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New U–Pb zircon ages and the duration and division of Devonian time

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Abstract

Newly determined U–Pb zircon ages of volcanic ashes closely tied to biostratigraphic zones are used to revise the Devonian time-scale. They are: (1) 417.6 ± 1.0 Ma for an ash within the conodont zone of *Icriodus woschmidti*/*I. w. hesperius* (early Lochkovian); (2) 408.3 ± 1.9 Ma for an ash of early Emsian age correlated with the conodont zones of *Po. dehiscens*–Lower *Po. inversus*; (3) 391.4 ± 1.8 Ma for an ash within the *Po. c. costatus* Zone and probably within the upper half of the zone (Eifelian); and (4) 381.1 ± 1.3 Ma for an ash within the range of the Frasnian conodont *Palmatolepis punctata* (*Pa. punctata* Zone to Upper *Pa. hassi* Zone). U–Pb zircon ages for two rhyolites bracketing a palyniferous bed of the *pusillites–lepidophyta* spore zone, are dated at 363.8 ± 2.2 Ma and 363.4 ± 1.8 Ma, respectively, suggesting an age of ~363 Ma for a level within the late Famennian *Pa. g. expansa* Zone. These data, together with other published zircon ages, suggest that the base and top of the Devonian lie close to 418 Ma and 362 Ma, respectively, thus lengthening the period by ~20% over current estimates. We suggest that the duration of the Middle Devonian (Eifelian and Givetian) is rather brief, perhaps no longer than 11.5 Myr (394 Ma–382.5 Ma), and that the Emsian and Famennian are the longest stages in the period with estimated durations of ~15.5 Myr and 14.5 Myr, respectively. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: U/Pb; absolute age; Devonian; time scales; K-bentonite

1. Introduction

The Devonian Period encompasses an extraordinary time in Earth history including the radiation of aquatic vertebrates, rise of vascular plants, emergence of air-breathing vertebrates and, near its end, a significant period of mass extinction and biotic turnover [1]. Knowing when these events occurred, and at what rates they occurred, is possible only if accurate and precise isotopic ages are determined for rocks with well-known biostratigraphic ages. At present, there are widely different estimates for the upper and lower boundary dates of the Devonian; these range between 417 and 400 Ma for the base [2,3] and between ~360 and 354 Ma for the top

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[4–7]. The differences reflect, in large part, the lack of reliable isotopic ages for Devonian rocks that are well constrained by index fossils.

We report new U–Pb zircon ages for six volcanic ashes and lavas with good biostratigraphic control spanning the entire Devonian, including samples of Lochkovian, Emsian, Eifelian, Frasnian, and Famennian age. Four of our samples are eruptive ashes (K-bentonites) intercalated within the richly fossiliferous and well-studied Lower, Middle, and Upper Devonian strata of the Appalachian Basin, and two others are volcanic strata from an uppermost Devonian caldera in New Brunswick, Canada. Using these dates, as well as published isotopic ages, we present a new chronometric calibration of Devonian time that greatly revises our present understanding of the length of the period and the duration of its stages.

2. Analytical methods

Our samples consist of altered volcanic ash (K-bentonites) and erupted lavas intercalated with strata whose fossil age is known well by high-precision conodont and pollen biostratigraphy. Absolute ages for the volcanic strata were determined by the U–Pb zircon method using refinements of the procedures developed by Krogh [8,9] and described previously by Tucker et al. [10]. Our method of time-scale calibration has been widely used (e.g. [11–13]) and proven reliable [14] provided that sources of age bias are eliminated from consideration. Such is the case for our samples where single grains and small populations of magmatic, concordant zircon have been isolated and analyzed precisely from 2 to 5 times in order to demonstrate the resolution of the method and the reproducibility of the ages.

Isotope ratios, elemental concentrations, and atomic ratios of U and Pb are reported in Table 1. Isotope ratio measurements of Pb and U were made with a Sector 54 TIMS by the method of peak-hopping using a Daly-type detector with ion-counting capability. In general, ion-beam intensities ranged between 5.0×10^{-15} A and 1.5×10^{-13} A for $^{206}Pb^+$, and between 5.0×10^{-14} and 2.5×10^{-13} A for ^{235}U (measured as UO_2^+), with typical measurement precision better than 0.06% (1σ) for the $^{207}Pb/^{206}Pb$ ratio and 0.05% (1σ) for the $^{238}U/^{235}U$ ratio. Daly bias and nonlinearity were periodically monitored with NIST and CBNM isotopic reference materials, and correction factors and errors for Daly gain were used in data reduction. Errors for the $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$, and $^{207}Pb/^{206}Pb$ ages were estimated using the method of Ludwig [15], and all age uncertainties are quoted at 95% confidence limits. Many of our analyses are concordant (±2 Ma) and those that are not are dispersed on a linear trend toward 0 Ma; these may be reasonably interpreted as perturbed by a small amount of secondary Pb-loss. Thus our cited ages are the calculated means of the $^{207}Pb/^{206}Pb$ ages, weighted according to the inverse variance of each analysis [16]. In all cases, the mean square of the weighted deviates (MSWD) is less than one indicating that assigned individual errors may be somewhat overestimated.

3. The data

3.1. K-bentonite, Kalkberg Formation (Helderberg Group), Cherry Valley, NY (early Lochkovian)

Altered volcanic ashes (K-bentonites) were first reported in the Kalkberg Formation of the Helderberg Group in roadcuts on U.S. Route 20 northeast of Cherry Valley, NY and in natural exposures in the nearby Richfield Springs and Cooperstown quadrangles [17,18]. In eastern New York, New Jersey, and northeasternmost Pennsylvania, most of the lower part of the Helderberg Group, including the Kalkberg Formation, contains *Icriodus woschmidti*, the nominate species of the lowest Devonian conodont zone [19–22]. It is likely that the Kalkberg K-bentonites are in the upper part of the *woschmidti* Zone because younger Helderberg units (Becraft and Alsen formations) produce conodonts diagnostic of the *A. delta* Zone [20,23].

Our K-bentonite sample was collected from the well-studied exposure of a single ash bed, ~8 cm thick, northeast of Cherry Valley, NY, where it occurs within the zone of *Icriodus woschmidti* and probably within the upper part of that zone. At Cherry Valley, the first occurrence of *I. woschmidti* ssp. is about 4 m above the base of the Coeymans Formation and approximately 20–30 m below the dated K-bentonite [24,25].

Elongate prisms of faceted zircon are abundant in our sample. Ten small fractions of zircon, weighing between 5 and 33 μg and representing 4–12 grains each, were selected for analysis (Fig. 1a; Table 1). Four fractions give concordant analyses, five others are variably discordant (2–3%), and all share a common $^{207}Pb/^{206}Pb$ age of ~417 Ma. A tenth analysis is significantly discordant (~9%) with a much older $^{207}Pb/^{206}Pb$ age (467 Ma), and is interpreted as having a trace amount of inherited zircon. Excluding analysis 10, our best estimate for the age of the Kalkberg K-bentonite and a level within the upper *I. woschmidti* Zone, is the weighted mean $^{207}Pb/^{206}Pb$ age of nine analyses, or 417.6 ± 1.0 Ma.

3.2. Sprout Brook K-bentonites, Esopus Formation (Tristates Group), Cherry Valley, NY (early Emsian)

Two K-bentonites are informally grouped as the K-bentonites at Sprout Brook. The dated ashes are 3.0 and 3.57 m above the base of the Esopus Formation. Conodonts are not known from the Esopus Formation and, thus, the K-bentonites near the base of the Esopus at Cherry Valley, NY cannot be precisely positioned within a conodont zone. The brachiopod fauna of the Esopus, although endemic, is most likely Emsian in age and probably early Emsian [26]. Above the Esopus are the barren beds of the Carlisle Center Formation that are succeeded by the Schoharie Formation. Conodonts from the Schoharie Formation in New York State suggest the *Po. serotinus* Zone, or approximately upper Emsian. The fauna includes *Icriodus latericrescens robustus* [20,27], a North American form whose lower range lies either within the *Po. inversus* or *Po. serotinus* Zone on the basis of the upper limit of its likely ancestor in polygnathid-bearing successions in Nevada and the lower limit of *I. l. robustus* within the same successions. The biostratigraphic position of the Sprout Brook K-bentonites is, therefore, generally constrained to the lower half of the Emsian, and probably within the zones of *Po. dehiscens*, *Po. gronbergi* or to the lower half of the *Po. inversus* Zone.

We report five analyses (11–15, Table 1) of long-prismatic zircon from the lower ash, and four analyses (16–19) from the higher ash. All five analyses of the lower ash are concordant (within error) and yield a weighted mean $^{207}Pb/^{206}Pb$ age of 408.3 ± 1.9 Ma (Fig. 1b); analyses 16–19, determined for the upper ash, are discordant (~2.8–11.4%) and have a weighted mean $^{207}Pb/^{206}Pb$ age of 406.8 ± 3.6 Ma. If we pool our analyses from both ashes, a weighted mean $^{207}Pb/^{206}Pb$ age of 408.0 ± 1.5 Ma is obtained. Because all analyses from the lower ash are concordant, and therefore more reliable, our preferred age for the Sprout Brook K-bentonites is 408.3 ± 1.9 Ma, our best estimate for a level within the combined zones of *Po. dehiscens*, *Po. gronbergi*, and the Lower *Po. inversus* of the Emsian.

3.3. Tioga K-bentonite, Wytheville, VA (Eifelian)

The Tioga K-bentonite does not correspond to a single ash, but rather seven or more beds (the Tioga zone) designated by letters A (lowest) to G (highest), that crop out within the Eifelian Stage of the Middle Devonian Series throughout the Appalachian Basin from Virginia to New York State. In New York State and Pennsylvania the Tioga zone either marks the contact between the Marcellus and Onondaga formations or lies within the upper part of the Onondaga that preserves a well-known and diverse Middle Devonian fauna (e.g. [20,28–30]). In New York State, the lowest member of the Onondaga lacks biostratigraphically diagnostic conodonts. *Po. costatus patulus* and probably *Po. c. partitus* [31] occur in the base of the succeeding Nedrow Member and is joined by *Po. c. costatus* midway through the Nedrow. *Po. c. partitus*, the nominate subspecies of the lowest Middle Devonian conodont zone, indicates that most of the Onondaga is no older than that zone. Conodonts of the *Po. c. costatus* Zone continue to the top of the Onondaga so that the upper Onondaga Tioga ash is within that zone. Throughout its exposure in the Appalachian Basin, the Tioga ash is positioned between fossiliferous strata of a single conodont zone (*Po. c. costatus* Zone), and thus it is an ideal time-marker for time-scale calibration.

Our date for the Tioga interval is based on single- and multi-grain zircon analyses from an ash at Wytheville, VA. We report four analyses, all of which are concordant at 95% confidence limits, and having a weighted mean $^{207}Pb/^{206}Pb$ age of 391.4 ± 1.8 Ma (Fig. 1c). We regard this as our best estimate of the age of our sample, and for a level within the conodont zone of *Po. c. costatus*. This date agrees well

Table 1
U–Pb zircon data, Devonian volcanic rocks and ashes

Fractions No. and properties[a]	Wt. (µg)[b]	Concentrations			Atomic ratios					Age (Ma)
		Pb rad (ppm)[b]	U (ppm)[b]	Pb com (pg)[c]	Th/U[d]	^{206}Pb/^{204}Pb[e]	^{207}Pb/^{206}Pb (±)[f]	^{207}Pb/^{235}U (±)[f]	^{206}Pb/^{238}U (±)[f]	^{207}Pb/^{206}Pb (±)[f]
Kalkberg K-bentonite										
1. 4 gr, −200, f, cl, c, n	5	22.4	326	2	0.429	2,866	0.05511 (5)	0.50804 (71)	0.06686 (8)	416.7 (1.9)
2. 12 gr, −200, f, cl, c, n	33	38.5	570	1	0.380	49,596	0.05508 (3)	0.50630 (66)	0.06667 (9)	415.6 (1.1)
3. 11 gr, −200, f, cl, c, n	31	25.4	372	2	0.427	22,048	0.05513 (3)	0.50578 (64)	0.06654 (8)	417.4 (1.1)
4. 8 gr, −200, f, cl, c, n	15	26.3	387	6	0.415	3,902	0.05513 (5)	0.50510 (100)	0.06645 (12)	417.4 (2.0)
5. 8 gr, −200, f, cl, c, n	13	31.9	471	3	0.425	7,103	0.05517 (2)	0.50122 (80)	0.06589 (10)	419.0 (0.9)
6. 7 gr, −200, f, cl, c, n	9	27.3	409	5	0.397	3,172	0.05513 (6)	0.49856 (99)	0.06559 (12)	417.6 (2.4)
7. 4 gr, −200, f, cl, c, n	8	31.8	472	6	0.446	2,824	0.05516 (5)	0.49737 (79)	0.06539 (9)	418.9 (1.9)
8. 8 gr, −200, f, cl, c, n	11	23.5	351	5	0.430	3,367	0.05514 (4)	0.49560 (90)	0.06519 (11)	417.7 (1.5)
9. 8 gr, −200, f, cl, c, n	11	32.9	494	7	0.436	2,954	0.05511 (9)	0.49170 (101)	0.06471 (11)	416.8 (3.5)
10. 12 gr, −200, cl, c, s-p[g]	18	12.9	185	4	0.398	3,423	0.05638 (7)	0.53078 (106)	0.06828 (12)	467.3 (2.8)
Esopus K-bentonite										
11. 15 gr, −200, f, cl, c, n	25	11.4	167	2	0.534	7,798	0.05486 (6)	0.49094 (105)	0.06491 (12)	406.4 (2.4)
12. 17 gr, −200, f, cl, c, n	33	11.9	175	4	0.511	6,365	0.05486 (4)	0.49068 (105)	0.06486 (14)	406.7 (1.7)
13. 4 gr, −200, f, cl, c, n	11	14.8	216	2	0.522	4,352	0.05488 (7)	0.49250 (111)	0.06508 (14)	407.5 (2.9)
14. 14 gr, −200, f, cl, c, n	25	21.9	317	4	0.566	7,742	0.05495 (4)	0.49125 (103)	0.06483 (14)	410.4 (1.5)
15. 2 gr, −200, f, cl, c, n	5	9.4	137	2	0.538	1,292	0.05511 (33)	0.49304 (323)	0.06489 (15)	416.7 (13.1)
16. 6 gr, −200, f, cl, c, n[h]	11	9.4	140	4	0.543	1,623	0.05485 (5)	0.47831 (81)	0.06324 (10)	406.3 (2.2)
17. 6 gr, −200, f, cl, c, n[h]	11	10.2	162	7	0.412	1,026	0.05488 (12)	0.46291 (130)	0.06118 (13)	407.3 (4.7)
18. 9 gr, −200, cl, c, n[h]	15	7.6	121	12	0.642	597	0.05492 (20)	0.43918 (167)	0.05800 (7)	408.8 (7.9)
19. 5 gr, −200, cl, c, n[h]	10	6.8	107	8	0.583	556	0.05490 (17)	0.45077 (159)	0.05955 (13)	408.2 (6.7)
20. 20 gr, +200, cl, c, p[g]	30	13.7	190	4	0.515	6,316	0.05724 (5)	0.53783 (110)	0.06815 (13)	500.6 (2.1)
21. 13 gr, +200, cl, c, p[g]	28	17.6	250	4	0.516	7,307	0.05597 (13)	0.51582 (189)	0.06685 (23)	451.0 (5.2)
Tioga K-bentonite										
22. 4 gr, −200, f, cl, c, n	9	21.1	334	6	0.361	1,983	0.05454 (4)	0.47153 (59)	0.06270 (6)	393.4 (1.8)
23. 1 gr, −200, f, cl, cln	4	33.5	541	8	0.323	1,005	0.05450 (10)	0.46669 (112)	0.06211 (9)	391.7 (4.3)
24. 3 gr, −200, f, cl, c, n	8	21.8	349	5	0.342	2,132	0.05451 (4)	0.46832 (56)	0.06232 (6)	391.9 (1.6)
25. 4 gr, −200, f, cl, c, n	9	20.3	324	2	0.333	5,126	0.05444 (4)	0.46821 (70)	0.06238 (9)	389.1 (1.7)
26. 3 gr, −200, f, cl, c, n	6	23.6	383	10	0.300	992	0.05441 (12)	0.46541 (125)	0.06204 (10)	388.0 (5.0)
27. 5 gr, −200, f, cl, c, n[i]	10	22.1	367	2	0.221	7,240	0.05453 (4)	0.46761 (69)	0.06219 (9)	393.0 (1.7)
28. 1 gr, +200, cl, c, s-p[g]	5	25.9	413	10	0.270	788	0.05516 (15)	0.48447 (147)	0.06370 (10)	418.9 (5.9)

Table 1 (continued)

Fractions No. and properties [a]	Wt. (µg) [b]	Concentrations			Atomic ratios					Age (Ma) ^{207}Pb/^{206}Pb (±) [f]
						^{206}Pb/^{204}Pb [e]	^{207}Pb/^{206}Pb (±) [f]	^{207}Pb/^{235}U (±) [f]	^{206}Pb/^{238}U (±) [f]	
Little War Gap K-bentonite										
29. 7 gr, −200, f, c, cr, cl, n	15	27.9	450	3	0.407	6,754	0.05423 (6)	0.45394 (77)	0.06072 (10)	380.4 (1.9)
30. 25 gr, −200, f, cl, c, n	76	25.8	419	8	0.396	15,042	0.05425 (3)	0.45301 (69)	0.06057 (9)	381.3 (1.1)
31. 1 gr, +200, f, c, cr, i, n	3	15.4	245	2	0.585	2,139	0.05422 (19)	0.43956 (168)	0.05880 (9)	380.0 (2.5)
32. 1 gr, +200, f, c, cr, i, n	3	25.9	435	3	0.384	1,394	0.05422 (17)	0.43851 (150)	0.05865 (7)	380.4 (2.6)
33. 3 gr, −200, f, cl, cr, n	11	15.2	249	1	0.517	5,368	0.05419 (9)	0.43186 (88)	0.05779 (8)	379.1 (1.9)
34. 1 gr, +200, f, cl, cr, n	3	29.6	512	5	0.355	1,124	0.05420 (12)	0.42961 (110)	0.05749 (11)	379.2 (5.1)
35. 4 gr, +200, f, c, cr, i, n	17	28.5	488	25	0.434	1,238	0.05436 (9)	0.42463 (121)	0.05665 (13)	386.1 (3.9)
36. 5 gr, +200, f, c, cr, n	20	22.5	372	9	0.505	2,879	0.05430 (5)	0.43186 (74)	0.05768 (9)	383.4 (2.2)
37. 10 gr, +200, f, c, cr, n	25	29.8	549	66	0.479	707	0.05436 (16)	0.38865 (133)	0.05185 (9)	386.2 (6.7)
38. 2 gr, −200, f, c, cr, i, n [g]	6	23.9	381	5	0.497	1,727	0.05495 (12)	0.45532 (117)	0.06010 (9)	410.2 (4.8)
39. 6 gr, −200, f, cl, cr, n [g]	18	28.0	454	11	0.445	2,926	0.05536 (6)	0.45556 (82)	0.05968 (10)	426.8 (2.3)
Carrow Formation										
40. 8 gr, −200, pb, c, s-p	19	13.4	224	7	0.405	2,033	0.05385 (5)	0.43353 (67)	0.05839 (8)	364.7 (2.0)
41. 15 gr, −200, cl, c, s-p	19	14.7	244	13	0.478	1,990	0.05379 (5)	0.42975 (61)	0.05795 (6)	362.1 (2.3)
42. 6 gr, −200, pb, c, s-p	11	8.2	135	4	0.523	1,298	0.05379 (6)	0.43107 (81)	0.05812 (10)	362.2 (2.3)
43. 1 gr, +200, cl, c, s-p	3	8.3	134	2	0.561	675	0.05389 (6)	0.43115 (108)	0.05803 (14)	366.4 (2.5)
Bailey Rock										
44. 10 gr, −200, cl, c, n	23	4.6	76.4	3	0.504	1,953	0.05374 (5)	0.42871 (73)	0.05786 (9)	360.2 (2.1)
45. 25 gr, −200, c, i, m-p	50	6.2	98.3	37	0.640	509	0.05387 (12)	0.42879 (127)	0.05773 (15)	365.5 (5.1)
46. 2 gr, +200, cl, c, p	33	5.8	86.7	2	0.888	3,971	0.05389 (5)	0.43074 (69)	0.05797 (9)	366.6 (2.1)
47. 5 gr, −200, cl, c, m-p	20	7.8	129		0.489	5,768	0.05382 (3)	0.43035 (65)	0.05800 (9)	363.4 (1.4)
48. 20 gr, −200, cl, c, n	30	5.2	83.5		0.581	2,552	0.05381 (6)	0.42925 (71)	0.05785 (9)	363.3 (2.3)

Notes:

[a] Cardinal number indicates the number of zircon grains analyzed (e.g. 15 grains); all grains were selected from non-paramagnetic separates at 0° tilt at full magnetic field in a Frantz Magnetic Separator; +200 = size in mesh (> 75 µm), c = colorless; cl = clear; cr = cracked; f = faceted; i = contains melt or fluid inclusions parallel to *c* axis; m-p = middle parts of prismatic grains; n = 5 : 1 prismatic needles; p = prismatic; pb = pale brown; s-p = short-prismatic. All grains were air-abraded following Krogh [9].

[b] Concentrations are known to ±30% for sample weights of about 20 µg and ±50% for samples ≤ 5 µg.

[c] Corrected for 0.0215 mole fraction common-Pb in the ^{205}Pb–^{235}U spike.

[d] Calculated Th/U ratio assuming that all ^{208}Pb in excess of blank, common-Pb, and spike is radiogenic ($\lambda\ ^{232}\mathrm{Th} = 4.9475 \times 10^{-11}\ \mathrm{y}^{-1}$).

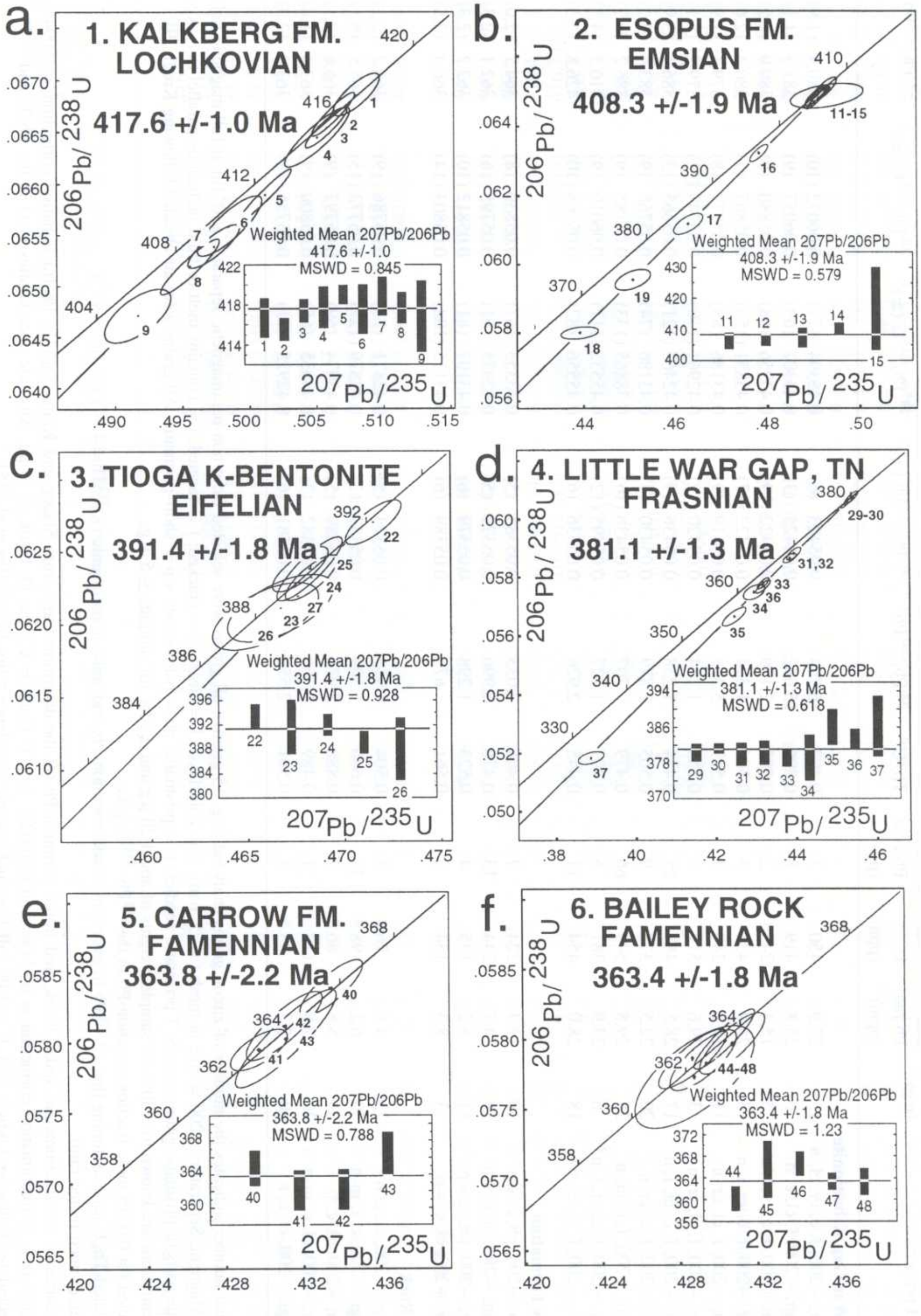
[e] Measured, uncorrected ratio.

[f] Ratio corrected for fractionation, spike, blank, and initial common-Pb (at the determined age from Stacey and Kramers [54]). Pb fractionation correction = 0.094%/amu (±0.025% 1σ), U fractionation correction = 0.111%/amu (±0.02% 1σ). U blank = 0.2 pg; Pb blank ≤ 10 pg. Absolute uncertainties (1σ) in the Pb/U and ^{207}Pb/^{206}Pb ratios calculated following Ludwig [15]. U and Pb half-lives and isotopic abundance ratios from Jaffey et al. [55].

[g] Denotes zircon analyses with isotopic evidence for inheritance; not used in the weighted average calculation.

[h] Denotes zircon fractions from the upper Esopus ash not used in the weighted average calculation.

[i] Denotes zircon fractions from the Tioga ash at Wardville, PA not used in the weighted average calculation.


a.
1. KALKBERG FM.
LOCHKOVIAN
417.6 +/-1.0 Ma
Weighted Mean 207Pb/206Pb
417.6 +/-1.0
MSWD = 0.845
206Pb/238U
207Pb/235U
.0640
.0645
.0650
.0655
.0660
.0665
.0670
.490
.495
.500
.505
.510
.515
404
408
412
416
420
414
418
422
1
2
3
4
5
6
7
8
9
b.
2. ESOPUS FM.
EMSIAN
408.3 +/-1.9 Ma
Weighted Mean 207Pb/206Pb
408.3 +/-1.9 Ma
MSWD = 0.579
206Pb/238U
207Pb/235U
.056
.058
.060
.062
.064
.44
.46
.48
.50
370
380
390
410
400
420
430
11-15
11
12
13
14
15
16
17
18
19
c.
3. TIOGA K-BENTONITE
EIFELIAN
391.4 +/-1.8 Ma
Weighted Mean 207Pb/206Pb
391.4 +/-1.8 Ma
MSWD = 0.928
206Pb/238U
207Pb/235U
.0610
.0615
.0620
.0625
.460
.465
.470
.475
384
386
388
392
380
396
22
23
24
25
26
27
d.
4. LITTLE WAR GAP, TN
FRASNIAN
381.1 +/-1.3 Ma
Weighted Mean 207Pb/206Pb
381.1 +/-1.3 Ma
MSWD = 0.618
206Pb/238U
207Pb/235U
.050
.052
.054
.056
.058
.060
.38
.40
.42
.44
.46
330
340
350
360
380
370
378
386
394
29-30
31,32
29
30
31
32
33
34
35
36
37
e.
5. CARROW FM.
FAMENNIAN
363.8 +/-2.2 Ma
Weighted Mean 207Pb/206Pb
363.8 +/-2.2 Ma
MSWD = 0.788
206Pb/238U
207Pb/235U
.0565
.0570
.0575
.0580
.0585
.420
.424
.428
.432
.436
358
360
362
364
368
40
41
42
43
f.
6. BAILEY ROCK
FAMENNIAN
363.4 +/-1.8 Ma
Weighted Mean 207Pb/206Pb
363.4 +/-1.8 Ma
MSWD = 1.23
206Pb/238U
207Pb/235U
.0565
.0570
.0575
.0580
.0585
.420
.424
.428
.432
.436
358
360
362
364
368
356
372
44-48
44
45
46
47
48

with the concordant monazite age of 390.0 ± 0.5 Ma for the same zone of ashes at Union County, PA [32], thus demonstrating that an age of the lower Eifelian is established securely by isotope dilution ages of zircon and monazite from widely separated localities determined in two different laboratories. We also report an additional analysis (26, Table 1) of zircon from a Tioga ash at Wardville, PA, of approximately the same age and also in the *Po. c. costatus* Zone, but which is not included in the mean age calculation.

3.4. K-bentonite (Center Hill), Little War Gap, Tennessee (Frasnian)

Roadcuts in the Devonian part of the Chattanooga Shale at Little War Gap, east Tennessee, expose four K-bentonite intervals, corresponding to beds 59, 61, 65, and 67 in the measured section of Dennison and Boucot [33]. The interval was originally identified as the Tioga zone by Dennison and Boucot [33], but later work by Harris [34] identified the Frasnian conodont *Palmatolepis punctata* from shale within the interval (beds 61–64). *Palmatolepis punctata* ranges from the base of its zone through at least the *Pa. hassi* Zone, but probably not into the succeeding *Pa. jamieae* or *Pa. rhenana* Zones. On this basis, we provisionally correlate the ashes at Little War Gap with the Center Hill ash of Frasnian age in central Tennessee [35], and suggest a biostratigraphic age within the zones of *Pa. punctata* to *Pa. hassi* for the dated ash at Little War Gap.

One of the four ash beds (bed 61 in Dennison and Boucot's [33] section), produced the greatest yield of long-prismatic, faceted zircon, and it was therefore targeted for isotopic dating. We report seven single-grain and small-fraction zircon analyses for this sample (Fig. 1d). Analyses 29–30, consisting of 7 and 25 long-prismatic zircons, are concordant at ~381 Ma whereas seven other analyses are variably discordant (3–8%) but have a common ^{207}Pb/^{206}Pb age (Table 1). The weighted average ^{207}Pb/^{206}Pb age of the nine analyses is 381.1 ± 1.3 Ma, our best estimate of the age of our sample. Two other analyses of zircon (38, 39, Table 1) have significantly older ^{207}Pb/^{206}Pb ages, and these are best interpreted as having incorporated a trace amount of inherited zircon.

3.5. Piskahegan Group, New Brunswick (late Famennian)

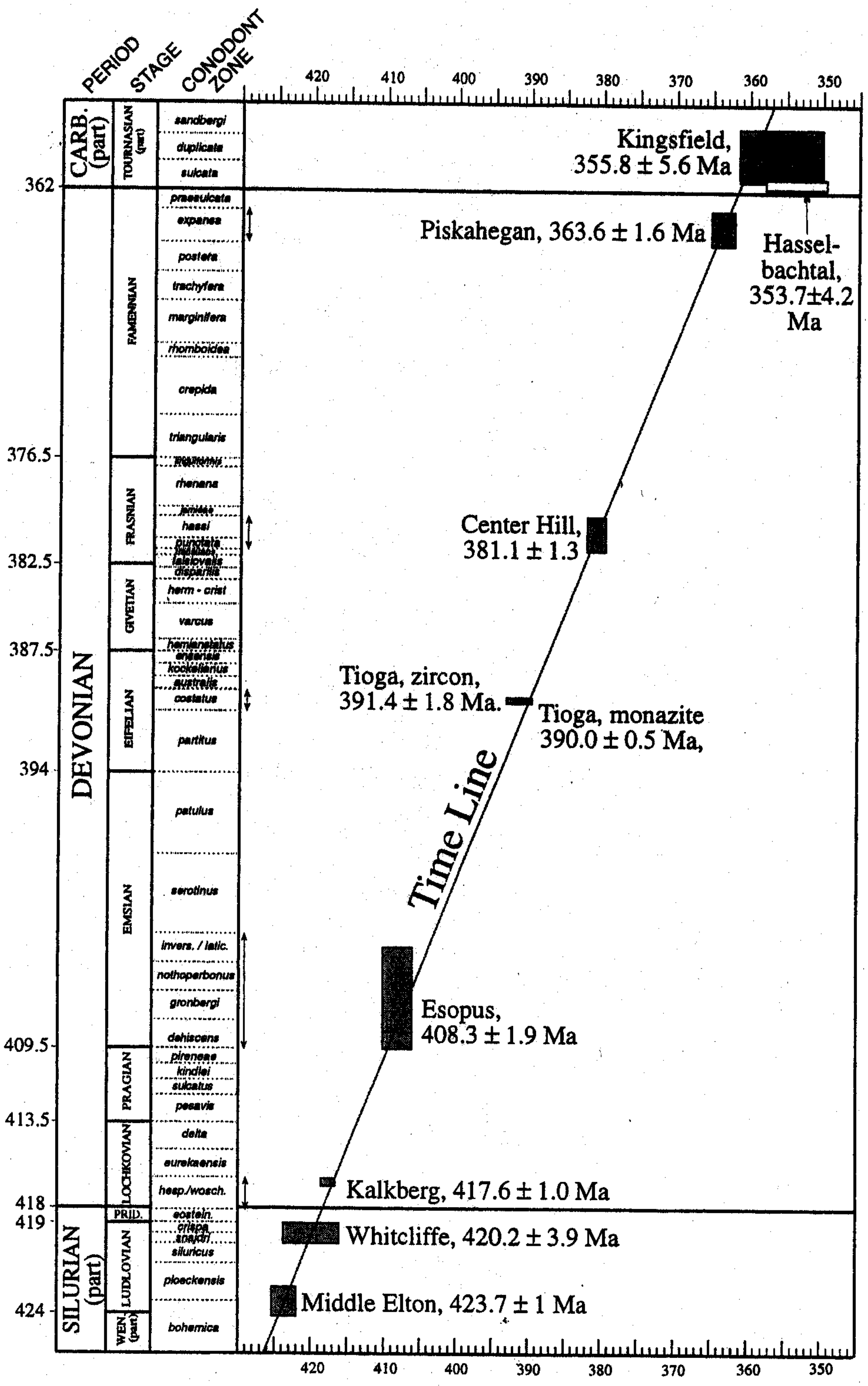
McGregor and McCutcheon [36] report late Famennian spores from the Carrow Formation of the Piskahegan Group, that is within the outflow facies of a Late Devonian caldera complex in southern New Bunswick [37]. According to these authors [36], the palyniferous horizon is most likely in the *pusillites–lepidophyta* spore zone (Fa2d), or less likely in the *flexuosa–cornuta* spore zone (Fa2c of the Belgian scale). This is about equivalent to a position within the Upper *Pa. g. expansa* conodont zone of Ziegler and Sandberg [38].

We report precise, concordant analyses of zircon from the volcanic rocks immediately beneath and either above or intrusive through the spore-bearing horizon (Carrow Formation). A weighted mean ^{207}Pb/^{206}Pb age of 363.8 ± 2.2 Ma was determined for the pumiceous tuff member of the Carrow Formation beneath the spore-bearing bed (Fig. 1e), and a weighted mean ^{207}Pb/^{206}Pb age of 363.4 ± 1.8 Ma (Fig. 1f) for the Bailey Rock Rhyolite which intrudes and (or) overlies the Carrow Formation. As the palyniferous horizon is bracketed between the two dated rhyolites, our preferred age for the Carrow Formation, and the Upper *Pa. g. expansa* Zone, is the mean of all ^{207}Pb/^{206}Pb ages or 363.6 ± 1.6 Ma.

4. Proposed Devonian time-scale

We use our new data plus selected other published isotopic ages for rocks of Late Silurian to earliest Carboniferous age to construct a new Devonian time-scale (Fig. 2). They include a ^{40}Ar–^{39}Ar plateau

Fig. 1. Concordia diagrams for the dated ashes and volcanic rocks. (a) Kalkberg Formation, New York State, early Lochkovian. (b) Sprout Brook K-bentonite, New York State, early Emsian. (c) Tioga K-bentonite, Wytheville, VA, Eifelian. (d) Little War Gap, K-bentonite, eastern Tennessee, Frasnian. (e) Pumiceous tuff of the Carrow Fm., Piskahegen Group, New Brunswick, late Famennian. (f) Bailey Rock Rhyolite, Piskahegen Group, New Brunswick, late Famennian.


PERIOD
STAGE
CONODONT ZONE
420
410
400
390
380
370
360
350
CARB. (part)
DEVONIAN
SILURIAN (part)
TOURNASIAN (part)
FAMENNIAN
FRASNIAN
GIVETIAN
EIFELIAN
EMSIAN
PRAGIAN
LOCHKOVIAN
PRID.
LUDLOVIAN
WEN. (part)
sandbergi
duplicata
sulcata
praesulcata
expansa
postera
trachytera
marginifera
rhomboidea
crepida
triangularis
linguiformis
rhenana
jamieae
hassi
punctata
falsiovalis
disparilis
herm - crist
varcus
hemiansatus
ensensis
kockelianus
australis
costatus
partitus
patulus
serotinus
invers. / latic.
nothoperbonus
gronbergi
dehiscens
pireneae
kindlei
sulcatus
pesavis
delta
eurekaensis
hesp./wosch.
eostein.
crispa
snajdri
siluricus
ploeckensis
bohemica
362
376.5
382.5
387.5
394
409.5
413.5
418
419
424
Kingsfield, 355.8 ± 5.6 Ma
Piskahegan, 363.6 ± 1.6 Ma
Hassel-bachtal, 353.7±4.2 Ma
Center Hill, 381.1 ± 1.3
Tioga, zircon, 391.4 ± 1.8 Ma.
Tioga, monazite 390.0 ± 0.5 Ma,
Time Line
Esopus, 408.3 ± 1.9 Ma
Kalkberg, 417.6 ± 1.0 Ma
Whitcliffe, 420.2 ± 3.9 Ma
Middle Elton, 423.7 ± 1 Ma

age for biotite from the Middle Elton Formation of early Ludlow (Gorstian) age [39], and U–Pb zircon and monazite ages for late Ludlovian, Eifelian, and early Tournaisian strata from the published literature [2,6,7,32].

To arrive at our estimates for the stage boundaries, we plotted the dated rocks on a Cartesian plot of time (the abscissa) versus stratigraphic age (the ordinate) as defined by conodont zonation [38,40]. Each of the data points has an assigned uncertainty, defined by the precision of the isotopic age and the sample's allowable biostratigraphic range, and they may therefore be plotted as a rectangle in Fig. 2. Errors for the isotopic dates are shown at 95% confidence limits, and stratigraphic uncertainties are estimated from published paleontologic descriptions. By shifting the boxes vertically, within limits dictated by the conodont zones, it is possible to achieve a satisfactory fit of boxes to a single line, called a 'time-line' in Fig. 2, from which boundary ages may be read directly.

Two scales were erected to evaluate the reliability of the construction method. One used biozones (or biochrons) of more-or-less equal duration between each of our dated ashes [38,41], and the other utilized zones of unequal length and scaled in proportion to an empirical scheme of graphic correlation (e.g. [3]) or biostratigraphic intuition (e.g. [40]). The agreement between stage boundary ages estimated by both methods is remarkably good, in the most extreme case differing by 1.5 Myr for the base of the Eifelian and Frasnian, and in many cases not differing at all. With the assumption that the conodont zones are not of equal length, our best estimates for the base of the Devonian stages are given in Figs. 2 and 3.

5. Discussion

In Fig. 3, our boundary dates are plotted graphically against the recent time scales of Fordham [3], Sandberg and Ziegler [41], Harland et al. [42], and Harland et al. [4] that forms the basis for the DNAG scale of Palmer [5]. Our upper and lower boundary dates for the Devonian do not conform completely to any single time-scale although our upper bound agrees better with Harland et al. [42] than any other. This is because Fordham [3] and Sandberg and Ziegler [41] have elected to place their upper bound at ~354 Ma in accordance with the determination of Claoué-Long et al. [6,7] for the K-bentonite of bed 79 in the Hasselbachtel stratotype.

Our estimate for the top of the Devonian is constrained by our age for the zone of *pusillites–lepidophyta* based on precise, concordant analyses with no detectable sign of inheritance or Pb-loss. It is unlikely that the fossil age of the spore zone may be revised downward [43] because several of the spore species have never been reported from older rocks, and an older, but still Late Devonian, age would require major downward extensions in the range of certain species whose biostratigraphy is well established. We thus interpret our age of ~363 Ma to date the Fa2d zone of the Belgian scale or about the Upper *Pa. g. expansa* Zone of Ziegler and Sandberg [38]. Assuming a duration of 1–2 Myr for the zone of *S. praesulcata*, we estimate the top of the Devonian to be ~362 Ma, in good agreement with the estimate of Harland et al. [42] but significantly older (~8 Myr) than the suggested boundary date of Claoué-Long et al. [6,7]. In constructing Fig. 2, we were able to intersect only a corner of the large Kingsfield rectangle with the 'best-fit' time-line. The Hasselbachtal K-bentonite, with its exquisite biostratigraphic control, could only have been made to intersect our time-line by forcing a five-fold increase in the duration of the combined conodont zones of *S. praesulcata* and *S. sulcata*.

The Silurian–Devonian boundary is now well-constrained at ~418 Ma by three dates in the Ludlovian and one in the lower Lochkovian. This leaves very little time — perhaps 1–2 Myr — for the entire Přídolí (base= 419 Ma) and not much more for the Ludlow (base= 424 Ma; Fig. 1). According to Zalasiewicz [44] and Jaeger [45], there are five

Fig. 2. Time-scale for the Late Silurian and Devonian. Each datum is represented by a rectangle whose horizontal dimension is the isotopic age with its 2σ error, and whose vertical dimension is the biostratigraphic range. Double-ended arrows identify the conodont zone(s) whose relative durations were assigned as discussed in the text. Numbers refer to items discussed in the text.

Period	Stage	This Paper	[41]	[3]	[42]	[4,5]
CARB. (part)	TOURNAISIAN	362	354	354	362.5	360
DEVONIAN	FAMENNIAN	376.5	364	367	367.0	367
	FRASNIAN	382.5	369	372	377.4	374
	GIVETIAN	387.5	376	381	380.8	380
	EIFELIAN	394	381	386	386.0	387
	EMSIAN	409.5	389	390	390.4	394
	PRAGIAN	413.5	393	396	396.3	401
	LOCHKOVIAN	418	400	408.5	408.5	408
SILURIAN (part)	PRIDOLIAN	419		418.5	410.7	414
	LUDLOVIAN	424		423.5	424.0	421

Fig. 3. Comparison chart of the proposed new time-scale and recently published scales.

graptolite zones in the Ludlow and seven in the Přídolí. No matter how much tinkering is done with the epoch boundaries these will be among the shortest biostratigraphical zones on record [46]!

Our data suggest that the Devonian is approximately 56 Myr long (418 Ma–362 Ma), or ~20% longer than the estimates of Palmer (48 Myr [5]), Harland et al. (46 Myr [42]), and Sandberg and Ziegler (46 Myr [41]). Interestingly, the estimate of Fordham [3] of ~54.5 Myr is based on a scheme of graphic correlation that predicts a length for the Period closely approximating ours. This may signify that Fordham's approach holds promise for future calibration improvements, provided that more isotopic dates become available, and refinements in the technique of graphic correlation continue (e.g. [47]).

With the period boundaries defined, our stage boundaries are positioned relative to the new ages for the Sprout Brook, Tioga, and Center Hill ashes. There are no good constraints on the position of the Lochkovian–Pragian boundary which we estimate at ~413 Ma. The zone of K-bentonites within the Forillon Series (Gaspé) [48] of late Pragian age remains a promising target for future work. The unexpected result from the Sprout Brook determination implies that the Pragian–Emsian boundary is older than 408.3 ± 1.9 Ma; we estimate that boundary date at ~409.5 Ma. Making the base of the Emsian older, and increasing its length, helps to reconcile a long-standing problem in New England geology wherein strata established as Emsian (and therefore younger than ~394 Ma; e.g. Palmer [5]) are intruded by plutons dated at ~409–400 Ma [49,50]. Our data demonstrate that the Sprout Brook ash has as its possible source the Picataquis–Central Maine volcanic and plutonic belt, themselves emplaced into Emsian sediments, dated at ~407–400 Ma [51,52], and overlain unconformably by sandstones of late Emsian or earliest Eifelian age [53].

Our determination for the Sprout Brook and Tioga ashes places the lower Emsian (zone of *Po. dehiscens*) close to ~408 Ma, and the lower Eifelian (*Po. c. costatus* Zone) near ~391 Ma. The latter determination agrees well with the published age of the Tioga interval in Pennsylvania [32]. With these dates, we estimate the length of the Emsian at ~15.5 Myr, and the base of the Eifelian at ~394 Ma. Similarly, with our age of 381.1 ± 1.3 Ma for the Center Hill ash we estimate the base of the Givetian, Frasnian, and Famennian at 387.5 Ma, 382.5 Ma, and 376.5 Ma, respectively. Thus, a significant find of the present study is the relative brevity of the Middle Devonian (combined Eifelian and Givetian) that now has an estimated duration of ~11.5 Myr It is the shortest of the Devonian epochs, and encompasses less time than either the Emsian or the Famennian stages. The Emsian and Famennian are the longest stages of the period at ~15.5 Myr and ~14.5 Myr, respectively.

Construction of these scales, and quantifying rates of geologic and biologic processes, continues to be a work in progress requiring close cooperation among stratigraphers, paleontologists, and geochronologists. We regard the present scale as an interim estimate whose accuracy will no doubt improve as new ash beds are found and better ages are obtained. Although poorly calibrated at present, continued application of U–Pb geochronology to well-studied rocks promises to establish a time-scale for the Paleozoic that approaches the precision and accuracy of the Mesozoic and Cenozoic scales.

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