Discussion of

A quantitative tool for detecting alteration in undisturbed rocks and minerals

I: water, chemical weathering and atmospheric argon

&

II: application to argon ages related to hotspots

by

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17th November, 2006, Romain Meyer, Michael Abratis, Henry Rauche

An additional process to increase radiogenic Ar in basalts.

In addition to Baksi’s exceptionally detailed description of alteration problems resulting in geological Ar-Ar age errors, a recent study of igneous rocks from the Central European Volcanic Province (CEVP) (Abratis et al., in press.) clearly points to an additional process responsible for wrong radiometric Ar ages. In this study, all data except for one outlier range between 20 and 14 Ma. The outlier, with an age of 29 Ma, is from a volcanic dyke in the NE Rhön, close to the Thuringian Forest.

The sample location is in the Werra district, a region in Germany famous for its former potash mining industry. These Permian (Zechstein) potash salt deposits were penetrated in the Cenozoic by basaltic magma dykes. This CEVP magmatism has been linked in the literature by many authors to a postulated mantle plume arriving in the subcontinental lithosphere, on the basis of mantle tomography, geochemistry and radiogenic age data (cf. references in: Lustrino and Wilson, in press).

Despite the tremendous thermal and tectonic stresses that must have accompanied injection of the magmas, the salt layers remained nearly unchanged. However, geochemical salt–magma interactions occurred; e.g., diffusion of K and Ar from the salt into the magma is apparent. The K and Ar geochemistry of these basalts illustrates such assimilation/contamination via (a) potash salt in the basaltic magma, and (b) fluid circulation in the proximal zone of the basaltic dykes (Steinmann et al., 1999). Basalts having undergone these interactions are enriched in highly radiogenic Ar from the salt deposit, and cannot indicate a real crystallisation age.

Thus, it is not only processes that occur after crystallisation (e.g. alteration) that can affect apparent radiogenic ages, but as is proposed for geochemical mantle plume “fingerprints”, melt–crust rock interactions can mask the initial signal. The lithology of the rocks through which the magma rises to the Earth’s surface can cause inaccurate estimates of the crystallization ages. Even if basalts are petrographically fresh, statistically acceptable ages of CEVP rocks from
Central Germany are difficult to obtain due to (a) the widespread distribution of Zechstein salt deposits, and (b) the likelihood that only the central parts of large dykes that penetrated into salt deposits are not affected by highly radiogenic Ar from the salt.

A good knowledge of the continental crust below continental volcanic provinces will permit better constraint of the intrinsic geochemical heterogeneity – in space and time – of mantle melts.

15th January, 2007, Ajoy K. Baksi

Meyer and colleagues raise an important point which was inadvertently left out in the final revision of my manuscript. Namely, alteration can, on occasion, lead to $^{40}\text{Ar}/^{39}\text{Ar}$ ages that are too old (see also Dalrymple and Lanphere, 1969). This appears to be often the case for intrusive rocks and is illustrated by study of results on a Deccan Trap sample from India.

A dyke from the Panvel area (D-921, see Baksi, 1994), was analyzed using a system with very low argon blanks (cf. Baksi et al., 1992). The results are presented in Figure 1. The whole-rock specimen contains excess argon and the isochron yields an age of ~ 62 Ma (i.e. ~ 3 Ma after the main pulse of Deccan volcanism). The the A.I. values for the isochron steps in Figure 1b fall in the range 0.04 - 0.0015. The cutoff for freshness is < 0.0006; the rock is “altered” and should not yield the correct crystallization age. However, it is suggested that the correct age is ~62 Ma.

![Figure 1](image.png)

Figure 1. (a) Age spectrum and isochron analysis of $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating analysis of dike D-921 from the Deccan Traps, India. All errors shown at the 1σ level. F = goodness of fit parameter, p = probability of occurrence; T = age, IR = initial ($^{40}\text{Ar}/^{39}\text{Ar}$) ratio. The rock contains “excess argon” and has an age of ~62 Ma (see text).

Note that the A.I. technique is successful in pinpointing some cases of alteration in sills – see the section dealing with the Gettysburg Sill in Baksi (this volume). Further investigation is required to fully understand the possible application of the A.I. technique to sills and dykes in general.

24th January, 2007, Alexei Ivanov
Baksi (this volume) suggests a very interesting approach for determining secondary alteration of samples through measurements of the amount of $^{36}$Ar. Briefly, in the present-day atmosphere $^{36}$Ar comprises up to 0.338% of the total argon or as much as ~0.003% of the total atmosphere. The mantle and mantle-derived volcanic rocks are thought to contain significantly less $^{36}$Ar. Argon is soluble in water. Thus, chemically weathered minerals contain an excess of atmospheric $^{36}$Ar. On basis of this, and a number of representative examples from K-Ar and $^{40}$Ar/$^{39}$Ar studies, Baksi (this issue) develops a set of equations and cutoff values for different minerals and basaltic rock compositions to estimate their degree of secondary alteration. Below is rather an addendum to Baksi (this issue) than a critique of his approach.

Baksi (this volume, 20th January comment to Hooper et al., this volume, and 15th January comment to Ivanov, this volume) may be too strict in accepting/rejecting published ages. I think that there cannot be a single cutoff value, even for the same type of dated material, and this is evident from analyses of plagioclases from the Central Atlantic Magmatic Province and the Rajahmundry Traps (Fig. 6b and 7a in Baksi, this volume). Especially, this may be true for whole-rock samples, because the whole rock is mixture of different minerals, each of which may be characterized by its own range of cutoff values. For instance, the occurrence of biotite in the whole rock will shift AI towards higher values. Small crystals of primary magmatic mica (biotite?) may occur in some dolerites (see Fig. 12 in Ivanov, this volume).

Baksi (this volume) acknowledges that recycling of atmospheric water through subduction may create high $^{36}$Ar in mantle-wedge-derived volcanic rocks. The water recycling may also be responsible, in origin, of at least some flood basalt provinces (see Ivanov, this volume and 17th January comment to Hooper et al., this volume). Thus, we may expect high $^{36}$Ar in the flood basalts, too. This necessitates performing special methodical $^{40}$Ar/$^{39}$Ar studies which may include dating of three matrix aliquots, two leached with HNO$_3$ and HF, and one unleached, from visually altered and fresh samples from island-arcs, flood basalt provinces and continental alkaline volcanic rock occurrences.

Another important question is the style and timing of alteration. Was it continuous or episodic, and if episodic when did the episodic alteration happen? The concept of timing of episodic alteration is illustrated in Fig. 2 with three models for a hypothetical 250-Ma sample:

- (model 1) alteration event at 200 Ma with 100% loss of radiogenic argon,
- (model 2) alteration event at 240 Ma with 50% loss of radiogenic argon, and
- (model 3) alteration event at 249 Ma with 100% loss of radiogenic argon.

Model 1 shows a 20% decrease of apparent age relative the true crystallization age, whereas models 2 and 3 yield less prominent apparent age decreases (3.5% and 0.4%, respectively). Of course, Fig. 2 gives an oversimplified view of the problem. Alteration (chemical weathering) redistributes potassium from primary minerals to tiny secondary clay minerals, which are less retentive of radiogenic argon and suffer from the nuclear-irradiation-related $^{39}$Ar recoil problem. This is probably the case for the plagioclase sample SCD-9, which shows a complex argon release pattern (Fig. 7a in Baksi, this volume).
In summary:

1. Samples of magmatic rocks and minerals with statistically acceptable plateaus and isochron $^{40}$Ar/$^{39}$Ar ages and AI values below the cutoff values represent true crystallization ages.

2. Samples of magmatic rocks and minerals with statistically acceptable plateaus and isochron $^{40}$Ar/$^{39}$Ar ages and AI values above the cutoff values are suspected of having apparent ages that are too young. They may yield true crystallization ages if they (a) are derived from a magmatic source with recycled atmospheric water through subduction, or (b) were altered soon after crystallization.

3. The AI approach is both simple and powerful. It should be used routinely in $^{40}$Ar/$^{39}$Ar dating for additional assessment of the age reliability.

![Figure 2](image)

Figure 2. Dependence of the difference between true and apparent ages on timing of episodic alteration and degree of associated radiogenic argon loss. $\Delta t = (t_{\text{apparent}}/t_{\text{true}}-1) \times 100$. See text for description of the models.

29th January, 2007, Ajoy K. Baksi

Ivanov raises pertinent questions regarding the utility of the alteration index (A.I.) method. Clarification is offered on a number of issues.

First, for plagioclase feldspars from mafic material, the cutoff value of A.I. < 0.00006 for freshness, appears to be valid. The results on HF-washed CAMP samples (Hames et al. 2000) show this best (Baksi, 2007a), and those on the hot HNO$_3$-leached samples (Verati et al. 2005) may be valid. The latter should be reanalyzed following HF leaching. The (acid) unleached samples (Deckart et al. 1997; Sebai et al.1991) do not give proper plateaus (Baksi, 2003) and fail the A.I. test for freshness (Baksi, 2007a). The Rajahmundry Traps data sets referred to by Ivanov
(comment of 24th January) are considerably tightened up by rejection of samples showing high A.I. (see Baksi, 2005). On extrusion into a shallow-marine or estuarine environment (Baksi, 2001; 2005), these rocks incorporated higher quantities of $^{36}$Ar than most whole-rock basalts.

Earlier, the A.I. method was not recommended for subduction zone rocks (Baksi, 2007a). Fig. 3 looks to its application to tholeiites and boninites from the Izu-Bonin-Marianas Arc in the Pacific Ocean. The plateau steps of Cosca et al. (1998) show elevated A.I. values, but less than initially envisaged (Baksi, 2007a). During the (high temperature) melt generation process, much of the $^{36}$Ar in the water driven off the subducted slab escapes and is released from volcanoes. Ivanov suggests some flood basalts may contain contributions from (earlier) subducted material. Melting of such rocks with A.I. values similar to those in Fig. 3 would release much of the $^{36}$Ar; furthermore, the solubility of argon in such melts is low (Lux, 1987) and would produce (flood) basalts with low (< 0.0006?) A.I. values.

The A.I. method should initially be applied only to mafic, extrusive material. Ivanov expresses concern regarding the cut-off recommended for alkali basalts that may contain minor quantities of hornblende and/or biotite. The Bengal Trap alkali basalt “Debagram” contains primary biotite (Baksi, 1995), was used to construct Fig. 4 in Baksi (2007a), and passes the A.I. test for freshness. Ivanov discusses alteration as being an episodic process. I suggest chemical weathering for EXTRUSIVE rocks is (quasi) continuous (see Fig. 18 in Baksi, 2007a). Many altered continental and oceanic basalts show A.I. values higher than the Izu-Bonin-Marianas arc rocks (see Figs. 3 &13 in Baksi, 2007a, and Figs. 10-19 in Baksi, 2007b). (Continuous) alteration at low temperatures leads to higher A.I. values than seen in (high temperature generated) subduction-zone rocks.

The high A.I. values in flood basalts result from alteration and lead to lowered ages. This is illustrated using results from the Columbia River Basalt (CRB). Hooper et al. (2002) and Hooper (2004) argue for > 90% of the volcanism occurring between ~16.1 and 15.0 Ma, utilizing in part the ages of Long and Duncan (1983). Fig. 4 examines the A.I. values for this latter work. The rocks are altered and yield (incorrect) low ages. Material recovered from the deepest borehole in the Grande Ronde Basalt (GRB/O) gave step ages of ~10 Ma; ~30% loss of $^{40}$Ar* resulted from (gross) alteration of the material dated. An alternative viewpoint is that most sections of the CRB are ~0.5 to 1.0 Ma older than envisaged by Hooper (see Baksi, 1993 and discussion by Baksi of the chapter by Hooper et al., this volume). This was based, in large part, on a ~17.5-Ma age for the Immaha Basalt (IB - Baksi and Farrar, 1990, Fig.1a). The MSWD value for the plateau section is 2.3, the probability of occurrence ~ 0.02, and the age must be rejected (Baksi, 2007a). The other ages of Baksi and Farrar (1990), adjusted to the calibrations of Renne et al. (1998), are 16.3 to 16.0 Ma for the R$_1$ through N$_2$ magnetostratigraphic units. Fig. 4 shows the A.I. for CRB rocks analyzed following HNO$_3$ leaching of crushed whole-rock material (Baksi, unpubl. data). Ages are ~16.3 Ma for the top of the IB and for the GRB they agree with the earlier ages of ~16.4 -16.0 Ma. All samples show acceptable A.I. values, are unaltered, and thus the ages are more reliable than the (acid untreated) rocks of Baksi and Farrar (1990).

In summary, I agree with Hooper et al. (see Discussion on chapter by Hooper et al., this volume) that most of the CRB volcanism occurred within ~0.75 Ma, but at ~16.5-16.0 Ma (cf. Jarboe et al., 2006) not 16.1–15.0 Ma. The age of 16.6-16.5 Ma for the Steens Basalt is not in dispute.
Scrupulous attention to $^{40}\text{Ar}/^{39}\text{Ar}$ ages (a) using only plateau/isochron ages that are statistically acceptable and (b) on rocks that are unaltered – using the A.I. test – can help resolve (magneto)stratigraphic problems. Samples (feldspars, whole-rocks, in particular) should be leached with acid (see Baksi, 2007b), prior to dating.

![Subduction zone rocks diagram]

Fig. 3. Alteration index values for rocks from the Izu-Bonin-Marianas trench – data from Cosca et al. (1998). Average values for plateau steps (open circles) shown with associated SEM values, and total gas values (filled circles). Dotted line shows cutoff for unaltered basaltic material. High values (i.e. high $^{36}\text{Ar}$ contents) result not from alteration but from interaction with water driven off the subducted slab (see Baksi, 2007a and comment text above).
Fig. 4. Alteration index values for Columbia River Basalts; average values for plateau steps shown with associated SEM. IB = Imnaha Basalt, GRB = Grande Ronde Basalt. Results of Long and Duncan (1983) – open circles; all samples are altered and resulting ages are rejected. Results on HNO$_3$-washed samples shown as filled circles (Baksi, unpubl. data). All samples show A.I. < 0.0006 (cutoff for freshness). The resulting age of ~16.4 Ma (IB) is preferred over the earlier result of Baksi and Farrar (1990) on an acid-untreated split of rock. Ages of ~16.4 – 16.0 Ma (GRB) are in agreement with the results of Baksi and Farrar (1990) – see text of comment above.

4th February, 2007, Ajoy K. Baksi

I make a final comment on my second, “application” chapter.

In evaluating the argon ages for “hotspot tracks” in the Pacific Ocean (Baksi, this volume), I overlooked the data for seamounts in the Northwest Pacific (Winterer et al. 1993). These “ages” are of importance, as the authors hypothesize ~40 Ma of volcanism on the Darwin Rise – a superswell. Earlier (Baksi, 2004), some of these ages were shown to be untenable on the basis of statistical evaluation of the plateaus postulated by these authors. Herein, I evaluate all ten sets of ages put forth by Winterer et al. (1993), looking to both the statistical validity of plateau sections of the age spectra, as well as the alteration state (index) of the whole-rock samples utilized by these authors.

Step ages were calculated following Dalrymple et al. (1981), using the isotopic data in Table 1, of Winterer et al. (1993). Some step ages differ from those listed by these authors. No effort was
made to adjust the ages from those reported relative to MMhb-1 at 520.4 to those preferred by Renne et al. (1998) The statistical analysis is straightforward – see Fig. 5. Only a single plateau was recovered, for Lamont Seamount-1, for a different set of steps than those used by Winterer et al. (1993). Most cases show very low probability values, notably Wilde/Lamont-2/Winterer/Isakov/MIT/Heezen Seamounts.

The two-step plateau for Allison seamount is rejected, as a minimum of three steps must form a plateau. The alteration index for each sample (Fig. 6) was calculated as \( \frac{36}{39} \)Ar, normalized for the production of \( ^{39} \)Ar from \( ^{39} \)K (see Baksi, 2007a). All samples are altered, most showing > 10 times the amount of \( ^{36} \)Ar expected for fresh whole-rock material. The statistically acceptable plateau age of Lamont-1 must be rejected, as the sample is badly altered. The finding that all samples are altered is in line with the observations that “extensive (residual) alteration in some of (the rocks)” and “many lavas, …….., are largely transformed to smectite, zeolite and authigenic K-feldspar” (Winterer et al., 1993, p. 310). Such specimens should not be dated, without recourse to acid leaching, to remove alteration products (Baksi, 2007b). In light of the ~100 Ma exposure of these rocks to seawater, pervasive alteration is expected. The radiometric work of Winterer et al. (1993) yielded no valid ages, and cannot be used to test predictions using seamount magnetic data, hot spot models, or the Pacific apparent polar wander path for the time period ~120 – 80 Ma.

Fig. 5. Age spectra for \( ^{40} \)Ar/\( ^{39} \)Ar stepheating analyses of rocks from Cretaceous guyots in the northwest Pacific Ocean (data from Winterer et al., 1993). All errors shown and listed at the 1σ level. Plateau sections and ages postulated by the authors, are shown in grey. The corresponding statistical parameters are shown in black. F = goodness of fit parameter, p = probability of occurrence. All of these ages are rejected as p < 0.15 – the cutoff value suggested by Sharp and Clague (2006) for statistical validity. This value is more stringent than the initial value of p < 0.05 suggested earlier (Baksi, 1999, 2005) and is preferred here. Only steps 2-6 of Lamont Seamount-1, yields a statistically acceptable “age”.
Fig. 6. Assessing the alteration state of rocks from the Cretaceous guyots of the northwest Pacific Ocean dated by Winterer et al. (1993). The A.I. and SEM for plateau steps are shown on a log scale. The cutoff value for fresh samples is A.I. < 0.0006 (dotted line) – see Baksi (2007a). All samples are altered and no accurate estimates of the time of crystallization can be recovered from these rocks.

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