# $^{40}$Ar/$^{39}$Ar Age Spectrum Dating of Biotite from Middle Ordovician Bentonites Eastern North America

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Middle Ordovician bentonites in sedimentary sequences of eastern North America are potentially useful time markers. Previous attemts to determine their radiometric age have yielded discordant results for various reasons. Biotites from thermally undisturbed bentonites from the interval of North American Midcontinent Conodont Faunas 7 and 8, corresponding to an age of Blackriveran to early Kirkfieldian, have been analyzed by $^{40}$Ar/$^{39}$Ar age spectrum techniques. Plateau ages of biotites from bentonites in the Stones River Formation (as used by Drahovzal & Neathery in 1971) in Alabama and the Carters Limestone of central Tennessee range from 453 to 456 Ma, providing a mean age for the above-mentioned biostratigraphic interval of about 454 Ma. Additional $^{40}$Ar/$^{39}$Ar dates from the Stones River Formation in Alabama, the Hermitage Formation of central Tennessee, and the Lexington and Tyrone Limestones of central and northern Kentucky, although analytically less reliable, provide a mean age of about 455 Ma. The age spectrum data show a direct correlation between apparent K/Ca ratio and apparent age as a function of argon extraction temperature. Biotites that have individual temperature steps with apparent K/Ca ratios above about 50 tend to define age plateaus, whereas temperature steps with apparent K/Ca ratios below about 50 tend to yield discordant ages. Comparison of plateau ages with their corresponding total gas ages suggest that conventional K/Ar dating of these biotites would generally yield only minimum age estimates for these bentonites.

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## Introduction

The primary obstacle to the production of a detailed radiometric time scale for the Ordovician and, in fact, the whole of the Palaeozoic, has been the lack of suitable datable material. Ideal materials (Fitch *et al.*, 1977) include datable sediments, lavas, tuffs, and bentonites interbedded with fossiliferous strata. Of these ideal materials, bentonites have a widespread occurrence in Middle Ordovician rocks in eastern North America.

Since the late 1950's, several attempts, using various techniques, have been made to date these bentonites isotopically. Faul & Thomas (1959) and Faul (1960) reported an average, conventional K-Ar age of 419 ± 5 Ma (old constants) for biotite from a bentonite near the top of the Stones River Formation (of Drahovzal & Neathery, 1971) of Alabama. Additionally, Faul (1960) reported Rb-Sr ages of bentonitic biotites from the Carters and Eggleston Limestones of Tennessee that range from 437 ± 50 to 466 ± 50 Ma (old constants). Edwards *et al.* (1959) and Adams *et al.* (1960) reported U/Pb ages ranging from 438 ± 10 to 453 ± 10 Ma (old constants) for bentonitic zircons from the Carters Limestone and Bays Formation of Tennessee. Ghosh (1972) reported conventional K/Ar ages for bentonitic biotites and a sanidine, from the Carters Limestone (equivalent to the upper part of the Stones River Formation), and from the Little Oak Limestone in Alabama that range from 424 to 453 Ma (old constants, no analytical errors given). Ross *et al.* (1981) have reported fission track ages for 3 zircon samples from bentonite beds in the Tyrone Limestone of Kentucky of 447 ± 15, 462 ± 15, and 438 ± 15 Ma. Additionally, Ross *et al.* (1981, 1982) reported

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zircon fission track ages of 454 ± 12, 456 ± 12, and 450 ± 10 Ma for bentonites from the Carters Limestone of Tennessee and the Decorah Formation and the Plattin Limestone of eastern Missouri, respectively.

The stratigraphic position from which the samples of the above mentioned analysis were collected has been limited to a narrow biostratigraphic interval by Fetzer (1973) on the basis of his own work as well as conodont and bentonite data in the literature. This interval ranges from North American Midcontinent conodont Fauna 7 to 8. On this basis it is obvious that all of the above mentioned analyses cannot be correct, even with corrections for new decay constants (Steiger & Jäger 1977), which would result in a maximum variation of any quoted age of less than 2%.

Isotopic ages from other portions of the Ordovician in North America are rather few and do not have adequate biostratigraphic and/or geologic control to allow for their use as points on a geological time scale. At best they can be used as age maxima or minima. A good example of these is the data given by Dallmeyer & Williams (1975) average $^{40}Ar/^{39}Ar$ incremental release age of 460 ± 5 Ma for the Bay of Islands ophiolite metamorphic aureole in Newfoundland, Canada. The biostratigraphic age of the emplacement of this complex has only been confined to the interval of the late Arenig to late Llandeilo due to complex structural relationships. This level of biostratigraphic control is inappropriate for constructing a geologic time scale. In addition, the age is a cooling age of hornblendes in the metamorphic aureole and, thus must be viewed only as a minimum age.

The age of the Ordovician-Silurian boundary, however, has been defined by $^{40}Ar/^{39}Ar$ total fusion ages of two hornblende samples from sedimentary breccias in the Lower Silurian *Monograptus cyphus* Zone of Esquibel Island, Alaska (Lanphere *et al.*, 1977). Although these samples are from the Lower Silurian, Lanphere *et al.* (1977) were able to suggest an age estimate for the boundary of 433–435 Ma, on the basis of their data and of a sedimentation model.

A variety of methods have been used in efforts to isotopically date Middle Ordovician bentonites. Unfortunately, as shown above, the various isotopic techniques have, in general, produced disordant results. While a complete discussion of the causes for this discordancy is beyond the scope of the present paper, a few brief comments on some basic assumptions used in most isotopic dating techniques would be of use to the reader in evaluating existing and future data.

Most of the isotopic dating techniques in use today rely on the decay of a radioactive parent nuclide to produce a stable daughter nuclide. For these dating techniques to reflect the age of the material being dated, several assumptions must be fulfilled:

1) The decay constants of the parent nuclide must be accurately known.
2) It must be possible to meansure, precisely, the isotopic composition and/or concentration of both the daughter and parent nuclides.
3) The sample being dated must have neither gained nor lost (except by radioactive decay) any parent nuclides since its formation.
4) The sample must have neither gained nor lost (except by decay of the parent nuclide) any stable daughter nuclides since its formation.

The decay constants (assumption 1) in use today for most isotopic dating techniques are those recommended by the Subcommission on Geochronology (Steiger & Jäger 1977). These constants are known to a precision of 1–2% and are internally consistent (Jäger & Hunziker 1979). The only commonly used isotopic dating technique for which various decay constants are used is the Fission Track method (Jäger & Hunziker 1979).

The ability to measure precisely the isotopic composition of both daughter and parent nuclides (assumption 2) has improved markedly in the past twenty years. In most techniques, it is now possible to measure isotopic compositions to a precision of 0.1% or less ($1\sigma$) and concentrations to a precision of about 1% or less. The only commonly used technique in which the analytical precision is worse than this, is the Fission Track dating method. The concentrations of daughter and parent nuclides are not measured directly in this method. Due to the method of measurement and also due to the inhomogeneous distribution of uranium in some minerals, the analytical precision of this technique cannot be better than about 3–4% (for a detailed explanation of Fission Track systematics, procedures, and statistics the reader is directed to Naeser 1976, and Johnson *et al.* 1979). While this level of analytical precision is inappropriate for use in the construction of a time scale, Fission Track data can be useful as corroborating evidence for samples dated by other techniques.

The closure (assumptions 3 and 4) of the isotopic system with respect to both daughter and parent nuclides is the most common problem encountered when trying to determine the age of a rock or mineral sample. Most, if not all, isotopic systems of Palaeozoic age have been open, to one degree or another, for some period of time since their formation. In the conventional K-Ar, Rb-Sr and Fission Track (track annealing in sphene and zircon) techniques there is no direct way of measuring the degree of system closure but the interpretation of the results is, at present, difficult to make for discordant data. The $^{40}Ar/^{39}Ar$ age spectrum technique, however does allow for the measure of system closure and, in many cases, if the disturbance has not been too severe, it is possible to accurately date disturbed systems. For a detailed explanation of the $^{40}Ar/^{39}Ar$ age spectrumtechnique, the reader is referred to Dalrymple & Lanphere (1971, 1974) and Dalrymple *et al.* (1981).

It is our conclusion from this brief examination of these basic assumptions that, currently, the most useful isotopic technique for high precision time scale studies in the Paleozoic is the $^{40}Ar/^{39}Ar$ age spectrum technique. It is important, however, that $^{40}Ar/^{39}Ar$ age spectrum results be confirmed by means of other isotopic dating techniques to ensure geological accuracy.

In the present study, the $^{40}Ar/^{39}Ar$ age spectrum technique has been employed to date biotites from Middle Ordovician bentonites of eastern North America. The samples analyzed were interbedded with fossiliferous carbonates located in the Middle Ordovician of Alabama, Tennessee, and Kentucky (Fig. 1) and are believed to represent the interval of North American Midcontinent Conodont Faunas 7 and 8 (Fetzer 1973). This interval corresponds to an age of Blackriveran to early Kirkfieldian (Sweet & Bergström 1976). Conodont Alteration Index values from conodonts in the associated carbonates range from $< 1.5$ to $< 3.0$ indicating paleotemperature maximums of $< 90°$ to $<200°C$ (Epstein *et al.* 1977). These temperatures are well below the argon closure temperature of biotite ($> 250°C$, Harrison & McDougall 1981). It is our opinion that this biostratigraphic interval (Faunas 7 to 8) is probably less than 2–3 million years in duration and, in terms of the resolution of isotopic dating techniques, can be considered a "Horizon".

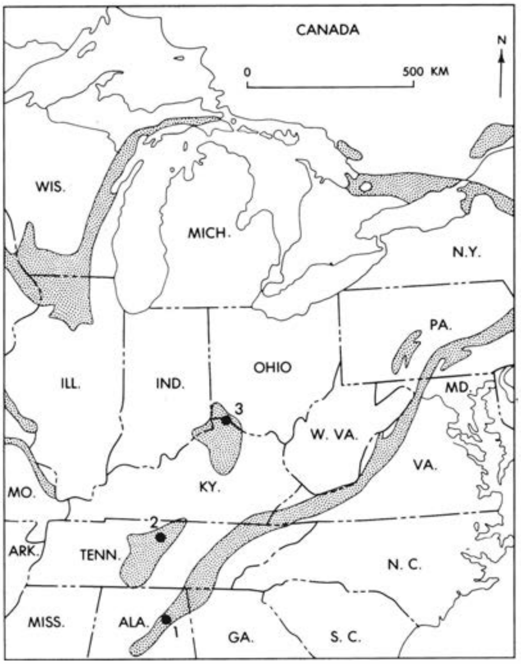

*Figure 1 – Middle Ordovician outcrops in eastern North America. Sample sites are indicated by numbered black dots. Samples 31D and 30B are from Location No. 1, 40 and 29 are from Location No. 2 and 1A, CM-10 and 5A are from location No. 3 (modified from Fetzer, 1973).*

## Analytical Techniques

All samples were processed using standard magnetic separator, heavy liquid, and paper shaking techniques to produce biotite separates of > 99% purity. The samples were then irradiated in the central thimble facility of the U.S. Geological Survey TRIGA reactor (Dalrymple *et al.* 1981) along with aliguants of monitor mineral MMhb-1. The geometry of the irradiation was arranged to ensure that all of the samples and monitors received the same neutron fluence. The purpose of this geometrical arrangement was to provide a constant J value so that the analytical results could be more critically compared. The samples were then analyzed and their $^{40}Ar/^{39}Ar$ ages calculated using:

$$t_u = \frac{1}{\lambda} \ln \left[ \left( {}^{40}Ar_R / {}^{39}Ar_K \right) J + 1 \right]$$

$$J = \frac{e^{\lambda t_m} - 1}{\left( {}^{40}Ar_R / {}^{39}Ar_K \right)_m}$$

where, $^{40}Ar_R$ = Radiogenic $^{40}Ar$

$^{39}Ar_K$ = Potassium derived $^{39}Ar$

$\lambda$ = Total decay constant for $^{40}K$ = $5.543 \times 10^{-10}$/yr

and, $t$ = Age of unknown Sample (u) and Monitor (m)

$t_m$ for MMhb-1 was taken to be 519.4 Ma (Dalrymple *et al.* 1981). This monitor mineral has been described in detail by Alexander *et al.* (1978).

The analytical precision reported for the individual temperature step analyses in this study is based on the estimated error in the $^{40}Ar_R/^{39}Ar_K$ ratio. As J was a constant for all samples analyzed in this study, this (the $^{40}Ar_R/^{39}Ar_K$ ratio) is the only possible source of analytical error for internal comparisons. Errors reported in Table 1 are at the 67% confidence level ($\sim 1\sigma$) but have been compared using the Critical Value Test reported by Dalrymple & Lanphere (1969: 120) at the 95% confidence level ($\sim 2\sigma$).

During preliminary analyses, it was noted that the biotites discussed in this study contained small, but significant, amounts of $^{37}Ar$. $^{37}Ar$ is produced during neutron irradiation by the reaction $^{40}Ca\ (n, \alpha)^{37}$ and, in addition to its use as a correction factor in calcium bearing samples, can be used, together with $^{39}Ar_K$, in the study of K/Ca ratios (for example, Harrison & McDougall 1981). In this study, a direct relationship between apparent K/Ca and apparent age as a function of argon release temperature was noted and it was possible to define for these specific samples a critical value for this ratio of $\sim 50$. Those having temperature steps with apparent K/Ca > 50 tended to form plateau age spectra as defined by Fleck *et al.* (1977). Samples with apparent K/Ca < 50, however, tended to yield spurious age results. The cause for this variance has not yet been determined. It may, however, be due to small amounts of inseparable, intimately intergrown chlorite or some other alteration product of the biotites.

The relationship of apparent K/Ca versus apparent age permitted the formulation of criteria for evaluation of the data reported in this study:

1) Is the age spectrum concordant or discordant?
2) If the age spectrum is discordant, does it define an age plateau (Fleck *et al.* 1977)?
3) If an age plateau is defined, are the apparent K/Ca ratios of at least two temperature steps above the critical value of 50?
4) If at least two temperature steps on the plateau have apparent K/Ca ratios above 50, do they together represent more than 50% of the total $^{39}Ar_K$ in the sample?

In all samples analyzed, the age spectra are discordant and, thus, fail criterion 1. The reader should note at this point that the failure of *all* samples analyzed to pass criterion 1 means that it is very likely all conventional K-Ar ages for these materials are spurious and of questionable value. Some samples, however, meet criteria 2–4, and, in our opinion have a high probability of being accurate indicators of geologic age. These samples will be discussed in the remainder of this report.

In a few cases, we were not able to separate enough biotite from our bentonite samples for a 7–9 step age spectrum experiment. In these cases, a 3–4 step age spectrum (3–4 step fusion) experiment was conducted. As it was not possible to apply all of the above criteria to these experiments, their reliability is somewhat lower than that of the more detailed experiments. In addition, 3–4 steps fusion experiments were conducted for all samples analyzed by the more detailed age spectrum experiments as a test of analytical reproducibility.

## Results

### I–59 Roadcut, Gadsden, Alabama

The roadcut is located on U.S. Interstate Highway 59, 19.3 km north of Gadsden, Alabama, and west of the trace of the Helena thrust fault. Six bentonites are present here in the upper Stones River Formation of Drahovzal and Neathery (1971) (Fig. 2) and two of them yielded biotite both of which meet $^{40}Ar/^{39}Ar$ age spectrum criteria 2–4. The biostratigraphic assignment of this bentonite complex, although somewhat uncertain due to poor conodont preservation, is believed to represent the interval of Fauna 7 and 8 (Fetzer 1973) of Blackriveran to Kirkfieldian age (Sweet & Bergström 1976, Ross *et al.* 1982). Sample 31D yields a plateau age of 454 ± 1.9 Ma (Fig. 3, Table 1) and a preferred 4-step fusion age (Table 1) of 454.2 ± 3.0 Ma. Sample 30B (Fig. 3, Table 1) yields a plateau age of 455.8 ± 1.4 Ma and a preferred 3-step fusion age (Table 1) of 453.3 ± 3.0 Ma. As all of these ages agree within the limits of analytical uncertainty and, because the age spectra passed criteria 2–4 these results are considered to be of the highest quality (Class I).

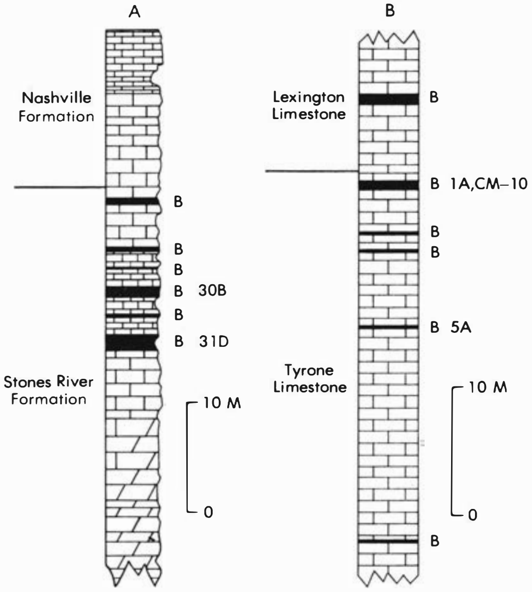

*Figure 2 – Partial columnar section of (A) I–59 roadcut near Gadsden, Alabama, includes portions of the Stones River and Nashville Formations of Drehovzal & Neathery, 1971, and (B) outcrop in mine at Carntown, Kentucky. B = bentonite horizon.*

### Carthage, Tennessee

The outcrop sampled is located in a new roadcut on Tennessee State Route 53, 4.4 km south of Cartage, Tennessee. One sample (our no. 40) from a 41 cm thick bentonite was collected and donated to the authors by A. Soderberg of the Tennessee Valley Authority. The bentonite is located, stratigraphically, 7.6 m below the contact of the Middle Ordovician Carters and Hermitage Limestones at the contact of the upper and lower members of the Carters Limestone and its equivalent to T-3 of Wilson (1949). The Carters Limestone, at this locality, contains late representatives of conodont Fauna 7 and early representatives of Fauna 8 (Fetzer 1973); they are probably of late Blackriveran to Rocklandian age (Sweet & Bergström 1976, Ross *et al.* 1982).

Sample 40 (Fig. 3, Table 1) yields a plateau age of 452.8 ± 0.5 Ma and a preferred 3-step fusion age (Table 1) of 454.2 ± 3.0 Ma. For the same reasons as described for the data from Gadsden, these data are also considered to be of highest quality (Class I).

### Watertown, Tennessee

The bentonite locality sampled (our sample no. 29) is on the farm of J. Fite near Watertown, Tennessee. Due to the poor outcrop at this locality, it was impossible to determine the precise stratigraphic position. However, this shaley bentonite is in the lower portion of the laminated argillaceous member of the Hermitage Limestone and has been identified as Wilson's (1949) T-5 by R. A. Miller of the Tennessee Division of Geology. Though slightly higher stratigraphically, the biostratigraphic assignment of sample 29 is the same as that of sample 40; late Conodont Fauna 7 to early Fauna 8 (Fetzer 1973) of late Blackriveran to Rocklandian

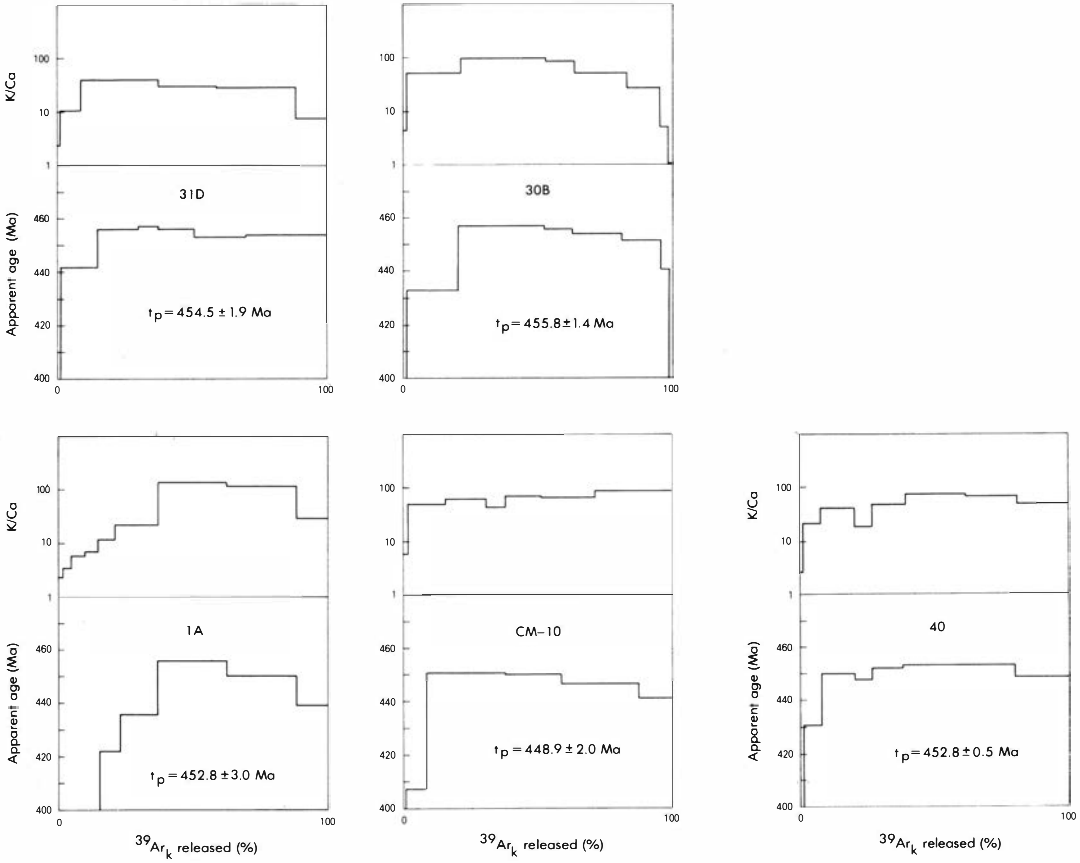

*Figure 3 – Age spectra and K/Ca plots for biotites from Middle Ordovician bentonites of eastern North America.*

age (Sweet & Bergström 1976, Ross *et al.* 1982).

Sample 29 was analyzed only by the 3-step fusion technique due to low biotite recovery and has a preferred age of 453.8 ± 3.6 Ma (Table 1). Even though the data are not of the highest analytical quality, they do agree, within the limits of analytical precision with other results from this horizon and thus are probably geologically meaningful (Class II data).

## Carntown, Kentucky

This sample is from the shaft of an underground mine near Carntown, Kentucky. Six bentonites have been found here in the Lexington and Tyrone Limestones (Fig. 2) and of these six bentonites, two, from the Tyrone, will be discussed. The rocks in which these two bentonites occur have been placed in the interval of latest conodont Fauna 7 (?) (Fetzer 1973) of late Blackriveran (Sweet & Bergström 1976) to Rocklandian age (Ross *et al.* 1982).

Sample 1A yields a plateau age (Fig. 3, Table 1) of 452.8 ± 3.0 Ma and a preferred 3-step fusion age of 457.7 ± 3.0 Ma. Although the age spectrum meets criteria 2–4, the 3-step fusion experiment shows that this sample is not reproducible in terms of total gas age and apparent K/Ca. In addition, a separate sample, CM-10, was collected from this bentonite at the same locality by D. Stith of the Ohio Geologi-

*Table 1 – Analytical data for samples discussed in this study.*

| Temp °C | 40-Ar / 39-Ar | 37-Ar[1] / 39-Ar $(x10^{-3})$ | 36-Ar / 39-Ar $(x10^{-2})$ | 39-Ar % of total | 40-Ar % Radiogenic | $39\text{-Ar}_K$[2] (moles $x10^{-12}$) | Apparent[3] K/Ca (mole/mole) | Apparent[4] Age (Ma) |
|---|---|---|---|---|---|---|---|---|
| 31 D Biotite Age Spectrum I-59 Roadcut, Gadsden, Alabama<br>J = .008898 Sample Wt = .0971 g | | | | | | | | |
| 350 | 36.67 | 81.6 | 4.497 | 1.4 | 63.8 | 0.16 | 6.0 | 344.1 ±15.0 |
| 600 | 32.62 | 9.8 | 0.594 | 13.6 | 94.6 | 1.70 | 50.1 | 441.7 ± 1.8 |
| 800 | 33.53 | 7.7 | 0.521 | 15.0 | 95.4 | 1.84 | 63.1 | 455.8 ± 1.8 |
| 900 | 34.37 | 11.2 | 0.770 | 7.6 | 93.4 | 0.93 | 43.8 | 457.2 ± 1.9 |
| 1000 | 33.57 | 6.9 | 0.531 | 13.2 | 95.3 | 1.62 | 70.7 | 454.9 ± 1.8 |
| 1050 | 33.21 | 7.4 | 0.491 | 20.1 | 95.6 | 2.47 | 66.1 | 452.9 ± 1.8 |
| 1150 | 33.95 | 5.6 | 0.730 | 28.6 | 93.6 | 3.51 | 86.9 | 453.4 ± 1.8 |
| Fuse | 165.65 | 263.3 | 48.44 | 0.2 | 13.6 | 0.03 | 1.9 | 332.4 ± 224.9 |
| | | | | | | Total-gas Age | | = 451.0 |
| | | | | | | Weight Average Plateau Age | | = 454.5 ±1.9 |
| 31 D Biotote 4-Step I-59 Roadcut, Gadsden, Alabama<br>J = 0.008898 Sample Wt = .0372 g | | | | | | | | |
| 550 | 46.30 | 40.1 | 6.309 | 4.7 | 59.7 | 0.26 | 12.2 | 400.5 ± 6.8 |
| 650 | 36.38 | 27.1 | 2.257 | 4.5 | 81.7 | 0.26 | 18.1 | 427.0 ± 5.5 |
| 1100 | 33.00 | 4.5 | 38.36 | 70.5 | 96.5 | 3.96 | 109. | 454.2 ± 3.0 |
| Fuse | 35.27 | 12.1 | 1.257 | 20.3 | 89.3 | 1.14 | 40.5 | 449.7 ± 3.1 |
| | | | | | | Total Gas Age | | = 449.6 |
| | | | | | | Preferred Age | | = 454.2 ±3.0 |
| 30 B Biotite Age Spectrum I-59 Roadcut, Gadsden, Alabama<br>J = .008898 Sample Wt = 0.0965 g | | | | | | | | |
| 350 | 37.60 | 113.3 | 4.530 | 1.1 | 64.4 | 0.16 | 4.3 | 355.3 ±15.4 |
| 650 | 31.64 | 9.2 | 0.492 | 19.3 | 95.4 | 2.67 | 53.1 | 433.0 ± 1.7 |
| 850 | 32.81 | 4.9 | 0.248 | 31.7 | 97.7 | 2.37 | 92.2 | 456.9 ± 1.8 |
| 950 | 33.50 | 5.2 | 0.516 | 10.8 | 95.4 | 1.49 | 93.4 | 455.7 ± 1.8 |
| 1000 | 33.94 | 9.3 | 0.708 | 19.4 | 92.8 | 2.67 | 52.8 | 454.0 ± 1.8 |
| 1050 | 33.71 | 18.0 | 0.701 | 13.5 | 93.8 | 1.86 | 27.3 | 451.4 ± 1.8 |
| 1100 | 38.77 | 98.8 | 2.703 | 3.3 | 79.4 | 0.45 | 5.0 | 440.6 ± 5.3 |
| Fuse | 106.34 | 468.1 | 29.32 | 0.8 | 18.6 | 0.11 | 1.1 | 294.5 ±44.8 |
| | | | | | | Total Gas Age | | = 447.9 |
| | | | | | | Weight Average Plateau Age | | = 455.8 ±1.4 |
| 30 B Biotite 3-Step I-59 Roadcut Gadsden, Alabama<br>J = .008898 Sample Wt = 0.0332 g | | | | | | | | |
| 700 | 31.85 | 20.4 | 0.509 | 24.3 | 95.3 | 87.1 | 24.0 | 435.0 ± 2.9 |
| 1100 | 33.85 | 22.3 | 0.696 | 73.2 | 93.9 | 2.62 | 22.0 | 453.3 ± 3.0 |
| Fuse | 69.39 | 194.5 | 18.05 | 2.4 | 23.1 | 0.09 | 2.5 | 243.2 ±31.0 |
| | | | | | | Total Gas Age | | = 444.0 |
| | | | | | | Preferred Age | | = 453.3 ±3.0 |

| Temp °C | 40-Ar / 39-Ar | 37-Ar[1] / 39-Ar (x$10^{-3}$) | 36-Ar / 39-Ar (x$10^{-2}$) | 39-Ar % of total | 40-Ar % Radiogenic | 39-Ar$_K$[2] (moles x$10^{-12}$) | Apparent[3] K/Ca (mole/mole) | Apparent[4] Age (Ma) |
|---|---|---|---|---|---|---|---|---|
| | 40 B Biotite Age Spectrum Carthage, Tennessee<br>J = .008898 Sample Wt = .0834 | | | | | | | |
| 350 | 50.28 | 185.1 | 12.82 | 0.9 | 24.6 | 0.11 | 2.7 | 190.5 ±23.1 |
| 600 | 35.45 | 23.0 | 1.843 | 6.7 | 84.6 | 0.85 | 21.3 | 430.7 ± 2.1 |
| 800 | 33.99 | 11.5 | 0.832 | 12.6 | 92.8 | 1.60 | 42.6 | 450.0 ± 1.9 |
| 900 | 35.22 | 25.8 | 1.310 | 6.7 | 89.0 | 0.85 | 19.0 | 447.7 ± 2.0 |
| 1000 | 34.10 | 9.9 | 0.813 | 12.5 | 92.9 | 1.59 | 49.6 | 452.2 ± 1.9 |
| 1050 | 33.06 | 6.3 | 0.442 | 22.6 | 96.0 | 2.87 | 73.3 | 452.9 ± 1.8 |
| 1150 | 33.12 | 6.9 | 0.461 | 19.2 | 95.9 | 2.43 | 70.8 | 452.9 ± 1.8 |
| Fuse | 33.3 | 10.0 | 0.655 | 18.9 | 94.2 | 2.39 | 49.0 | 448.4 ± 1.8 |
| | | | | | | Total Gas Age | | = 447.6 |
| | | | | | Weight Average Plateau Age | | | = 452.8 ±0.5 |
| | 40 Biotite 3-Step Carthage, Tennessee<br>J = .008898 Sample Wt = 0.0243 g | | | | | | | |
| 700 | 34.25 | 49.7 | 1.656 | 13.0 | 85.7 | 0.50 | 9.9 | 422.4 ± 3.5 |
| 1150 | 33.03 | 6.05 | 0.397 | 73.1 | 73.1 | 2.84 | 81.0 | 454.2 ± 3.0 |
| Fuse | 36.61 | 19.7 | 1.972 | 13.9 | 13.9 | 0.54 | 24.9 | 440.6 ± 3.7 |
| | | | | | | Total Gas Age | | = 448.2 |
| | | | | | | Preferred Age | | = 454.2 ±3.0 |
| | 29 Biotite 3-Step Watertown, Tennessee<br>J = .008898 Sample Wt = 0.0063 g | | | | | | | |
| 650 | 34.95 | 107.8 | 2.964 | 16.5 | 74.9 | 0.14 | 4.6 | 381.4 ± 14.4 |
| 1100 | 35.12 | 24.75 | 1.116 | 70.5 | 80.6 | 0.60 | 19.8 | 453.8 ± 3.6 |
| Fuse | 50.50 | 80.79 | 6.780 | 13.1 | 60.3 | 0.11 | 6.1 | 436.6 ± 19.8 |
| | | | | | | Total Gas Age | | = 439.8 |
| | | | | | | Preferred Age | | = 453.8 ±3.6 |
| | 1A Biotite Age Spectrum Carntown, Kentucky<br>J = .008898 Sample Wt = 0.0920 g | | | | | | | |
| 350 | 24.29 | 206.9 | 5.939 | 1.3 | 27.8 | 0.18 | 2.4 | 106.3 ± 11.6 |
| 450 | 19.49 | 142.4 | 1.947 | 2.9 | 70.5 | 0.41 | 3.4 | 210.2 ± 3.1 |
| 600 | 29.74 | 84.02 | 1.330 | 5.1 | 86.8 | 0.72 | 5.8 | 376.4 ± 2.4 |
| 700 | 30.66 | 70.19 | 1.179 | 5.8 | 88.6 | 0.82 | 7.0 | 394.2 ± 1.7 |
| 800 | 31.74 | 41.02 | 0.820 | 7.7 | 92.4 | 1.09 | 11.9 | 422.0 ± 1.8 |
| 900 | 32.99 | 21.90 | 0.883 | 14.2 | 92.1 | 2.00 | 22.4 | 435.5 ± 1.8 |
| 1000 | 33.13 | 3.59 | 0.389 | 25.4 | 96.5 | 3.57 | 137. | 455.7 ± 1.8 |
| 1050 | 34.10 | 4.27 | 0.870 | 26.0 | 92.4 | 3.66 | 115. | 450.0 ± 1.8 |
| Fuse | 34.29 | 16.95 | 1.227 | 11.6 | 89.4 | 1.64 | 28.9 | 439.1 ± 1.9 |
| | | | | | | Total Gas Age | | = 428.4 |
| | | | | | Weight Average Plateau Age | | | = 452.8 ± 3.0 |

| Temp °C | 40-Ar / 39-Ar | 37-Ar[1] / 39-Ar ($x10^{-3}$) | 36-Ar / 39-Ar ($x10^{-2}$) | 39-Ar % of total | 40-Ar % Radiogenic | 39-$Ar_K$[2] (moles $x10^{-12}$) | Apparent[3] K/Ca (mole/mole) | Apparent[4] Age (Ma) |
|---|---|---|---|---|---|---|---|---|
| | 1A Biotite 3-Step Carntown, Kentucky<br>J = .008898 Sample Wt = 0.0440 g | | | | | | | |
| 700 | 31.01 | 25.31 | 0.595 | 14.7 | 94.3 | 0.96 | 19.4 | 421.0 ± 2.8 |
| 1100 | 32.47 | 3.95 | 0.114 | 73.3 | 98.9 | 4.80 | 127. | 457.7 ± 3.0 |
| Fuse | 33.30 | 16.32 | 0.818 | 12.0 | 92.7 | 0.79 | 30.0 | 441.9 ± 3.0 |
| | | | | | | | | ± |
| | | | | | | Total Gas Age | | = 450.4 |
| | | | | | | Preferred Age | | = 457.7 ± 3.0 |
| | CM-10 Biotite Age Spectrum Carntown, Kentucky<br>J = .008898 Sample Wt = 0.0888 g | | | | | | | |
| 350 | 43.04 | 208.6 | 12.04 | 0.6 | 17.4 | 0.08 | 2.4 | 117.2 ± 33.4 |
| 650 | 30.89 | 45.45 | 9.469 | 7.9 | 90.9 | 1.07 | 10.8 | 406.1 ± 1.8 |
| 850 | 32.66 | 11.86 | 3.740 | 29.2 | 96.6 | 3.92 | 41.3 | 450.4 ± 1.8 |
| 950 | 32.90 | 15.84 | 4.594 | 20.9 | 95.5 | 2.80 | 30.9 | 450.1 ± 1.8 |
| 1100 | 32.55 | 16.67 | 4.397 | 28.8 | 96.0 | 3.87 | 29.4 | 446.5 ± 1.8 |
| Fuse | 33.64 | 62.42 | 9.589 | 12.6 | 91.6 | 1.69 | 7.9 | 440.9 ± 1.9 |
| | | | | | | Total Gas Age | | = 442.8 |
| | | | | | Weight Average Plateau Age | | | = 448.9 ± 2.0 |
| | CM-10 Biotite 3-step Carntown, Kentucky<br>J = .008898 Sample Wt = 0.0399 g | | | | | | | |
| 700 | 30.57 | 48.72 | 1.153 | 14.4 | 88.8 | 0.69 | 10.1 | 394.0 ± 3.2 |
| 1100 | 32.27 | 9.36 | 0.165 | 68.2 | 98.5 | 3.24 | 52.4 | 453.3 ± 3.0 |
| Fuse | 34.02 | 72.25 | 1.475 | 17.4 | 87.2 | 0.83 | 6.8 | 426.4 ± 3.0 |
| | | | | | | Total Gas Age | | = 440.2 |
| | | | | | | Preferred Age | | = 453.3 ± 3.0 |
| | 5A Biotite 4-Step Carntown, Kentucky<br>J = .008898 Sample Wt = 0.0489 g | | | | | | | |
| 550 | 25.03 | 114.0 | 2.483 | 6.3 | 70.7 | 0.41 | 4.30 | 266.2 ± 4.1 |
| 650 | 29.92 | 87.03 | 1.350 | 4.1 | 86.7 | 0.27 | 5.6 | 377.9 ± 4.9 |
| 1100 | 32.69 | 7.93 | 0.188 | 78.4 | 98.3 | 5.10 | 61.8 | 457.7 ± 3.0 |
| Fuse | 33.70 | 19.24 | 1.002 | 11.1 | 91.2 | 0.73 | 25.5 | 440.1 ± 3.5 |
| | | | | | | Total Gas Age | | = 440.9 |
| | | | | | | Preferred Age | | = 457.7 ± 3.0 |

[1] $^{37}$Ar corrected values were determined using a decay constant of 8.25 x $10^{-4}$ disintegrations/hour for $^{37}$Ar.

[2] $^{39}Ar_K$ concentrations were calculated using the measured sensitivity of the mass spectrometer and thus have a precision of about 5%.

[3] Apparent K/Ca ratios were calculated using the equation given in Fleck, Sutter and Elliot (1977).

[4] The isotopic composition of argon was measured with a VG-Isotopes MM 1200 B mass spectrometer at the U.S. Geological Survey in Reston, Va. Samples were irradiated in the Central Thimble facility of the U.S. Geological Survey TRIGA reactor in Denver, Co. and $(^{36}Ar/^{37}Ar)_{Ca}$, $(^{39}Ar/^{37}Ar)_{Ca}$ and $(^{40}Ar/^{39}Ar)_K$ ratios used were those reported by Dalrymple *et al.* (1981). The monitor mineral used in this study was MMhb-1, which has been described by Alexander, Michelson & Lanphere (1978).

*Table 2 – Summary of highest quality (Class I) and supporting (Class II) age data.*

| | | Results of Age Data | |
|---|---|---|---|
| Sample | Locality | Age (Ma) | Preferred Age for Unit |
| | | Class I | |
| 31D (1) | Gadsden, Ala | 454.5 ± 1.9 | 454.4 |
| 31D (2) | Gadsden, Ala | 454.2 ± 3.0 | |
| 30B (1) | Gadsden, Ala | 455.8 ± 1.4 | 454.6 |
| 30B (2) | Gadsden, Ala | 453.3 ± 3.0 | |
| 40 (1) | Carthage, Tenn | 452.8 ± 0.5 | 453.5 |
| 40 (2) | Carthage, Tenn | 454.2 ± 3.0 | |
| | | Mean age 454.1 ± 2.1[3] (3.1)[4] Ma | |
| | | Class II | |
| 29 (1) | Watertown, Tenn | 453.8 ± 3.6 | 453.8 |
| 1A (1) | Carntown, Ky | 452.8 ± 3.0 | 454.6 |
| 1A (2) | Carntown, Ky | 457.7 ± 3.0 | |
| CM-10 (2) | Carntown, Ky | 453.3 ± 3.0 | |
| 5A (2) | Carntown, Ky | 457.7 ± 3.0 | 457.7 |
| | | Mean age 455.1 ± 4.9 Ma[3] | |

(1) Age Spectrum
(2) 3–4 Step Fusion
(3) Standard Error of the Mean, 2 σ
(4) Probable Error (includes uncertainty in age of monitor MMhb-1)

cal Survey. CM-10 yields a plateau age of 448.9 ± 2.0 Ma (Fig. 3, Table 1) and a preferred 3-step fusion age of 453.3 ± 3.0 Ma (Table 1). The plateau age spectrum of CM-10 fails criteria 1, 3, and 4. The 3-step fusion results, however, agree with the results of the age spectrum experiment of sample 1A. The conclusion to be drawn from this comparison is that this bentonite is not homogeneous in terms of the chemical composition of its biotite as reflected by apparent K/Ca ratios. Even though this sample is not reproducible in terms of apparent K/Ca ratios, the age results of both analyses of 1A and the 3-step fusion results of CM-10 are in excellent agreement with the results from Gadsden, Alabama, and Carthage, Tennessee. Due to this agreement, we believe that these data, while not of the highest quality have a good probability of being geologically meaningful and that they can be used as supportive data (Class II).

Sample 5A, also from the Tyrone Limestone, was analyzed only by the 4-step fusion technique due to the small amount of biotite in our sample. It yields a preferred age (Table 1) of 457.7 ± 3.0 Ma. Even though these data could not be properly tested by criteria 1–4, the K/Ca ratio of the preferred age fraction and the agreement in age with other samples analyzed from this "Horizon" leads us to believe that it is probably geologically meaningful (Class II).

## Discussion

The age data presented in this report are of two qualities (Class I and II), defined on the basis of criteria 1–4. Class I data are of higher analytical quality than Class II and have both a low analytical error and a low probability of geologic error due to their reproducibility over a wide geographic area. Class II data are of somewhat lower analytical quality but, due to their close agreement in age with Class I data, also have a low probability of geologic error. Both Class I and Class II data are reviewed in Table 2. The estimated analytical error placed on the mean of both Class I and Class II data are at the 95% confidence level ($\sim 2\sigma$). The probable error includes a 0.5% uncertainty in J which is based on the uncertainty in the age of the monitor mineral MMhb-1.

The best age, from our data, for the interval of North American Midcontinent Conodont Faunas 7 and 8 of Blackriveran to early Kirkfieldian age is, thus, 454.1 ± 2.1 Ma. The Class II data support this conclusion and yield an age for this "Horizon" of 455.1 ± 4.9 Ma. A recent study by Ross et al. (1982) of zircon from bentonites in the Carters Limestone (equivalent in the upper part of the Stones River Formation) of Alabama and the Plattin and Decorah Formations of eastern Missouri lend support to these results. Using the fission track dating technique, they were able to establish ages of 450 ± 8, 454 ± 10, and 456 ± 11 Ma, respectively, and suggested a mean of 453 ± 3 Ma for this stratigraphic interval.

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