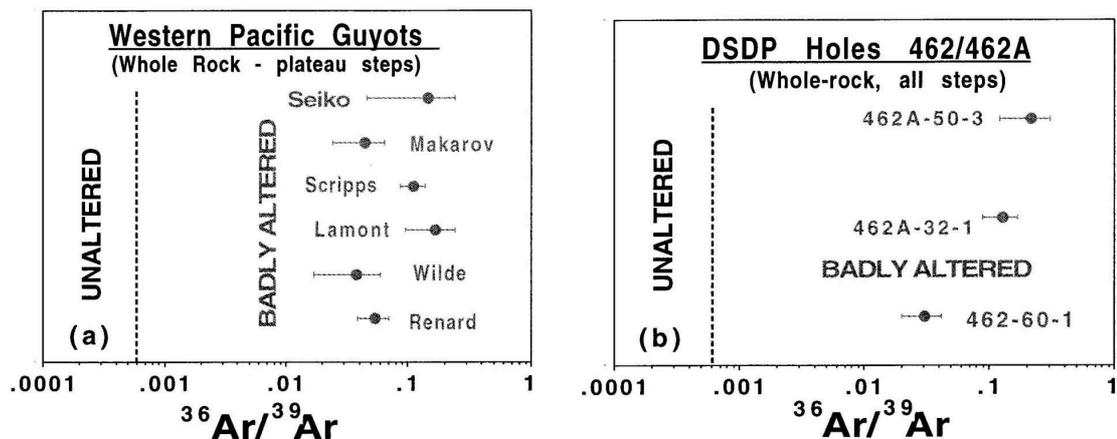


Figure 17. Assessing the alteration of (whole-rock) Western Pacific samples. The A.I. and SEM shown on *log* scales. (a) Plateau steps for rocks from Guyots (Ozima et al., 1977); all rocks are

badly altered and no proper ages were recovered (see text). (b) Evaluation of basalts and an altered dolerite from DSDP Hole 462/462A, analyzed by Ozima et al. (1978). The rocks are badly altered, containing ~200 times the amount of ^{36}Ar of fresh basaltic material and display the efficacy of the A.I. technique in detecting alteration, not readily discernible by optical techniques.

Saito and Ozima (1977) analyzed samples from the Line volcanic chain, the Suiko Seamount and the Necker Rise. A summary of their results is listed in Table 2. Many of their ages are unacceptable for the same reasons as outlined above for the work of Ozima et al. (1977). Isochron ages for 128D, 133D, 137D-9, 144D, were calculated with subatmospheric (< 295.5) initial argon ratios. Only three samples yield statistically acceptable ages. The A.I. for all samples (plateau steps only) is shown in Figure 18. All rocks are severely altered, containing ~100 times more ^{36}Ar than fresh basaltic material. No crystallization ages were recovered.

Galapagos. Whole-rock material from this area were analyzed using modern instrumentation (Sinton et al., 1996). Most samples are young (< 10 Ma) and the resulting plateau ages appear to have acceptable statistics, but show high error estimates. Their A.I. (listed in parentheses) shows all rocks have suffered alteration. Specimen 17-4 (~0.0012) appears to be less altered, whereas samples 1-46, 4-19, 5-1, 10-5 and 20-2 (~0.005 – 0.008) are more altered, containing ~10 times more ^{36}Ar than fresh material (< 0.0006). Their ages are *minimum* estimates of the time of crystallization. The conclusions of Sinton et al. (1996) regarding the velocity of the Nazca Plate relative to the Galapagos hotspot, and possible changes in Pacific hotspot motion, are rejected, as they are based on inaccurate radiometric ages.

TABLE 2. Results for $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating studies on whole-rock samples from the Line Islands, Necker Rise and Suiko Seamount. Age spectra calculated using the $(^{40}\text{Ar}/^{36}\text{Ar})_i$ values of Saito and Ozima (1977). F = goodness of fit parameter, p = corresponding probability value (see text). Errors listed at the 1σ level.

Sample No	$(^{40}\text{Ar}/^{36}\text{Ar})_i$	Plateau Age (Ma)	F (p)
119D	293±13	63.9±0.3	3.9 (~0.004)
128D	275±9	No plateau	Not applicable
130D	299±3	73.9±1.8	1.15 (~0.33)

133D	269±3	No plateau	Not applicable
134N	308±10	46.7±0.4	6.62 (<10 ⁻⁵)
137D-10	277±11	50.4±0.8	4.67 (~0.003)
137D-12	275±21	49.9±0.4	10.7 (< 10 ⁻⁶)
137D-9	246±8	No plateau	Not applicable
144D	278±9	80.1±2.4	0.91 (~0.44)
142D	281±6	No plateau	Not applicable
KH68-3	314±3	60.1±0.1	0.31 (~0.91)

Hawaiian-Emperor Chain. The age progression for this island-seamount is included in almost every introductory textbook. Subaerial rocks are altered based on their ³⁶Ar contents. I look to the older ages (primarily ⁴⁰Ar/³⁹Ar stepheating ages on whole-rock material) that were used to suggest an age of ~43 Ma, and its subsequent use for plate tectonic velocities and other calculations (over the fixed Hawaiian plume). The plateaus are not questioned on a statistical basis. I evaluate the alteration state of the material used in earlier studies to estimate the age of the bend in the Chain.

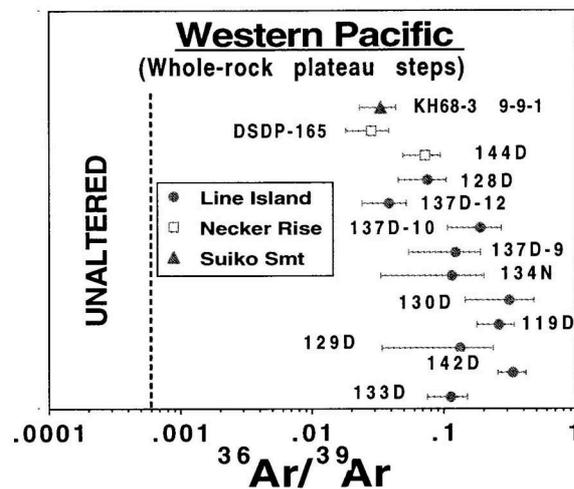


Figure 18. Assessing the alteration of whole-rock samples from the Line volcanic chain, Suiko Seamount and Necker Rise (see Table 2). The average A.I. for the best sites within the rocks (plateau steps), with SEM are shown on a *log* scale. All rocks are badly altered and the ages are rejected as accurate values for the time of crystallization.

K-Ar dating and $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion work on samples from the Koko Seamount. led to an age of ~ 47 Ma (Clague and Dalrymple, 1973). A single basalt sample (44-5) shows $\sim 3 - 5$ times atmospheric argon as fresh material. In $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion studies, two basaltic samples (43-71 and 43-80) yield A.I. values 3 - 5 times higher than for unaltered material. The samples are altered and the *minimum* age of the Koko Seamount is 47 Ma.

Clague et al. (1975) carried out K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ studies on alkalic basalts from the northern end of the Hawaiian Ridge and the southernmost part of the Emperor Seamounts. The Yuryaku Seamount lies close to the bend in the chain. The basalts from this location are partially altered, and Clague et al. (1975) suggested that $^{40}\text{Ar}/^{39}\text{Ar}$ methods yielded better results than K-Ar dating. Two samples gave plateau ages of ~ 42 Ma, and their total fusion ages fell in the range 42 - 49 Ma with 1 sigma errors of $\pm 2 - 9$ m.y.. The A.I. of the plateau steps on these rocks (Fig. 19) indicates the best sites within the rocks are altered. The average age of $\sim 42 - 44$ Ma for the Yuryaku Seamount is a *minimum* value. Dalrymple and Clague (1976) studied alkalic and tholeiitic basalts from the Diakakuji and Kimmei Seamounts. The former lies almost exactly at the bend in the Chain and the latter lies ~ 200 km to the NNW. K-Ar analysis yielded low “ages” as the rocks are altered. $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion ages on basalts and plagioclase separates fell in the range $\sim 42 - 46$ Ma. The A.I. for these samples (see Fig. 19) show $^{36}\text{Ar}/^{39}\text{Ar} > 0.01$ (basalts – the cutoff value is < 0.0006 for fresh rocks) and $^{36}\text{Ar}/^{37}\text{Ar} \sim 0.0007$ to 0.0010 (plagioclase – the cutoff value is < 0.00006). These samples are altered and total fusion ages can, at best, serve as *minimum* values for the time of crystallization.

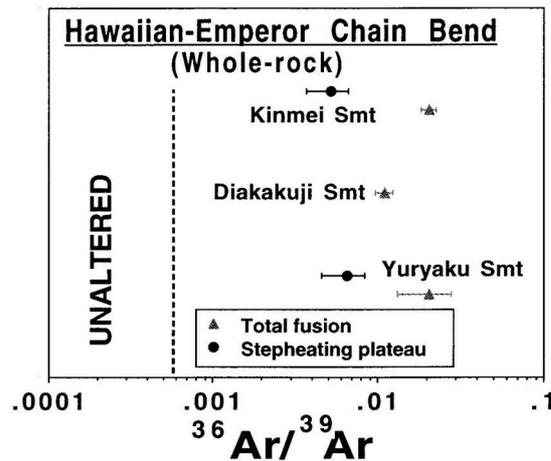


Figure 19. Assessing the accuracy of $^{40}\text{Ar}/^{39}\text{Ar}$ ages for rocks, used to obtain an age of 43 Ma for the bend in the Hawaiian-Emperor Chain. Data from Clague and Dalrymple (1973), Clague et al. (1975) and Dalrymple and Clague (1976). A.I. for $^{40}\text{Ar}/^{39}\text{Ar}$ analyses on rocks from the Yuryaku/Diakakuji/Kimmei Seamounts shown, with SEM on a *log* scale. Total fusion values show rocks are altered. Stepheating analyses on the Kimmei and Yuryaku Seamounts show lower A.I. values, but plateau steps are derived from altered sites/phases. The age of the bend must be > 43 Ma (see text).

Four rocks were subjected to $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating. For 52-50 from the Kimmei Seamount, the A.I. of the plateau steps (Fig. 19) is ~10 times higher than acceptable for fresh rocks; the age of 38 Ma is an underestimate of the time of crystallization. In summary, an age of 43 Ma is, at best, a *minimum* value for the age of the bend in the Hawaiian-Emperor Chain. More recent work on mineral separates (Sharp and Clague, 2006) gives an age of 50 Ma for the initiation of the bend. These samples were acid washed prior to analyses. Plagioclase show A.I. values of ~0.00005; the material is fresh and the plateau ages are good estimates of crystallization values. A detailed critique of these ages and changes in plate velocities in the Pacific for the period ~80-35 Ma, is under preparation.

Gilbert Ridge and Tokelau Seamounts. Koppers and Staudigel (2005) determined ages for these features that have sharp (60°) bends, similar to that in the Hawaiian-Emperor Chain. All three bends should be synchronous at ~43 - 47 Ma, if they were formed by Pacific Plate motion over stationary hotspots. The $^{40}\text{Ar}/^{39}\text{Ar}$ data suggest the bends in the Gilbert Ridge and Tokelau Seamounts were

formed at ~ 67 and ~ 57 Ma, respectively. Koppers and Staudigel (2005) conclude *their findings are not compatible with the stationary hotspot paradigm*. The mineral separates from rocks in both areas give plateaus that generally meet the statistical requirements for validity and appear to be relatively unaltered. Koppers and Staudigel (2005) also reported plateau ages for 11 groundmass separates that had been acid leached. Scrutiny of these data show that only one sample each from Tofetolu and Siapo, meet the statistical requirements for validity (see Fig. 20 and 21). Their alteration index suggests most of the samples are quite fresh. The Tofetolu and Siapo-7 samples gave statistically valid plateau ages, but these may not be correct estimates of time of crystallization. The Tofetolu groundmass gave a plateau age of 65.30 ± 0.58 Ma, whereas the plagioclase separate gave a *measurably older* age of 67.11 ± 0.24 Ma. The plateau age of Siapo-7 groundmass cannot be confirmed, since no plateau ages for plagioclase from this location are available (A.A.P. Koppers, pers. comm., 2005). Plagioclase separates yield better ages than whole-rock samples. It is therefore critical to examine all aspects of a recent work on dating *crystalline groundmass separates* (Koppers et al., 2000), from the statistical and A.I. points of view. These detailed data sets are currently *unavailable*.

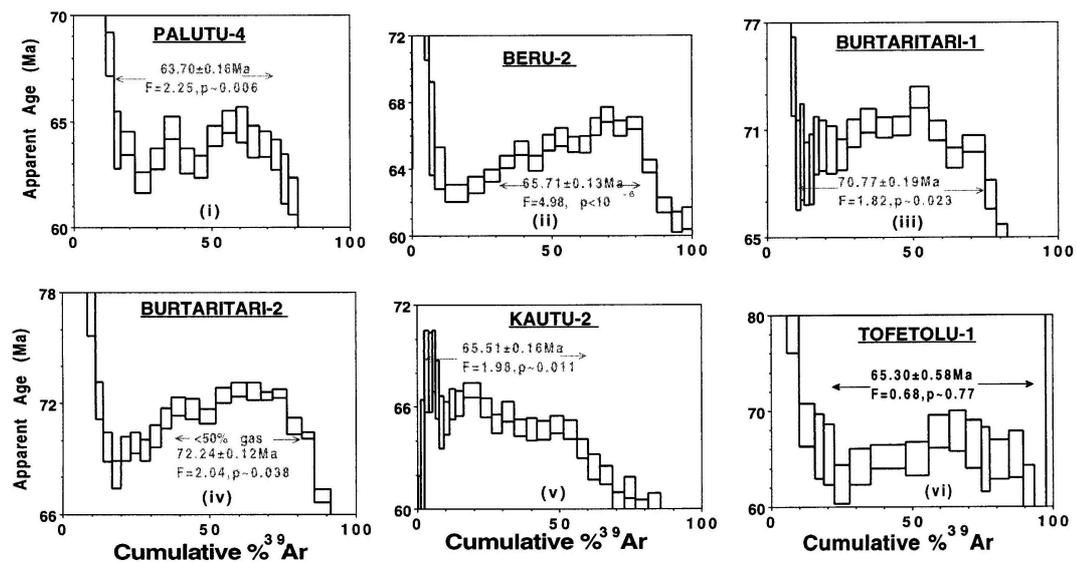


Figure 20. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for acid leached groundmass samples from the Gilbert Ridge, analyzed by Koppers and Staudigel (2005). Symbols and legend as in Fig. 1a. All except the

Tofetolu-1 sample show excess scatter ($p < 0.05$) and are disturbed specimens They do not yield valid plateau ages as stated by Koppers and Staudigel (2005). The plagioclase separate ages on the Gilbert Ridge (Koppers and Staudigel, 2005), appear to be statistically valid.

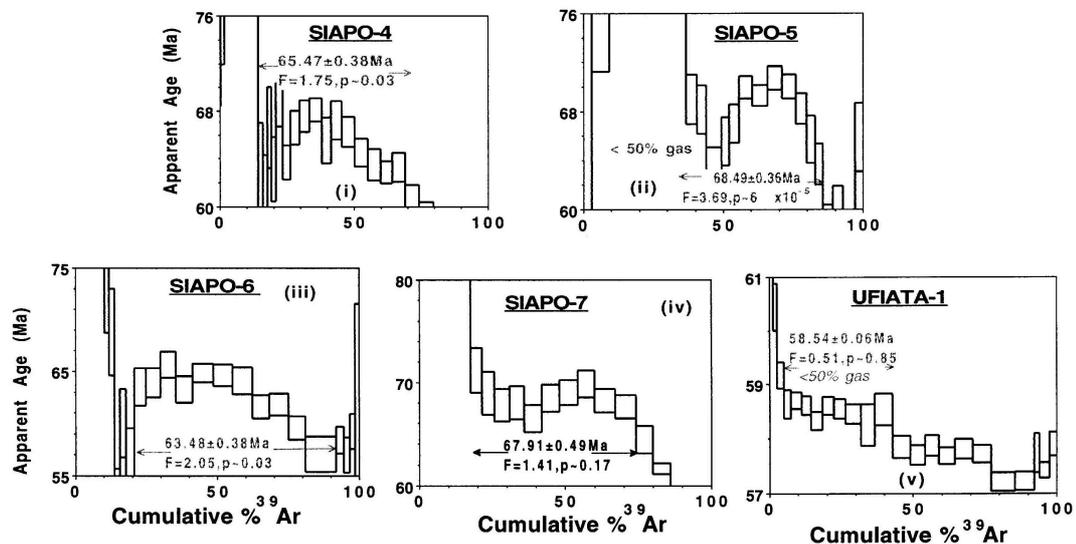


Figure 21. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for acid leached groundmass samples from the Tokelau Seamounts, analyzed by Koppers and Staudigel (2005). Symbols and legends as in Fig. 1a. All except Siapo-7 show excess scatter ($p < 0.05$), and are disturbed specimens; Ufiata-1 displays at best a marginal ($< 50\%$ gas) plateau. They do not yield valid plateau ages as stated by Koppers and Staudigel (2005). The plagioclase separate ages on the Tokelau Seamounts (Koppers and Staudigel, 2005), appear to be statistically valid.

Many workers including Koppers and Staudigel (2005), use FCT-3 Biotite as the monitor with an age of 28.03 Ma, referencing the work of Renne et al. (1998). The latter did *not* analyze FCT-3 Bio. The correct age of FCT-3 Bio relative to the calibrations of Renne et al. (1998) is in the range 28.15-28.23 Ma (see Baksi et al., 1996, Baksi, 2003).

Easter Chain volcanism. O'Connor et al. (1995) presented ages for volcanism along this chain. They utilized plagioclase separates leached in 6% HF prior to $^{40}\text{Ar}/^{39}\text{Ar}$ dating. Many samples contained excess argon, but careful stepheating led to (statistically speaking) good plateau ages. The A.I. fall in the range 0.00002 – 0.00006, i.e. all plagioclase samples were *unaltered* (see Fig. 22). Careful selection of samples, their pretreatment with acid, and good laboratory techniques, can lead to accurate ages. An intriguing facet of their work is the recovery of some plateau ages that are “too

good” (see Fig. 23). The simplest solution, is to reduce the estimated errors in each step by a factor of ~5. The SEM on the plateau ages would be reduced correspondingly.

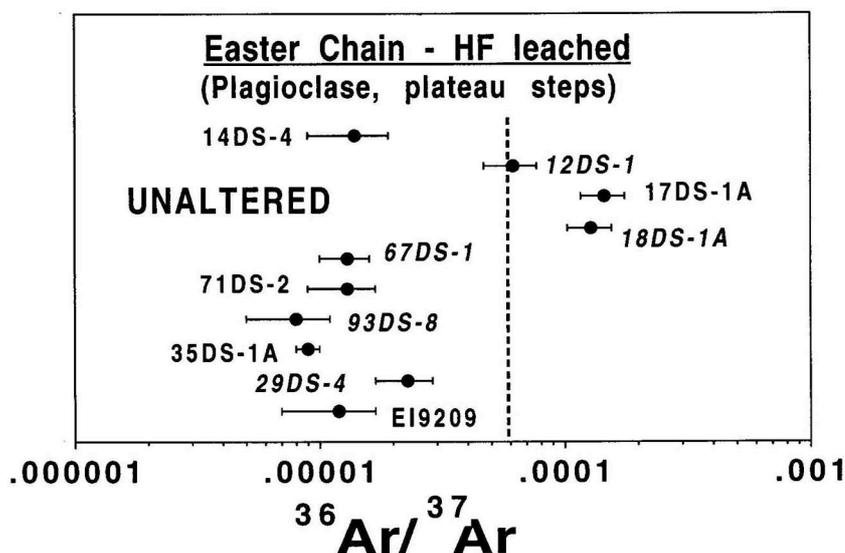


Figure 22. Assessing the alteration state of plagioclase samples from the Easter Chain dated by O'Connor et al. (1995). Average A.I. and SEM of plateau steps shown on a *linear* scale. All samples are quite fresh, proving the efficacy of HF in removing alteration products (see text).

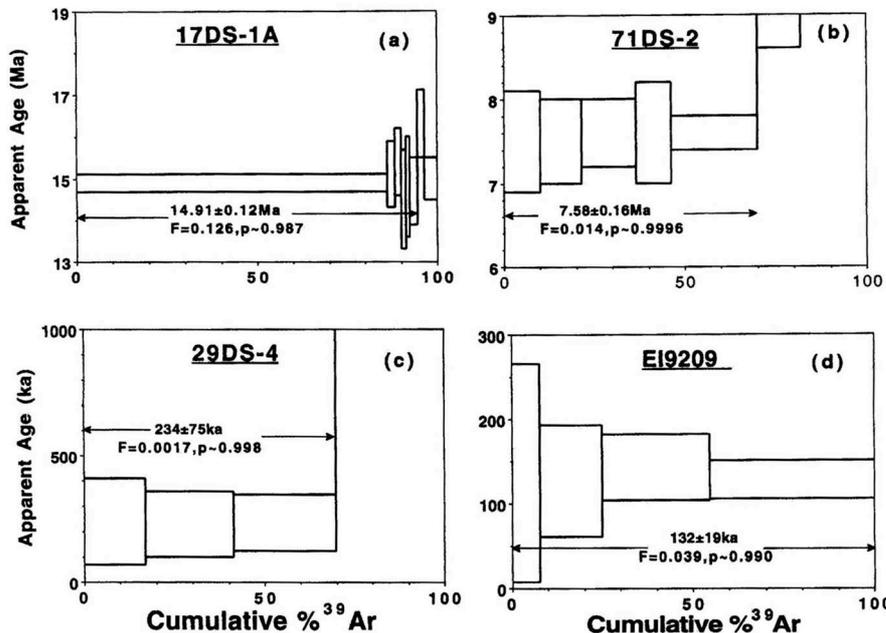


Figure 23. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for four (out of 10) HF leached plagioclase separates from the Easter Chain analyzed by O'Connor et al. (1995). Symbols and legends as in Fig. 1a. All plateau ages are statistically valid, but the statistics are “too good”, suggesting the errors reported by these authors should be reduced to ~20% (see text).

CONCLUSIONS

The ages of most of the major continental flood basalt provinces are being narrowed by use of $^{40}\text{Ar}/^{39}\text{Ar}$ dating techniques. Care must be used to use fresh (acid leached) specimens, and the resulting plateau/isochrons must be rigorously tested for statistical validity, as well as by the A.I. technique for freshness of the phases dated. In numerous cases, confusion/difficulty has resulted from the lack of full tables of analytical data. Journals must insist on the authors making such data sets available in print or on request. For elucidating the *duration* of such volcanic/magmatic events, as well as possible temporal overlap with other geological phenomena (e.g. faunal extinction events), all material must be dated by a single technique. If this is the $^{40}\text{Ar}/^{39}\text{Ar}$ method, the samples should be neutron irradiated in a single batch (cf. McWilliams et al., 1992), to eliminate errors associated with the uncertainty in the determination of irradiation (J) parameter. Lack of such data, does not permit unequivocal confirmation of the oft postulated link between flood basalt volcanism and global faunal extinction events.

Very few sea-floor rocks yield proper crystallization ages as based on argon dating studies (see Table 3). This is unsurprising in light of their alteration state, resulting from prolonged contact with a medium conducive to alteration – seawater. Analyses prior to ~1990 yielded very few reliable ages (e.g. Duncan, 1978, 1991). Whole-rock material was dated without acid leaching and grains were not selected for freshness utilizing binocular examination. Use of material in chunk or mini-core form (e.g. Pringle, 1993) caused further problems. During this earlier period, work on mineral separates gave somewhat better ages. The A.I. method reveals that samples were almost invariably altered and cannot be expected to give accurate estimates of the time of crystallization. Work carried out in the last 10 - 15 years used modern instrumentation, permitting use of smaller subsamples (often < 10 mg). Even in these cases, alteration (particularly in whole-rock material), can escape detection; this is confirmed by evaluation of the alteration index of each specimen. The studies of Sinton et al. (1996, 1998) used altered material and resulting ages are not proper estimates of the

time of crystallization. The necessity for acid leaching of all specimens prior to dating is emphasized. The work of Koppers and Staudigel (2005) indicates that HF treatment of plagioclase, and HNO₃ leaching of whole-rocks, can generally removed altered material. Attention must be directed to calculation of the A.I. for all steps and it is critical that the resulting ages be statistically evaluated for validity on age spectrum and/or isochron plots. The whole-rock ages of Koppers and Staudigel (2005) are *not* valid estimates of crystallization age; their plagioclase ages are proper estimates and hence their conclusions regarding the timing of bends in the Gilbert Ridge and Tokelau Seamounts (asynchronous with that of the Hawaiian-Emperor Chain) appear valid.

TABLE 3. Summary of the validity of published argon ages on seafloor rocks linked to hotspot (tracks).

Sample – geographic location	Statistical evaluation of plateau/isochron	Alteration state of material dated	Validity of ages
Caribbean flood basalts	Poor – not all data sets available	Poor (see Fig. 10)	All ages are minimum values
Ontong Java Plateau	OK? – but few/no data sets available	Poor (see Fig. 11)	Age appear to be a minimum value
Costa Rica	Poor – not all data sets available	Poor (see Fig. 12)	All ages are minimum values
Ninetyeast Ridge	Very poor (see Baksi, 2005)	Very poor (see Fig. 13a)	No proper ages recovered
Mascarene Plateau-Chagos Ridge	Very poor (see Baksi, 2005)	Very poor (see Fig. 13b)	Only one specimen gives a proper age
New England Seamounts	Poor (see Baksi, 2005)	Poor (see text)	Ages are minimum values
Walvis Ridge - Rio Grande Rise	Poor (see Baksi, 2005)	Poor (see Fig. 14a)	Ages are minimum values
St. Helena - Gough Chains	Poor (see Fig. 15)	Poor (see Fig. 14b)	Only one specimen gives a proper age
Coast Range - Oregon	Poor (see Baksi, 2005)	Poor (see text)	Ages are minimum values
Musicians Seamounts	Generally good	Poor (see Fig. 16)	Ages are minimum values
Western Pacific Guyots	Very poor (see Table 1)	Very poor (see Fig. 17a)	No proper ages recovered
Line Island/ Suiko Seamounts	Very poor (see Table 2)	Very poor (see Fig. 18)	No proper ages recovered
Hawaiian-Emperor Chain	Good	Poor (see Fig. 19)	Ages are minimum values

Tokelau Seamounts (whole-rock)	Poor (see Fig. 20)	Generally good (see text)	No proper ages recovered; plagioclase ages are valid
Gilbert Ridge (whole-rock)	Poor (see Fig. 21)	Generally good (see text)	No proper ages recovered; plagioclase ages are valid
Easter Chain	Good (see Fig. 23)	Very good (see Fig. 22)	Good ages – errors overestimated?

Recommendations for argon dating of sea-floor rocks. Sea floor rocks are recovered at considerable expense and it is tempting to attempt radiometric dating of all material. The argon dating methods remain the best tool. In many cases, the material recovered is severely altered and dating should *not* be attempted. “If the reliability of a sample is not certain beforehand, then the results will be ambiguous” (Dalrymple and Lanphere, 1969, p. 184). This guideline has often not been followed; the literature has numerous “ages” for sea-floor rocks that are not accurate measures of their time of crystallization.

The following procedure is recommended in approaching such work in future. (a) Carefully screen all samples petrographically and by microscopic examination. (b) Using only the freshest material, work with coarse crushed samples (see above) and not with chunks of whole-rocks. (c) Carry out acid leaching of all specimens prior to dating; HF for feldspar samples and HNO₃ for material containing ferromagnesian phases (see Baksi and Archibald, 1997). (d) Following total fusion on a weighed amount of (neutron *unirradiated*) material, calculate the amount of ³⁶Ar present (by the manometric mode of mass spectrometry – see Baksi, 1973). ⁴⁰Ar/³⁹Ar step-heating work should only be attempted on the freshest material, selected following the guidelines outlined herein and Baksi (2006). Plagioclase separates give better results than whole-rock material. All results must be critically examined for statistical validity and for freshness of the phases dated using the A.I. technique. With careful work along these lines a (small) body of reliable crystallization ages will emerge. These can then be examined for trails of hotspot tracks, possible coincidence with other geological phenomena, and calculation of the duration and/or rates of magmatic events.

ACKNOWLEDGMENTS

Comments and suggestions made by the editors of this volume, and the official reviewers, helped in shaping this manuscript. I thank those who made available tables of analytical data from their published papers. Carlo Pedretti placed da Vinci's quotations in the temporal frame. I express my gratitude to the late John Reynolds; his work helped establish modern inert gas work, and his imprint on scientists utilizing the argon dating techniques, is indelible.

REFERENCES CITED

- Allegre, C.J., Birck, J.L., Capmas, F., and Courtillot, V., 1999, Age of the Deccan Traps using ^{187}Re - ^{187}Os systematics: *Earth and Planetary Science Letters*, v. 170, p. 197-204.
- Baksi, A.K., 1973, Quantitative unspiked argon runs in K-Ar dating: *Canadian Journal of Earth Sciences*, v. 10, p. 1415-1419.
- Baksi, A.K., 1974a, Isotopic fractionation of a loosely held atmospheric argon component in the Picture Gorge Basalts: *Earth and Planetary Science Letters*, v. 21, p. 431-438.
- Baksi, A.K., 1974b, K-Ar study of the SP Flow; *Canadian Journal of Earth Sciences*, v. 11, p. 1350-1356.
- Baksi, A.K., 1994, Geochronological studies on whole-rock basalts, Deccan Traps, India: Evaluation of the timing of volcanism relative to the K-T boundary: *Earth and Planetary Science Letters*, v. 121, p. 43-56.
- Baksi, A.K., 1999, Reevaluation of plate motion models based on hotspot tracks in the Atlantic and Indian Oceans: *Journal of Geology*, v. 107, p.13-26.
- Baksi, A.K., 2003, Critical evaluation of $^{40}\text{Ar}/^{39}\text{Ar}$ ages for the Central Atlantic Magmatic Province: Timing, duration and possible migration of magmatic centers in Hames, W.E., McHone, J.G., Renne, P.R., and Ruppel, C .eds.: *The Central Atlantic Magmatic Province: Insights from Fragments of Pangea*. American Geophysical Union Monograph 136, p. 77-90.

- Baksi, A.K., 2004, Critical evaluation of radiometric ages used for tracking hotspots in the Pacific Ocean: *Eos* (Transactions American Geophysical Union), v. 85, no. 47, Fall Meeting Supplement, Abstract 51B-0544.
- Baksi, A.K., 2005, Evaluation of radiometric ages pertaining to rocks hypothesized to have been derived by hotspot activity, in and around the Atlantic, Indian and Pacific Oceans in Foulger, G.R., Natland, J.H., Presnall, D.C., and Anderson, D.L., eds.: *Plates, plumes and paradigms: Geological Society of America Special Paper 388*, p. 55-70.
- Baksi, A.K., 2006, A quantitative tool for detecting alteration in undisturbed rocks and minerals – I: water, chemical weathering and atmospheric argon: submitted to Foulger, G.R. and Jurdy, D.M., eds.: *The Origin of Melting Anomalies, Plates, plumes and planetary processes*, Geological Society of America Special Publication.
- Baksi, A.K., and Archibald, D.A., 1997, Mesozoic igneous activity in the Maranhao province, northern Brazil: $^{40}\text{Ar}/^{39}\text{Ar}$ evidence for separate episodes of magmatism: *Earth and Planetary Science Letters*, v. 151, p. 139-153.
- Baksi, A.K., Archibald, D.A., and Farrar, E., 1996, Intercalibration of $^{40}\text{Ar}/^{39}\text{Ar}$ dating standards: *Chemical Geology*, v. 129, p. 307-324.
- Clague, D.A., and Dalrymple, G.B., 1973, Age of Koko Seamount, Emperor Seamount Chain: *Earth and Planetary Science Letters*, v. 17, p. 411-415.
- Clague, D.A., Dalrymple, G.B., and Moberly, R., 1975, Petrography and K-Ar ages of dredged volcanic rocks from the western Hawaiian Ridge and the southern Emperor Seamount chain: *Geological Society of America Bulletin*, v. 86, p. 991-998.
- Clouard, V., and Bonneville, A., 2005, Ages of seamounts, islands, and plateaus on the Pacific Plate, in Foulger, G.R., Natland, J.H., Presnall, D.C., and Anderson, D.L., eds.: *Plates, plumes and paradigms: Geological Society of America Special Paper 388*, p. 71-90.
- Courtillot, V., Feraud, G., Maluski, H., Vandamme, D., Moreau, M.G. and Besse, J., 1988,

- Deccan flood basalts and the Cretaceous-Tertiary boundary; *Nature*, v. 333, p. 843-846.
- Dalrymple, G.B., 1991, *The age of the Earth*, Stanford University Press, Stanford, 474 pp.
- Dalrymple, G.B., and Clague, D.A., 1976, Age of the Hawaiian-Emperor bend: *Earth and Planetary Science Letters*, v. 31, p. 313-329.
- Dalrymple, G.B., and Lanphere, M.A., 1969, *Potassium-Argon Dating*, Freeman, San Francisco, 258 pp.
- Dalrymple, G.B., Alexander, E.C., Lanphere, M.A. and Kraker, G.P., 1981, Irradiation of samples for $^{40}\text{Ar}/^{39}\text{Ar}$ dating using the Geological Survey TRIGA Reactor: Reston, Virginia, U.S. Geological Survey Professional Paper 1176, 55 pp.
- Duncan, R.A., 1978, Geochronology of basalts from the Ninetyeast Ridge and continental dispersion in the eastern Indian Ocean: *Journal of Volcanology and Geothermal Research*, v. 4, p. 283-305.
- Duncan R.A., 1982, A captured island chain in the Coast Range of Oregon and Washington: *Journal of Geophysical Research*, v. 87, p. 10,827-10,837.
- Duncan, R.A., 1984, Age progressive volcanism in the New England Seamounts and the opening of the central Atlantic Ocean: *Journal of Geophysical Research*, v. 89, p. 9980-9990.
- Duncan, R.A., 1991, Age distribution and volcanism along aseismic ridges in the eastern Indian Ocean: *Proceedings of the Ocean Drilling Program*, v. 121, p. 507-517.
- Duncan, R.A. and Pyle, D.G., 1988, Rapid extrusion of the Deccan flood basalts at the Cretaceous-Tertiary boundary; *Nature*, v. 333, p. 841-843.
- Duncan, R.A., and Hargraves, R.B., 1990, ^{40}Ar - ^{39}Ar geochronology of basement rocks from the Mascarene Plateau, Chagos Bank and Maldiva Ridge: *Proceedings of the Ocean Drilling Program*, v. 115, p. 43-51.
- Hoffman, C., Feraud, G., and Courtillot, V., 2000, $^{40}\text{Ar}/^{39}\text{Ar}$ 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*, v. 180, p. 13-27.
- Knight, K.B., Renne, P.R., Halkett, A., and White, N., 2003, $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Rajahmundry Traps, Eastern India and their relationship to the Deccan Traps: *Earth and Planetary Science Letters*, v. 209, p. 257.
- Koppers, A.A.P., and Staudigel, H., 2005, Asynchronous bends in Pacific seamount trails: A case for extensional volcanism? *Science*, 307, p. 904-907.
- Koppers, A.A.P., Staudigel, H. and Wijbrans, J.R., 2000, Dating crystalline groundmass separates of altered Cretaceous seamount basalts by the $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating technique: *Chemical Geology*, v. 160, p. 139-158.
- Langmuir, I., 1989, Pathological science (transcribed and edited by Hall, R.N.): *Physics Today*, v. 42, p. 36-48.
- Lanphere, M.A., and Dalrymple, G.B., 1978, The use of $^{40}\text{Ar}/^{39}\text{Ar}$ data in evaluation of Disturbed K-Ar systems: U.S. Geological Survey Open-File Report 78-701, p. 241-243.
- Mahoney, J.J., Macdougall, J.D., Lugmair, G.W., and Gopalan, K., 1983, Kerguelen hotspot source for Rajmahal Traps and Ninetyeast Ridge? *Nature*, v. 303, p. 385-389.
- Mahoney, J.J., Storey, M., Duncan, R.A., Spencer, K.J., and Pringle, M., 1993, Geochemistry and age of the Ontong Java Plateau, in , in Pringle, M.S., Sager, W.W., Sliter, W.V., eds: *The Mesozoic Pacific: geology, Tectonics, and Volcanism*, American Geophysical Union Monograph 77, p. 233-261.
- McDougall, I. and Harrison, T.M., 1999, *Geochronology and thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ method*; Oxford University Press, New York, 269 pp.
- McWilliams, M.O., Baksi, A.K., Bohor, B.F., Izett, G.A. and Murali, A.V., 1992, High-precision relative ages of K/T boundary events in North America and Deccan Trap volcanism in India; *Eos*, Transactions of the American Geophysical Union, v. 73, p. 363.
- Merrill, C. and Turner, G., 1966, Potassium-argon dating by activation with fast neutrons:

- Journal of Geophysical Research, v. 71, p. 2852-2857.
- O'Connor, J.M., and Duncan, R.A., 1990, Evolution of the Walvis Ridge-Rio Grande Rise hot spot systems: Implications for African and South American plate motions over plume: Journal of Geophysical Research, v. 95, p. 17475-17502.
- O'Connor, J.M., and Le Roex, A.P., 1992, South Atlantic hot-spot plume systems: 1. Distribution of volcanism in time and space: Earth and Planetary Science Letters, v. 113, p. 343-364.
- O'Connor, J.M., Stoffers, P., and McWilliams, M.O., 1995, Time-space mapping of Easter Chain volcanism: Earth and Planetary Science Letters, v. 136, p. 197-212.
- Ozima, M., Honda, M., and Saito, K., 1977, ^{40}Ar - ^{39}Ar ages of guyots in the western Pacific and discussion of their evolution: Geophysical Journal of the Royal Astronomical Society, v. 51, p. 475-485.
- Ozima, M., Saito, K., and Takagami, Y., 1978, ^{40}Ar - ^{39}Ar geochronological studies on rocks drilled at holes 462 and 462A, Deep Sea Drilling Project Leg 61: Initial Reports of the Deep Sea Drilling Project, v. 61, p. 701-703.
- Pringle, M.S., 1993, Age progressive volcanism in the Musicians Seamounts; a test of the hotspot hypothesis for the late Cretaceous Pacific, in Pringle, M.S., Sager, W.W., Sliter, W.V., eds.: The Mesozoic Pacific; geology and volcanism; American Geophysical Union Monograph 77, Washington, D.C., p. 187-215.
- Renne, P.R., 2000, $^{40}\text{Ar}/^{39}\text{Ar}$ age of plagioclase from Acapulco meteorite and problem of systematic errors in cosmochronology: earth and Planetary Science Letters, v. 175, p. 13-26.
- Renne, P.R., Swisher, C.C., Deino, A.L., Karner, D. B., Owens, T.L., and DePaolo, D.J., 1998, Intercalibration of standards, absolute ages and uncertainties in ^{40}Ar - ^{39}Ar dating: Chemical Geology, v. 145, p. 117-152.
- Roddick, J.C., 1983, High precision intercalibration of ^{40}Ar - ^{39}Ar standards; Geochimica et Cosmochimica Acta, v. 47, p. 887-898.

- Saito, K., and Ozima, M., 1977, ^{40}Ar - ^{39}Ar geochronological studies on submarine rocks from the western Pacific area: *Earth and Planetary Science Letters*, v. 33, p. 353-369.
- Seidemann, D.E., 1978, $^{40}\text{Ar}/^{39}\text{Ar}$ studies of deep-sea igneous rocks: *Geochimica et Cosmochimica Acta*, v. 42, p. 1721-1734.
- Sharp, W.D., and Clague, D. A., 2006, 50-Ma initiation of the Hawaiian-Emperor Bend records major change in Pacific Plate motion: *Science*, v. 313, p. 1281-1284.
- Sinton, C.W., Christie, D.M., and Duncan, R.A., 1996, Geochronology of Galapagos Seamounts: *Journal of Geophysical Research*, v. 101, p. 13689-13700.
- Sinton, C.W., Duncan, R.A. and Denyer, P., 1997, Nicoya Peninsula, Costa Rica: a single suite of Caribbean oceanic plateau magmas: *Journal of Geophysical Research*, v. 102, p. 15507-15520.
- Sinton, C.W., Duncan, R.A., Storey, M., Lewis, J., and Estrada, J.J., 1998, An oceanic flood basalt province within the Caribbean plate: *Earth and Planetary Science Letters*, v. 155, p. 221-235.
- Steiger, R.H., and Jager, E., 1977, Subcommittee on geochronology: convention of the use of decay constants in geo- and cosmochronology. *Earth and Planetary Science Letters*, v. 36, p. 359-362.
- Turrin, B.D., Donnelly-Nolan, J.M. and Hearn, B.C., Jr., 1994, ^{40}Ar - ^{39}Ar ages from the rhyolite of Alder Creek, California: Age of the Cobb Mountain normal polarity subchron revisited: *Geology*, v. 22, p. 251-254.
- Venkatesan, T.R., Pande, K., and Gopalan, K., 1993, Did Deccan volcanism pre-date the Cretaceous/Tertiary boundary? *Earth and Planetary Science Letters*: v. 119, p. 181-189.
- Walker, D.A. and McDougall, I., 1982, $^{40}\text{Ar}/^{39}\text{Ar}$ and K-Ar dating of altered glassy volcanic rocks: the Dabi volcanics, P.N.G: *Geochimica et Cosmochimica Acta*: v. 46, p. 2181-2190.
- York, D., 1969, Least squares fitting of a straight line with correlated errors: *Earth and Planetary*

Science Letters, v. 5, p. 320-324.

York, D., Hall, C.M., Gaspar, M.J., and Lynch, M., 1984, Laser-probe $^{40}\text{Ar}/^{39}\text{Ar}$ dating with ultra-sensitive mass spectrometer: Eos, Transactions of the American Geophysical Union, v. 65, p. 303.