Precise dating of biotite in distal volcanic ash: Isolating subtle alteration using $^{40}$Ar/$^{39}$Ar laser incremental heating and electron microprobe techniques

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ABSTRACT

Precise dating of K-rich minerals in volcanic rocks via the $^{40}$Ar/$^{39}$Ar geochronometer has become crucial to resolving many geological problems. In some cases, ash beds containing biotite phenocrysts but lacking sanidine are the only datable horizons at key stratigraphic intervals, necessitating comparison of sanidine and biotite ages within the same chronostratigraphic framework. To assess the integrity of biotite and evaluate the accuracy of ages obtained from this often problematic mineral, incremental heating $^{40}$Ar/$^{39}$Ar experiments were performed on large, millimeter-sized, euhedral biotite crystals from four key Eocene tuffs in the Green River and Wind River Basins and are compared with sanidine $^{40}$Ar/$^{39}$Ar ages. Unaltered biotite crystals with homogenous K-compositions from two tuff beds yielded concordant plateau ages that are indistinguishable from cogenetic sanidine ages. In contrast, biotite crystals from two other tuffs yielded discordant spectra, with relatively young initial steps followed by older, down-stepping apparent ages. Plateau ages from the discordant experiments are older than the sanidine ages by 1 to 14%. Integrated (total fusion) ages from these experiments exhibit scatter toward both younger and older ages that correlate with the degree of spectral discordance. Electron microprobe transects reveal that biotite crystals yielding discordant age spectra contain 1–10 µm thick K-depleted (<8% K$_2$O) alteration zones along internal cleavage planes that are absent in biotite crystals yielding concordant age spectra. We propose that these altered zones promote open-system behavior. Phenomena such as loss of K or $^{40}$Ar*, $^{39}$Ar$_e$ recoil into internal K-depleted phases, and $^{39}$Ar$_e$ recoil entirely out of internally corroded biotite crystals are all potential mechanisms that can be related to this alteration. Due to the presence of these multiple potential pathways that promote the gain or loss of isotopes, such altered biotite crystals are unsuitable for high-resolution $^{40}$Ar/$^{39}$Ar dating, comparisons with sanidine ages, or calibration of the geomagnetic polarity timescale.

Keywords: Biotite, sanidine, $^{40}$Ar/$^{39}$Ar, recoil, Bridger Formation, Wagon Bed Formation, Wind River Formation, EPMA, tephra, tuff, volcanic ash

INTRODUCTION

Advances in the $^{40}$Ar/$^{39}$Ar dating of small samples from ash beds have facilitated geochronologic studies of unprecedented accuracy and precision in sedimentary strata (e.g., McDougall et al. 2005). For example, recent geochronology in Eocene basins of the western United States has permitted order-of-magnitude improvements in the temporal resolution of mammalian evolution, correlation of local paleobotanical temperature and precipitation estimates to global paleoclimate records, and direct measurement of lake cycle periodicity (Wing et al. 1991; Wilf 2000; Pietras et al. 2003; Smith et al. 2003). High-K sanidine is the ideal mineral, but in many cases is not available or is contaminated with xenocrysts or detrital grains (Mader et al. 2001; Smith et al. 2003). Biotite phenocrysts are commonly more abundant and are easily separated from many ash-fall deposits, but are also far more susceptible to alteration, which can lead to $^{40}$Ar* loss, K loss, and $^{39}$Ar recoil effects during irradiation (Clauer et al. 1982; Cerling et al. 1985; Onstott et al. 1995). Several studies have measured a discordance between sanidine and biotite ages (e.g., Hilgen et al. 1997; Lanphere 2000), or have empirically measured or modeled the effects of irradiation-derived recoil of $^{39}$Ar$_e$ on apparent ages for biotite and other minerals (e.g., Onstott et al. 1995; Paine et al. 2004). We present a systematic comparison of sanidine and biotite ages from a well-documented succession of widespread ash beds, along with mineralogical and chemical data from biotite crystals to assess the sources of discrepancies.

We used $^{40}$Ar/$^{39}$Ar incremental heating experiments and electron-microprobe analysis to examine biotite crystals from four Eocene tuff beds that also contain sanidine phenocrysts in the Green River and Wind River Basins of Wyoming (Fig. 1; Table 1). Further descriptions and analytical details are provided in the data repository. All of these beds consist of ash-fall deposits containing euhedral phenocrysts encased in altered matrix, and represent important temporal calibration points for paleontologic, magnetostratigraphic, and sedimentologic studies in the Wind River and Green River Basins (Sinclair and Granger 1911; Van
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dix Figures 1–3 (further descriptions and analytical details are

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Sanidine

Sanidine $^{40}\text{Ar}/^{39}\text{Ar}$ ages represent a baseline from which to assess the accuracy of biotite ages. Sanidine fusion and incremental heating analyses that exhibit Gaussian apparent age distributions with few outliers yield weighted mean ages of 48.15 ± 0.08, 48.76 ± 0.09, 47.70 ± 0.12, and 51.74 ± 0.09 Ma for the Henrys Fork, Church Buttes, White Lignitic, and Halfway Draw tuffs, respectively. Multi-crystal sanidine incremental heating experiments gave 100% concordant plateau ages, which are indistinguishable from fusion ages (Smith et al. 2008). Based on the apparent absence of fluvial reworking of sampled tuffs (Table 1) and largely unimodal sanidine age distributions, we interpret their weighted mean ages to represent the best estimate of the age of eruption and deposition of these ash beds. All ages and age differences for both sanidine and biotite are given with 2σ analytical uncertainties relative to 28.34 Ma for the Taylor Creek rhyolite sanidine standard (Renne et al. 1998).

Biotite

Large, millimeter-sized, euhedral biotite crystals were separated following hand crushing, then concentrated using a Frantz magnetic separator, and subjected to a 15 min ultrasonic bath in distilled water to break apart incipient cleavage separations prior to final hand selection for irradiation. All irradiations were performed at the Oregon State University Triga reactor, and were monitored using sanidine from the Taylor Creek rhyolite (TC; cf. Appendix Fig. 1'). Individual crystals and 3-crystal aliquots were incrementally heated in 3–6 steps using a CO$_2$ laser (Fig. 2). Age plateaus are here defined as three or more contiguous, concordant steps containing at least 50% of the total $^{39}\text{Ar}$ released. Steps were considered concordant if the MSWD resulting from their inclusion was less than the Student’s t-distribution limit for the number of included steps (Koppers 2002). When MSWD exceeded 1, analytical errors have been multiplied by the square root of the MSWD. Plateau ages are the weighted mean of included analyses, whereas integrated (total fusion) ages combine the Ar released during all heating steps.

Henrys Fork tuff (HeF). Fourteen of 14 incremental heatings of biotite crystals from the Henrys Fork tuff yield 100% concordant, reproducible age spectra, which yield plateau ages ranging from 47.95 ± 0.44 to 48.66 ± 0.44 Ma (Fig. 2). Integrated ages for these experiments are in all cases indistinguishable from plateau ages (Fig. 3a; Appendix Table 2'). The weighted means of all 14 plateau and integrated ages: 48.31 ± 0.12 (MSWD = 1.07) and 48.32 ± 0.13 Ma (MSWD = 0.86), respectively, are both statistically indistinguishable from the sanidine age of 48.15 ± 0.08 Ma (Fig. 3a; Table 1). The MSWD values suggest that non-analytical sources of uncertainty are minimal. An inverse isochron plot of all Henrys Fork biotite analyses gives an atmospheric $^{40}\text{Ar}/^{39}\text{Ar}$ intercept of 310 ± 26 (Appendix Fig. 2'), indicating negligible presence of excess $^{40}\text{Ar}$.

White Lignitic tuff (WL-1). Eleven of 12 incremental heatings of biotite crystals from the White Lignitic tuff yield 100% concordant age spectra (Fig. 2B). The heating step excluded from the sole discordant experiment represents only 4% of the total $^{39}\text{Ar}$ for this experiment [Figs. 2B(g)]. The plateau comprising the remaining 96% of the $^{39}\text{Ar}$ yields a weighted mean age that is statistically indistinguishable from the sanidine age, but it is nevertheless excluded from the grand weighted mean age. Together, plateau ages from the 11 concordant experiments yield a grand weighted mean age of 47.52 ± 0.14 Ma (MSWD = 1.40) that is indistinguishable from its sanidine age (Fig. 3b; Table 1). Similarly, the weighted mean of all integrated ages for White

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![Map of study area showing the location of sampled tuff beds, Eocene basins, and two possible source areas for tuff beds. Modified from Witkind and Grose (1972) and Love and Christiansen (1985). The Challis Volcanic Field in central Idaho (Snider and Moe 1989), not shown, may have also have contributed ashes to the region. C, H, W, and HD refer to the Church Buttes, Henrys Fork, White Lignitic, and Halfway Draw tuffs, respectively. Houten 1964; Love 1970; Evanoff et al. 1998; Smith et al. 2008). Complete descriptions and detailed stratigraphic context of these tuff beds can be found in Appendix Table 1.1

$^{40}\text{Ar}/^{39}\text{Ar}$ experiments on co-genetic sanidine and biotite

Sanidine $^{40}\text{Ar}/^{39}\text{Ar}$ ages represent a baseline from which to assess the accuracy of biotite ages. Sanidine fusion and incremental heating analyses that exhibit Gaussian apparent age distributions with few outliers yield weighted mean ages of 48.15 ± 0.08, 48.76 ± 0.09, 47.70 ± 0.12, and 51.74 ± 0.09 Ma for the Henrys Fork, Church Buttes, White Lignitic, and Halfway Draw tuffs, respectively.

1 Deposit item AM-08-019, Appendix Tables 1 and 2; Appendix Figures 1–3 (further descriptions and analytical details are provided in the data repository). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
Lignitic tuff/biotite crystals: 47.50 ± 0.14 Ma (MSWD = 0.98) is indistinguishable from its sanidine age (Fig. 3b). Inverse isochron analysis, though imprecise due to limited isotopic spread, yields a near-atmospheric 40Ar/39Ar value of 277 ± 14 that is inconsistent with the presence of excess 40Ar (Appendix Fig. 2).

Church Buttes tuff (ChB). Only 5 of 12 incremental heating experiments on single biotite crystals from the Church Buttes tuff yielded 100% concordant age spectra (Fig. 2C). Plateau ages from these five experiments [Figs. 2C(b, c, g, h, and j)] range from 48.80 ± 0.28 to 49.26 ± 0.36 Ma, and yield a grand weighted mean age of 49.04 ± 0.13 Ma, only 0.28 ± 0.16 Ma older than the sanidine age (Fig. 3c; Table 1). Only one of the remaining 7
experiments produced a plateau [Fig. 2(f)], based on the last 5 of 6 steps, which yields a weighted mean age 4.19 ± 1.30 Ma older than the sanidine age. The remaining 6 experiments [Figs. 2C(a, d, e, i, k, and l)] all gave strongly discordant age spectra. Relative to the sanidine age, most of these spectra are comprised of young initial steps followed by overly old increments, which ramp down toward the sanidine age. Integrated ages for Church Buttes biotite experiments exhibit considerable variance (MSWD = 14 if all experiments are included), with scatter toward older apparent ages (Fig. 3c). This scatter is positively correlated to the degree of internal discordance of individual experiments (Fig. 4d). However, if the 4 oldest integrated ages are excluded (using the MSWD <1.5 criteria outlined above), a weighted mean age of 49.09 ± 0.15 Ma results that is only 0.33 ± 0.18 Ma older than the sanidine age (Fig. 3c).

**Halfway Draw tuff (HD-1).** Due to their smaller grain size (<500 µm) and lower ⁴⁰Ar* content (often <70%), biotite crystals from the Halfway Draw tuff yielded less precise ages than were obtained from millimeter-sized, more-radiogenic (typically >90% ⁴⁰Ar*), biotite crystals separated from the other three analyzed tuff beds (Fig. 2D). Consequently, we conducted incremental heatings on both single crystals and three-crystal aliquots of biotite. Although a violation of stated plateau criteria, two-step plateau ages were calculated in several cases from experiments that only produced three heating steps. Despite the limited age resolution afforded by the small gas volume released from these grains, only 1 of 14 incremental heating experiments on Halfway Draw biotite crystals resulted in a 100% concordant age spectrum [Fig. 2D(b)]. This solitary concordant experiment was also the most radiogenic (97% ⁴⁰Ar*), and yielded a plateau age of 53.21 ± 2.10 Ma that is statistically indistinguishable from the sanidine age (Table 1). All of the remaining non-concordant experiments exhibit age spectra consisting of relatively young apparent ages followed by age steps that exceed the sanidine age.

**Figure 2.** Back-scattered electron images (BSE), wavelength-dispersive spectrometer (WDS) electron-probe microanalysis transects orthogonal to cleavage (A,B)-plane of biotite grains, and ⁴⁰Ar/³⁹Ar age spectra of incremental heating experiments for biotite crystals from the (A) Henrys Fork, (B) White Lignitic, (C) Church Buttes, and (D) Halfway Draw tuff beds. Scale bar for BSE images is 20 × 2 µm. WDS transects proceed from left to right across grains at 2.5 µm spacing. Beam size is 2 µm. O refers to excess O, other values are oxide percentages (see text and Table 2 caption for explanation). When possible, weighted mean plateau ages are indicated for each experiment in the center of each plot. Heating steps excluded from age calculation are unfilled. Integrated (total fusion) ages are indicated at the base of individual age spectra boxes. The 2σ envelope of uncertainty for the weighted mean age of sanidine experiments (Smith et al. 2008) is indicated by black bars between age spectra boxes.
Discordance resulting in MSWD values of 49, 73, and 131 if all steps are included precludes the calculation of plateau ages from three experiments [Figs. 2D(f, k, l)]. For the 10 remaining experiments, plateaus constructed from the final 2 to 4 heating steps yielded weighted mean ages that range from 48.45 ± 2.82 Ma to 59.34 ± 1.70 Ma. The MSWD if all plateau ages are included in a weighted mean is 8.7, mirroring the internal age scatter (Fig. 4). Because this scatter is composed of both older and younger outliers away from a central cluster of ages, the selection of analyses to include in the weighted mean of plateau ages becomes highly subjective. As an example, we selected the largest possible number of plateau ages that can be included in a weighted mean calculation with an MSWD < 1.5 (Fig. 3d). Excluding two younger ages and four older ages, this weighted mean is 55.06 ± 0.86 Ma (MSWD = 1.10), 3.32 ± 0.87 Ma older than the sanidine age (Fig. 3d; Table 1). Integrated ages for Halfway Draw biotite incremental heatings also exhibit considerable variance, with an MSWD of 10.1 if all experiments are included (Fig. 3d). Unlike the plateau ages for these experiments, this scatter is skewed toward younger rather than older apparent ages and does not directly correlate with the internal discordance of individual experiments (Fig. 4d).

If younger outliers are excluded from the weighted mean calculation using a MSWD < 2 criteria, the remaining integrated ages yield a weighted mean age of 51.53 ± 0.44 Ma (MSWD = 1.60) indistinguishable from the sanidine age (Fig. 3d; Table 1).

**Electron Probe Microanalysis of Biotite Phenocrysts**

Biotite crystals from the separates used for ⁴⁰Ar/³⁹Ar dating were analyzed using an electron microprobe to quantify the composition and extent of potential alteration phases and damaged zones that could affect ⁴⁰Ar/³⁹Ar results. Measurements were made with a Cameca SX51 instrument at the University of Wisconsin-Madison operated with an accelerating voltage of 15 kV, beam current of 10 nA, a 2–5 µm defocused beam, and with 10 s peak and 10 s background counting times. F Kα was calibrated with a thallium acid phthalate crystal (TAP) and O Kα was measured with a 60 Å W/Si layered dispersive element (LDE), with O Kα background offset positions ±3000 sin theta units. Major elements in biotite (Si, Al, Mg, Fe, and Ti) were calibrated using a UW-Madison EPMA biotite standard (Wards biotite from Bancroft, Ontario, extensively characterized by UW Probe Lab; composition in Table 2), and natural and synthetic standards were used for the other elements. BaLα was calibrated using a LiF crystal, minimizing interference from TiKα, and cross interferences were corrected within the matrix correction (Donovan et al. 1993). A reconnaissance study performed on one sample indicated that rhabdophane (REE phosphate) might explain some small (micrometer scale or smaller) inclusions.
in some of the more altered biotite crystals; USNM Ce- and La-orthophosphates were therefore used as standards. Nash (1992) showed that quantitative EPMA of O is valuable for estimating OH/H$_2$O in hydrous silicate minerals and glasses. “Excess O” is defined as O above and beyond that accounted for in stoichiometric apportionments: some will be due to Fe$_2$O$_3$ (where the stoichiometric analysis assumes iron as FeO), and some due to OH/H$_2$O in interlayer sites and intergrown alteration phases. Peak interference and background position issues (e.g., Fe L$_1$, Si K$_\alpha$, Al K$_\alpha$ and K$_\beta$) were minimized by the LDE’s inherent suppression of most $\alpha > 1$ X-rays and differential mode pulse-height settings. Problems with peak shifts and mass absorption coefficients were eliminated by the use of a biotite standard. Optimally, the standard and unknown should be carbon coated simultaneously to minimize analytical discrepancies between the two for absorption of low energy X-rays (e.g., O and F) and incident beam retardation (Armstrong 1993); however, in this case they were coated separately, and interference colors on a polished brass plug were used to calibrate a 200 Å thickness of carbon. Errors due to carbon coat differences are estimated using the GMRFilm computer program (Waldo 1988). For a worst-case difference of 50 Å between standard and unknown, the error in O K$_\alpha$-ratio (unknown X-ray intensity divided by standard X-ray intensity) would be 1.6%, F 0.65%, and other major elements 0.2–0.4%. Because the standard and unknowns are similar materials, there is no significant difference between the matrix correction factors, and thus the relative error in O wt% content is also 1.6%. For comparative purposes, even if the error in the O measurement is assumed to be 2% or even double that, the analytical uncertainty in O is adequate to differentiate the observed differences between analyses. Overall, EPMA totals were considered a test of the degree of alteration that the various biotite populations had suffered. In evaluating the level of confidence to place in the final composition, the analytical total for a grossly unaltered biotite crystal should be 98.5–100.5 wt% (there could be 0.5 wt% unmeasured elements, e.g., Li, Cs, etc., with the “excess O” being around 2–3 wt%). Deviations from such totals indicate the probability that alteration phases are present.

Table 2 presents a summary of 272 EPMA analyses of biotite crystals. Compositional data are presented alongside $^{39}$Ar/$^{40}$Ar age spectra in Figure 2 to facilitate comparisons between them. With explicitly measured O, many of the biotite crystals show no gross sign of chemical alteration (i.e., low totals and heterogeneous K composition), whereas others do, especially in “lowest K$_2$O” analyses, likely due to K removal and hydration. The low totals of “lowest K$_2$O”

![Figure 2](https://example.com/figure2.jpg)
Exposure to surface waters (Banfield and Eggleton 1988; Acker and Bricker 1992; and volcanic biotite crystals, and can proceed rapidly at low temperatures upon decrease FeO (Banfield and Eggleton 1988; Fordham 1990). 

\[ (\text{Na,Ca})(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \]

inconsistent with the addition of either kaolinite (Al\(_2\)O\(_3\)\(\cdot\)2H\(_2\)O) or related phases, but are pervasive in nearly all Halfway Draw biotite crystals, which have K\(_2\)O consistently less than 8 wt\%. Major-element correlation diagrams show that K-depletion in both Church Buttes and Halfway Draw biotite crystals correlates with a slight decrease in Al\(_2\)O\(_3\), enrichment of excess CaO, and virtually no change in FeO (Fig. 5). These changes are most consistent with partial alteration to vermiculite \[(\text{Mg,Fe,Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \] or related phases, but inconsistent with the addition of either kaolinite \[(\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \] or montmorillonite \[(\text{Na,Ca})(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \] because replacement by these phases would decrease FeO (Banfield and Eggleton 1988; Fordham 1990).

Vermiculitization commonly occurs during the weathering of both plutonic and volcanic biotite crystals, and can proceed rapidly at low temperatures upon exposure to surface waters (Banfield and Eggleton 1988; Acker and Bricker 1992; Nanzo et al. 1999). Conversion of biotite to vermiculite proceeds along cleavage planes, and typically initiates with the removal of K from interlayer sites, followed by oxidation of Fe\(^{3+}\) in adjoining octahedral sites to Fe\(^{2+}\), and introduction of H\(_2\)O into interlayer sites (Banfield and Eggleton 1988; Pozzuoli et al. 1992). Transmission electron microscopy (TEM) studies of vermiculite and kaolinite in biotite indicate that these minerals are commonly intergrown with unaltered biotite at a much finer scale (often <0.01 pm) than is possible to observe with an electron microscope (Banfield and Eggleton 1988; Dong et al. 1995; Lo et al. 2000). Thus, if a simple linear mixing relationship is assumed, the observed 5 \(\mu\)m wide cleavage-parallel zones of lowest K\(_2\)O (4.5%) within Church Buttes biotite crystals \[e.g., \text{Fig. 2C(1)}\] are likely composed of a finely intercalated mixture of unaltered biotite having 8.1% K\(_2\)O with 45% vermiculite containing <0.5% K\(_2\)O, rather than one homogeneous phase. In addition to vermiculite, biotite crystals from the Halfway Draw tuff also exhibit spotty <10 \(\mu\)m diameter K-depleted areas (4.2 vs. 6.8% K\(_2\)O) that are enriched in P, Ce, and La, indicative of the presence of up to ~40% fine rhabdophane \[(\text{Ce,La})_3\text{PO}_4\cdot\text{H}_2\text{O} \] in the analyzed area \[\text{Fig. 2D(3); Table 2}\]. Rhabdophane is known to result from the weathering of apatite inclusions in biotite (Banfield and Eggleton 1989). Zones of rhabdophane are discontinuous in both cross section and plan view \[\text{Fig. 2D(2) and 2D1, and Appendix Fig. 3B(b)}\], suggesting that it may have replaced randomly distributed ~5 \(\mu\)m long apatite inclusions within biotite crystals. Larger (>5 \(\mu\)m) inclusions of apatite, zircon, and

**Figure 2.**—Continued. Halfway Draw tuff

**Cumulative \(^{39}\)Ar Released**
monazite occur in biotite from all samples, but are most prevalent in the Halfway Draw biotite crystals (Appendix Fig. 3).

**Summary: ⁴⁰Ar/³⁹Ar Ages and Electron Microprobe Analyses**

In situ chemical analyses and laser incremental heating ⁴⁰Ar/³⁹Ar experiments on biotite crystals correlate the presence and spatial distribution of K-depleted alteration phases with discordant ⁴⁰Ar/³⁹Ar age spectra and scatter of integrated ages. Biotite crystals from the Henrys Fork and White Lignitic tuffs are almost entirely free of alteration phases and yield concordant age spectra that give plateau ages consistent with the sanidine ages for these beds (Figs. 2A and 2B). On the other hand, biotite crystals from the Church Buttes tuff exhibit variable degrees of alteration, ranging from largely unaltered crystals to crystals with significant vermiculitization (Fig. 2C). Significantly, incremental heatings of these grains produce both concordant and discordant age spectra. The most discordant of these age spectra also yield the most inaccurate integrated ages, which in this case are skewed toward older apparent ages (Fig. 4c). Biotite from the Halfway Draw tuff are, as a whole, the most consistently and pervasively altered, with virtually all observed grains exhibiting less than 8% K₂O (Fig. 2D; Table 2). Age spectra from these grains are more significantly and consistently discordant than the spectra of biotite crystals from all other studied ashes (Fig. 2D).

**Discussion**

Sources of discordance and inaccuracy

Several phenomena have been suggested as the cause of discordance and inaccuracy in ⁴⁰Ar/³⁹Ar data, including (1) ⁴⁰Ar* loss due to alteration or metamorphism; (2) K loss due to alteration; (3) excess ⁴⁰Ar; (4) inheritance, both xenocrystic and detrital; (5) recoil of ³⁹Ar from entirely out of crystals; and (6) internal redistribution via recoil of ³⁹ArK from K-rich areas into K-poor areas. The generalized effects of these phenomena on age spectra and integrated age distributions are summarized in Table 3. Due to the apparent similarities in detectable morphology of these processes and the possibility of several overlapping phenomena in a single sample, incremental heating experiments alone are unable to adequately differentiate among the cause(s) of discordance and inaccuracy in biotite ages. However, via comparison of electron-microprobe data, biotite ⁴⁰Ar/³⁹Ar incremental heating results, and cogenetic sanidine ⁴⁰Ar/³⁹Ar ages, ⁴⁰Ar* loss and ³⁹ArK recoil are isolated to be the most likely causes. We propose a mechanism that ties both of these phenomena to an ultimate cause: the partial alteration of biotite to interstratified K-depleted phases.

Several lines of evidence argue against excess ⁴⁰Ar or K loss as major sources of discordance and inaccuracy in the analyzed biotite crystals. Previous incremental heating studies indicate that excess initial ⁴⁰Ar causes downstepping age spectra due to early outgassing of sites with more excess ⁴⁰Ar (Foland 1983). Similarly, samples having experienced K loss in greater proportion than ⁴⁰Ar* loss can also yield downstepping age spectra because altered areas degas first during step heating (Table 3; Cerling et al. 1985; Sharp et al. 1996). Both phenomena can lead to integrated age scatter toward older apparent ages. Excess ⁴⁰Ar is most commonly observed in metamorphic rocks (Foland 1983;
Baxter et al. 2002), whereas K loss has only been documented in volcanic glasses (Cerling et al. 1985; Sharp et al. 1996). Although most discordant age spectra from Church Buttes tuff and Halfway Draw tuff biotite crystals have segments of downstepping apparent ages (Figs. 2C and 2D), all exhibit underestimated initial heating steps and yield atmospheric $^{36}$Ar/$^{40}$Ar intercepts (Appendix Fig. 2), both of which are inconsistent with either excess $^{40}$Ar or K loss. Renne (1995) interpreted “hump-shaped” age spectra similar to those obtained in this study to indicate the presence of high-temperature excess $^{40}$Ar within plutonic biotite crystals that were overprinted by low-temperature $^{40}$Ar* loss. However, in light of the correlation of interstratified K-poor phases with discordance observed in this study, we propose that in ash-fall deposits such spectra are more indicative of the recoil of $^{39}$Ar within a K-heterogeneous mineral (Turner and Cadogan 1974; Onstott et al. 1995).

**Discordant age spectra and $^{39}$Ar$_K$ recoil**

The reaction of reactor-produced fast neutrons (1.5–9 MeV) with $^{39}$K atoms required to produce $^{39}$Ar$_K$ for $^{40}$Ar/$^{39}$Ar analysis can cause $^{39}$Ar$_K$ atoms to be displaced a short distance (~0.08 µm) from the original lattice position of target $^{39}$K atoms (Turner and Cadogan 1974; Onstott et al. 1995; Villa 1997). This undesirable side effect of the $^{39}$K(n,p)$^{39}$Ar reaction is of serious geochronologic concern if the mineral being dated is either fine-grained or heterogeneous enough for recoiled $^{39}$Ar$_K$ to escape its lattice or be displaced into regions of lower K content. Recoil of $^{39}$Ar$_K$ causes discordant age spectra in grains possessing submicrometer-scale K heterogeneity, such as exsolved K-feldspars with albite lamellae, clays, and biotite crystals with intergrown alteration phases, because $^{39}$Ar$_K$ recoiled from the edges of K-rich areas is implanted into adjacent K-poor areas (Hess et al. 1987; Lo and Onstott 1989; Odin et al. 1991; Dong et al. 1995; Onstott et al. 1995; Min et al. 2001). TEM studies of weathered biotite crystals (Banfield and Eggleton 1988; Dong et al. 1995) indicate that K-poor interlayered vermiculite akin to that detected in both Church Buttes and Halfway Draw biotite crystals typically occurs at the scale of individual octahedral silicate sheets (~10 Å), well below the effective $^{39}$Ar$_K$ recoil grain-size threshold (Dong et al. 1995; Lin et al. 1999). In such composite grains, $^{39}$Ar$_K$ becomes homogenized throughout the grain, whereas radiogenic $^{40}$Ar* remains heterogeneously distributed according to the primary K

**TABLE 3. Potential sources of discordance and inaccuracy in biotite $^{40}$Ar/$^{39}$Ar ages**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Effect on Generalized age spectra</th>
<th>Integrated age scatter</th>
<th>$^{40}$Ar/$^{39}$Ar intercept</th>
</tr>
</thead>
</table>
| $^{39}$Ar$_K$ recoil | Older ages?                     | =295.5?                | Use integrated age (Dong et al. 1995),
|                    |                                 |                        | Use only 100% concordant plateau age (Min et al. 2001) |
| $^{40}$Ar* loss    | Younger ages                    | <295.5                 | Exclude younger initial steps |
| K loss             | Older ages                      | >295.5                 | Exclude older initial steps |
| Excess $^{40}$Ar   | Older ages?                     | >295.5                 | Use inverse isochron age (Singer and Pringle 1996) |
| Inheritance        | Older ages                      | =295.5                 | Exclude older outliers (Deino and Potts 1990) |

Notes: For generalized age spectra diagrams: gray bars indicate incremental heating steps, with up indicating older apparent ages; black line indicates “true” age.

**Figure 4.** Cumulative distribution function showing offset of plateau and integrated ages relative to sanidine age (indicated by dashed line). Ages are plotted relative to their MSWD if all heating steps are included.
distribution (Turner and Cadogan 1974; Hess et al. 1987; Onstott et al. 1995). Age spectra of $^{39}$Ar$_e$ recoil-affected crystals [e.g., Fig. 2C(i)] typically begin with underestimated apparent ages, which reflect loss of $^{39}$Ar$_e$ from unaltered biotite into K-depleted phases, in this case interstratified vermiculite or rhabdophane. Young initial steps are followed by heating steps of overestimated apparent age, which reflect the degassing of zones of unaltered biotite peripheral to K-poor areas that have lost $^{39}$Ar$_e$ into these phases during irradiation. If thick enough zones of fresh biotite still exist within the grain, such as is likely the case with many Church Buttes tuff biotite crystals (Fig. 2C), successive heating increments stair-step down toward younger more accurate apparent ages as less affected interior domains are progressively outgassed. However, if alteration phases are pervasive throughout the grain, as is likely the case with many Halfway Draw tuff biotite crystals (Fig. 2D), even the final heating steps may yield overestimated apparent ages.

**Figure 5.** Major-element correlation diagrams showing compositional variations of Al$_2$O$_3$, excess O, CaO, and FeO relative to K$_2$O content. Error bars indicate 2σ analytical uncertainty of individual measurements. Excess O likely represents conversion of Fe$^{2+}$ to Fe$^{3+}$ but also may reflect the addition of H$_2$O.

**Integrated age scatter: $^{39}$Ar$_e$ recoil**

Inheritance, either detrital or xenocrystic, is often invoked by geochronologists to explain scatter toward older integrated ages (e.g., Deino and Potts 1990; Smith et al. 2003; Machlus et al. 2004). Inherited grains by definition record an age that is older than the eruption age of the ash beds they contaminate, but are not necessarily expected to yield disturbed age spectra (Table 3). However, the oldest integrated ages for Church Buttes tuff biotite are derived from grains that also yield the greatest age spectra discordance (Fig. 4). We suggest therefore that loss of $^{39}$Ar$_e$ out of these grains due to recoil during irradiation (Turner and Cadogan 1974; Onstott et al. 1995; Paine et al. 2004) is the most likely cause of their overestimated ages, rather than contamination by inherited grains. Modeling and experimental studies indicate that age offset resulting from escape of recoiled $^{39}$Ar$_e$ should be negligible for grains larger than ~1 µm (Dong et al. 1995; Onstott et al. 1995; Lin et al. 1999), though Paine...
poor alteration phases. Given the smaller grain size and greater loss and age spectra discordance caused by internal alteration has been shown to reduce K-Ar (Clauer et al. 1982; Odin Min et al. 2001). Accordingly, the weighted mean of integrated ages from crystals containing interlayered K-poor phases should theoretically recombine the absolute quantity of $^{39}$Ar recoiled out of Church Buttes tuff biotite grains, we emphasize the importance of the discordance itself as a predictor of inaccuracy.

**Integrated age scatter: $^{40}$Ar* loss**

Integrated ages from crystals containing interlayered K-poor phases should theoretically recombine the $^{39}$Ar atoms that were recoiled from the edges of unaltered biotite domains into low-K domains within the same grain, and thus be more accurate than plateau ages if no net loss of $^{39}$Ar has occurred (Dong et al. 1995; Min et al. 2001). Accordingly, the weighted mean of integrated ages from Halfway Draw tuff biotite crystals is indistinguishable from its sanidine age, but only if several younger analyses are excluded (Fig. 3d). Because no evidence for thermal resetting was observed in sanidine age spectra (cf. Smith et al. 2008), the most likely explanation for such younger outliers is post-depositional $^{40}$Ar* loss caused by diagenesis and/or weathering. Such alteration has been shown to reduce K-Ar (Clauer et al. 1982; Odin et al. 1991) and $^{40}$Ar/$^{39}$Ar total fusion apparent ages (Hilgen et al. 1997) for weathered biotite, presumably because a relatively higher proportion of radiogenic $^{40}$Ar* daughter than $^{40}$K parent is liberated during phase changes. The hypothesis of $^{40}$Ar* loss in Halfway Draw tuff biotite crystals is supported by our observation of pervasive intergrown alteration phases (Fig. 2A, Table 2) and a bulk biotite K-Ar age by Evernden et al. (1964) that is 1 Ma younger than its sanidine age. The coincidence of $^{40}$Ar* loss and age spectra discordance caused by internal $^{39}$Ar recoil is unsurprising because both can be related to interstratified, K-poor alteration phases. Given the smaller grain size and greater degree of alteration in Halfway Draw tuff biotite crystals, it seems unlikely that $^{39}$Ar recoil loss occurred in the Church Buttes tuff biotite crystals but not in those from the Halfway Draw tuff. The seemingly accurate integrated ages for Halfway Draw tuff biotite crystals may thus be only a coincidence of $^{40}$Ar* loss and $^{39}$Ar recoil canceling out one another, an effect that could be further explored via encapsulation experiments. Conversely, it also seems improbable that Church Buttes tuff biotite crystals entirely avoided $^{40}$Ar* loss during their partial conversion to vermiculite, unless this alteration occurred soon after the time of deposition. It is equally plausible, however, that Church Butte integrated ages reflect various competing open-system phenomena.

**CONCLUDING REMARKS**

There are significant but predictable differences in the reliability of $^{40}$Ar/$^{39}$Ar ages obtained from biotite phenocrysts in distal ash-all deposits. $^{40}$Ar/$^{39}$Ar step heating experiments conducted for this study have isolated three distinct modes of discordance and inaccuracy in biotite ages relative to sanidine ages. These include (1) discordant spectra, typically consisting of underestimated initial age steps followed by heating steps, which yield overestimated plateau ages; (2) scatter of integrated ages toward overestimated apparent ages; and (3) scatter of integrated ages toward underestimated apparent ages. We attribute these effects to the alteration of biotite crystals and subsequent recoil of $^{39}$Ar from altered zones during irradiation and conclude that the reliability of a biotite age is best predicted by two key indicators: the concordance of the age spectra, and the homogeneity of the K-O distribution. Biotite crystals that exhibit homogeneous K contents (>8% K2O) and give concordant age spectra yield $^{40}$Ar/$^{39}$Ar ages entirely suitable for use in high-resolution chronostratigraphy. This is the case for biotite crystals from the Henrys Fork and White Lignitic tuff beds, which yield plateau and integrated ages that are indistinguishable from the ages for co-genetic sanidine. In contrast, biotite crystals that are compromised by intergrown K-depleted phases such as vermiculite or rhabdophane exhibit discordant age spectra that yield inaccurate $^{40}$Ar/$^{39}$Ar. For example, if the weighted mean of Halfway Draw tuff plateau ages (55.06 ± 0.85 Ma) is taken at face value, the age of the base of the Lostcabinian “land mammal subage” becomes 2.5 Ma older than presently understood (~52.6 Ma, Wing et al. 1991; Smith et al. 2004), making it nearly coincident with the Paleocene-Eocene transition and stratigraphically inconsistent. For ashes with biotite crystals exhibiting variable alteration from grain to grain, such as the Church Buttes tuff, we suggest that only 100% concordant spectra should be used in age calculations.

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