[AMERICAN JOURNAL OF SCIENCE, VOL. 254, SEPTEMBER 1956, P. 574-583]

RELATIVE AGES OF EASTERN MASSACHUSETTS GRANITES BY TOTAL LEAD RATIOS IN ZIRCON

G. R. WEBBER, P. M. HURLEY, and H. W. FAIRBAIRN

ABSTRACT. The relative lead content of a number of accessory zircon samples separated from eastern Massachusetts granites was determined spectrographically. Selected samples, analyzed for absolute lead content by C. L. Waring of the U. S. Geological Survey, provided a calibration for the remainder. Contents of uranium and thorium were determined by scintillation spectrometer, and the values for total alpha activity calculated from these were checked by total alpha count. The average ratio of thorium to uranium was such that 85% of the radiogenic lead was derived from uranium.

If Waring's calibration values are correct, the lead ratios show two principal ages for the granites as follows:

260 MY: Localities near Peabody, Rockport, and Cape Ann; north of North Attleboro; north end of Whitinsville; near Fitchburg.

355 MY: Localities north-east of Milford and east of Wrentham.

From the geological relationships it is probable that the granites north and south of Boston known as the Quincy type, as well as part of the area mapped as Dedham granodiorite, and some of the granites extending southward into Connecticut, are all approximately 260 MY. At least one area of granite mapped as Dedham granodiorite was intruded earlier, at 350 MY.

INTRODUCTION

This investigation has employed the method originated by E. S. Larsen, Jr. and associates of the U. S. Geological Survey (Larsen, Keevil, and Harrison, 1952; Larsen, Waring, and Berman, 1953) for the determination of the age of granite by measurement of the total lead in the accessory zircon by optical spectrograph, and the rate of lead production by alpha count. The zircon was obtained from the granite by use of heavy liquids and magnetic separation, with the modified mechanical procedures described by Fairbairn (1955).

The samples of granite, from 50 to 100 lbs., were collected from a number of quarries and roadside outcrops in eastern Massachusetts. Details of their location are given in table 1. The classification of the Massachusetts granites, given by Emerson (1917), is as follows:

Fitchburg granite	Late Carboniferous or Post Carboniferous
Quincy granite	Early Carboniferous
Milford granite	Devonian ?
Dedham granodiorite	Devonian ?
Northbridge granite gneiss	Archean ?

Unfortunately there is a notable lack of fossils in sediments associated with Massachusetts granites. Cambrian fossiliferous strata are found near Quincy (about 10 miles southeast of central Boston) and at Hoppin Hill (about 30 miles southwest of central Boston). At Quincy, the Middle Cambrian Braintree slate is intruded by Quincy granite, a distinctive rock similar petrographically to the granites at Peabody and Cape Ann and correlated with them by field workers. From this evidence it is probable that the Cape Ann and Peabody rocks are post-Middle-Cambrian.

The relationship of the Dedham granodiorite to the Cambrian is more controversial. Rock which has been mapped as Dedham varies considerably petrographically, and it is not unlikely that very different intrusives are included in the classification. At Hoppin Hill, near the Massachusetts-Rhode Island border, the relationship between Hoppin Hill slate (Lower Cambrian) and adjacent granite (classified as Dedham) has been a subject of considerable discussion. Warren and Powers (1914) contended that the granite is younger than the sediments. For a summary of the problem and additional references, see Dowse (1950), who concludes that the granite is older than the sediments and therefore Precambrian in age. Quincy granite in Rhode Island is overlain by basal strata of the Carboniferous Narragansett Basin (Emerson, 1917, p. 188).

TABLE 1
Sample Locations

Sample No.	Rock	Quarry	Locality
3004	Hornblende-augite granite*	Linehan	3 miles WSW of Peabody
3005	Hornblende granite	Flat Ledge	0.5 mile NNW of Rockport
3006	Hornblende granite	Blood Ledge	2 miles WNW of Rockport
3011	Mica diorite	Leavitt	2 miles W of Leominster, near Fitchburg
3012	Biotite granite	Norcross	2 miles NE of Milford
3013	Biotite granite gneiss	Blanchard	1.5 miles WNW of Uxbridge, near Whitinsville
3014	Hornblende granite	Curry	2.5 miles ESE of Wrentham
3105	Granite	(Outcrop)	1.7 miles E of Wrentham
3106	Biotite granite	West	1.7 miles NNE of Milford
3107	Granite gneiss	(Outcrop)	North end of Whitinsville
3108	Muscovite-biotite granite gneiss	Fletcher	1.2 mile NW of West Chelmsford Station
3051	Granodiorite	(Outcrop)	3 miles N of North Attleboro
3052	Granodiorite	(Outcrop)	8.2 miles N of North Attleboro

* The rocks in most of these localities have been described by Dale (1923).

In areas where Quincy-type granite and Dedham-type granite occur it has been reported that the Quincy is intruded into the Dedham (Emerson, 1917, p. 187-188). In Rhode Island, Quincy granite is intrusive into Milford granite. Emerson states that the Milford granite is intrusive into the Northbridge granite gneiss (p. 155).

The mica diorite from the Leavitt Quarry is on the eastern border of an area mapped by Emerson as Fitchburg granite. The Fitchburg pluton has been tentatively assigned to late Devonian by M. P. Billings (Billings, Rodgers, and Thompson, 1952).

The Quincy granite has been correlated with the White Mountain magma series of New Hampshire by some writers (Williams and Billings, 1938) on

the basis of its alkaline nature. The White Mountain magma series has been dated as probably Mississippian by Billings. Age determinations of the Conway granite of the White Mountain magma series made by Larsen, Gottfried, Waring and others are tabulated by Faul (1954, p. 267). They range from 201 to 255 million years (average 235 MY).

EXPERIMENTAL PROCEDURES

Preparation of zircon.—The granite samples were crushed and ground, and 15 to 30 lbs. of material between the sizes −60 and +200 mesh were obtained from each sample.

Magnetite and tramp iron were removed by permanent magnets and a transverse belt arranged above a thin, moving stream of the sized sample. Magnetite will normally clog up any device used for the magnetic separation of the essential constituents of the rock. Biotite and other dark minerals were removed in a Carpco magnetic separator, leaving the zircon with the light-colored minerals for separation by heavy liquids. Acetylene tetrabromide, methylene iodide and Clerici solution were then used to separate zircon and other heavy accessory minerals. A Frantz magnetic separator was used to separate the zircon from sphene, monazite, and other constituents of higher magnetic susceptibility. Pyrite and other sulphides were dissolved by treating the final sample in hot nitric acid. Remaining impurities were hand-picked from the zircon sample.

The zircon concentrate was then separated into different fractions according to its weak magnetic properties, since it had been found that generally the more magnetic zircon had a higher content of uranium, along with other impurities. The purpose of this fractionation on the basis of magnetic susceptibility, and uranium content, was to test the constancy of age ratios on the same original zircon sample, despite differences in radioactivity and lead content. The separations were made on the Frantz separator using a full field of 1.4 amperes and varying the inclination of the separator. The fraction that is magnetic at 5 degrees is the most magnetic, and the fraction that is non-magnetic at 2 degrees is the least magnetic. These designations are used to distinguish the different fractions in table 2.

Measurement of uranium, thorium and alpha activity.—The uranium and thorium content of the zircon samples was determined by a method described by Hurley (1956), utilizing a scintillation spectrometer. The contribution of the gamma rays from the uranium and thorium series was differentiated by a count of the 238 kev gamma rays from lead 212 in the thorium series. The results are given in table 3. It can be seen that, whereas the decay rate of uranium is roughly three times greater than that of thorium, the production of radiogenic lead in the zircon is dominantly from the uranium series. Thus the age ratios are essentially Pb206/U238, if the assumption is correct that there was essentially no lead in the zircon crystals at the time of their formation. On these small zircon samples the precision of the scintillation spectrometer measurements is not quite good enough for this type of work, but the over-all accuracy of the measurements, after allowing for lack of precision, can be good owing to the possibility of direct comparison with well analyzed

TABLE 2
Lead Analyses

Sample no.	Magnetic fraction*	Replicate Lead Analyses Pb ppm							Average Pb ppm
3004A	+5°	47	45	48	42	48	49		47±1.5**
3004B	+2°–5°	23	20	21	21	22	21		21±0.7
3004C	–2°	19	16	20	22	19	19		19±0.6
3005A	+5°	134	164	125					140±6.5
3005B	+2°–5°	82	84	90	86	86	87		85±2.8
3005C	–2°	45	71						58±3.3
3006A	+2°	33	32	30	45	39	44		37±1.2
3006B	–2°	28	29	28	27				28±1.1
3011A	–2°	49	47	44	47				47±1.9
3012A	+2°	87	68	74					76±3.5
3012B	–2°	64	49	56					57±2.6
3013A	+5°	66	74	66	65	89	66	74	71±2.1
3013B	+2°–5°	65	84	70	58	66	67		68±2.2
3013C	–2°	71	73	75					73±3.4
3014B	–2°	67	72	68	74				70±2.8
3105A	+5°	110							110±8.8
3105B	+2°–5°	89	90						90±5.1
3105C	–2°	77	82	72					77±3.5
3106A	+5°	110	121	120					117±5.4
3106B	+2°–5°	120	129	100					116±5.3
3106C	–2°	81	90	72	72	94			82±3.0
3107A	+5°	71	78	77					75±3.4
3107B	+2°–5°	76	66	55	66	65			66±2.4
3107C	–2°	39							39±3.1**
3051	+2°	57	49	59					55±2.5
3052	+2°	68	65	65					66±3.0
3108A	–2°	286							286±23

* Angle on Frantz separator used in magnetic separation.

** Standard deviation precision error based on replicate lead analyses.

uranium and thorium standards. These analyses may therefore be used to check the absorption factor and efficiency in determinations of the alpha activity by direct alpha counting procedures.

The samples were then measured in an alpha counter for alpha particle emission from a thick source. In calculating the alpha activity in alphas/mg hr. within a sample of material, from the measured alpha emission in alphas/cm² hr. from a thick source of the sample in a counter of known geometry, it is necessary to know both the absorption factor and the lower limit of alpha energy that will be recorded by the alpha counter. A source absorption factor for zircon was calculated to be 0.493 by the method described by Nogami and Hurley (1948). In this calculation it was assumed that all alpha particles emerging from the sample would be counted if they had a residual air range exceeding 0.5 centimeter.

The results of the alpha activity determinations by thick source alpha counting are also shown in table 3, after a constant correction factor of 1.16

TABLE 3
Radioactivity Measurements

Sample no.	Uranium ppm	Thorium ppm	Activity calculated from U and Th α/mg hr.	Measured activity from alpha count α/mg hr.	Value used in age calculation α/mg hr.
3004A	1210	375	475	445	455 ± 34**
3004B	510	205	205	185	190 ± 14
3004C	405	130	160	200*	185 ± 14
3005A	2765	1890	1180	1250	1225 ± 130
3005B	2270	1200	940	975	960 ± 67
3005C	1320	740	550	570*	560 ± 40
3006A	970	550	405	405	405 ± 22
3006B	630	380	265	270	270 ± 20
3011A	1130	380	450	560*	510 ± 50
3012A	1350	480	540	465*	500 ± 37
3012B	955	445	390	390	390 ± 23
3013A	2040	1090	850	830	840 ± 60
3013B	1875	750	755	680	710 ± 70
3013C	650	480	280	310*	300 ± 22
3014B	1325	680	545	450	490 ± 37
3105A				715*	715 ± 54
3105B				680*	680 ± 50
3105C				515*	515 ± 38
3106A	2400	915	960	955	955 ± 57
3106B	2080	705	825	820	820 ± 54
3106C	1425	490	555	605	590 ± 39
3107A	1640	1000	690	720	710 ± 70
3107B				615*	615 ± 60
3107C				375*	375 ± 28
3051	1500	390	585	640	615 ± 60
3052	1820	900	750	750	750 ± 65
3108A				830	830 ± 69

* Sample composed of whole zircon, crystals, not ground.
** Standard deviation precision error based on replicate alpha counts.

had been applied. This factor was determined by plotting the alpha activity determined by alpha count against the alpha activity calculated from the separate uranium and thorium measurements using the scintillation spectrometer. As mentioned previously, although the precision of the scintillation spectrometer measurements is poor, the absolute accuracy of the method is preferred over the calculated absorption factor and efficiency used in the determination of alpha activity from total alpha counts. This adjustment of 16% is therefore applied as an efficiency correction for the counter. It is assumed that the error stems from the counter missing the alpha particles of lowest energy barely emerging from the sample, rather than from the absorption factor, because approximately this difference has also been found between this particular proportional counter and an ionization chamber that gives graphical records of alpha pulses. Alpha particle standards cannot be

used to determine this efficiency factor unless the standard is a homogeneous "infinitely" thick source.

Spectrographic measurement of lead.—In spectrographic analysis the problem of absolute accuracy generally consists of obtaining accurate standards composed of the same substance as the samples to be analyzed. The lead content of zircons of late Paleozoic age is low enough so that precise chemical analyses of the lead in standard samples are difficult to make. The ideal method of analysis would be by isotope dilution using a mass spectrometer, and it is hoped that such standards may become available to spectrographic laboratories working on lead measurements of this kind in the future. Because no standards were available for this work, four samples of zircon covering the range of lead content in most of the samples of interest were sent to the U. S. Geological Survey for analysis. It was felt that until such time as absolute standards measured by mass spectrometer become available the best alternative would be to tie in with the analyses made by C. L. Waring of the U. S. Geological Survey who has developed the techniques and standards used in the lead measurements for the laboratory of E. S. Larsen, Jr. and co-workers.

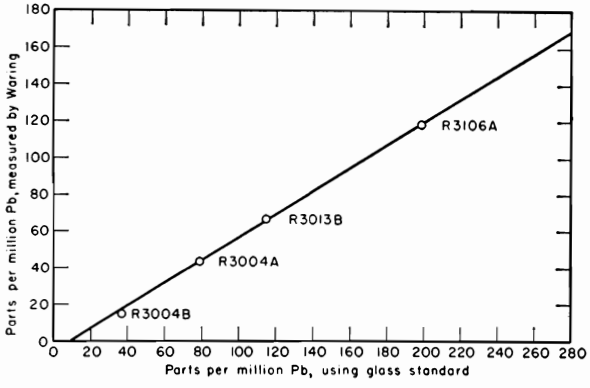

Fig. 1. Calibration of spectrographic analysis of lead in zircon samples.

All the zircon samples, including the four sent to Waring, were first analyzed for relative lead content by the emission spectrograph, using a calibration scale that was found by adding different amounts of a lead-barium glass of known composition to a certain sample of zircon. In figure 1 is shown the relationship between this calibration scale and that used by Waring, as given by the four common analyses. No reason for the failure of the calibration using the standard glass is ventured at this time, but it is mentioned as a warning to those making lead measurements in future by optical spectrograph.

Spectrographic procedures were fairly standard. The zircon was ground to a fine powder in an agate mortar, weighed, and mixed with NaCl so that the resultant mixture contained 80% zircon and 20% NaCl by weight. The sodium chloride was added to improve the arcing qualities of the zircon. The lead line at 4057.820 angstroms was used, in a grating spectrograph (Wads-

worth Mount. 21-ft. instrument) with a dispersion of 2.54 angstroms per millimeter. The lead comes off early. followed after about 35 seconds by an intense line of zirconium which obliterates the lead line's being measured. The arcing was made therefore on the basis of constant time—namely, 30 seconds. All other conditions of arcing and development were maintained as constant as possible.

The results of the lead analyses are given in table 2. Replicate analyses on the same samples give an indication of the precision of the method. As in the case of the activity measurements, it can be seen that there is generally a higher concentration of lead in the more magnetic fractions of each zircon sample.

TABLE 4
Age Results

Granite type, Emerson (1917)	Locality	Sample no.	Age ratio MY
Quincy	Peabody	3004A	260 ± 21 *
		3004B	290 ± 23
		3004C	260 ± 21
	Cape Ann	3005A	290 ± 33
		3005B	230 ± 18
		3005C	265 ± 25
	Cape Ann	3006A	235 ± 15
		3006B	265 ± 22
	Average age for this type	260 MY	
Milford	Milford	3012A	385 ± 38
		3012B	365 ± 33
	Milford	3106A	310 ± 28
		3106B	360 ± 33
		3106C	355 ± 32
	Average age for this type	355 MY	
Dedham	Wrentham	3014B	365 ± 35
	Wrentham	3105A	390 ± 43
		3105B	335 ± 31
		3105C	380 ± 33
	Average age for this locality	365 MY	
Dedham	North of N. Attleboro	3052	220 ± 22
		3051	225 ± 25
Fitchburg	Fitchburg	3011	230 ± 25
Northbridge gneiss	Whitinsville	3107A	270 ± 30
		3107B	270 ± 29
		3107C	265 ± 31
Northbridge gneiss	Uxbridge	3013A	215 ± 17
		3013B	245 ± 26
		3013C	620 ± 53
Ayer granite	W. Chelmsford	3108A	480 ± 51

* Standard deviation precision error.

DISCUSSION OF RESULTS

Calculated age ratios are given in table 4. For samples as young as these the simple formula

$$\text{Age} = K(\text{Pb})/A \text{ my}$$

is sufficiently accurate. A is alpha activity in alphas/mg hr., and Pb is the lead content in parts per million. The factor K varies, depending on the ratio of thorium-produced lead to uranium-produced lead in the zircon, between 1985 for all thorium lead to 2670 for all uranium lead. The average Th/U ratio in these zircons is 0.46. Because the distintegration rate of thorium is only 0.32 that of uranium, the ratio of thorium production of lead to uranium production of lead is only 0.15 on the average in these samples. From this the value of K = 2580 was obtained to be used as an average factor for the calculation of the ages.

The principal localities and average age ratios at each point are shown in figure 2. Details are omitted, including the field classifications of the granites.

The samples of the so-called Quincy-type granite show fairly close ages grouped about a mean value of 260 MY. Some of the so-called Dedham granodiorite, north of North Attleboro, Massachusetts, and other granitic rocks to the southwest of Boston near the Connecticut and Rhode Island borders also show this age. A small area in the vicinity of Milford and Wrentham contained granites that were grouped about an age of 355 MY, showing

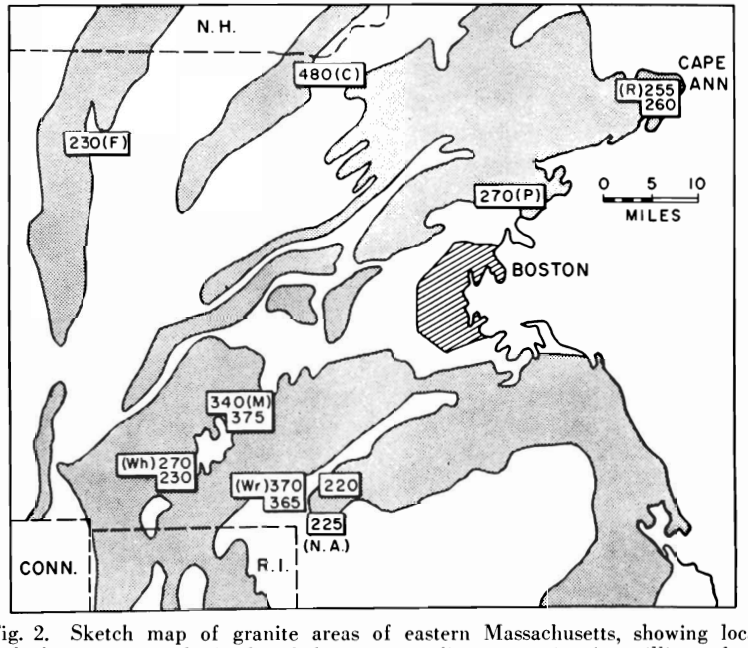

Fig. 2. Sketch map of granite areas of eastern Massachusetts, showing localities from which zircon was obtained and the corresponding age ratios (in millions of years). C—West Chelmsford, F—Fitchburg, M—Milford, N.A.—North Attleboro, P—Peabody, R—Rockport, Wh—Whitinsville, Wr—Wrentham.

that some of the rocks mapped as Dedham granodiorite are of an earlier period of intrusion.

These two ages, 260 MY and 355 MY, are fairly close to the rather common ages that have been appearing in the literature for many years for granitic rocks of the Appalachian province. The Quincy granite group of rocks (Peabody, Cape Ann, etc.) appears to be an extension of an alkaline belt of intrusives that includes the White Mountain magma series of New Hampshire and a number of alkaline masses extending northward into Canada. Whatever the actual geological age of these rocks might be, it appears that in time of implacement they form a homogeneous group with a number of other types of plutonic rocks appearing rather prominently in the northern part of the Appalachian province.

The discrepant age ratio found in the zircon from the Northbridge granite gneiss near Uxbridge (Whitinsville locality) appears to be more than simply precision error in analysis. It may be that these gneissic rocks were partly recrystallized during the time of emplacement of the granites to the northeast and east, with the zircon lowest in radioactivity (and therefore in damage resulting from radioactivity) having suffered the least recrystallization. This suggests that either the gneiss might have been Precambrian to start with, or the zircon may have been in part relict from Precambrian sediments.

The age ratio for zircon from the Fletcher quarry (West Chelmsford) likewise does not fit the pattern shown by the other localities. In this case, however, opinion regarding the history of parent granite is mixed, to say the least, some writers such as Currier and Jahns (1952) ascribing its origin to metasomatism. From this standpoint the age ratio of 480 MY could be interpreted as derived from zircon of mixed origin, in part from old (Precambrian ?) rocks, in part from much more recently crystallized granite of the 240 or 355 MY groups. Although relatively little zircon could be collected from this granite, there is evidence of slight rounding in some grains and of a crystal habit somewhat different from other granite zircons in eastern Massachusetts. More age determinations, from critical localities, are needed for the granites in the Chelmsford area.

The present results neither confirm nor negate the proposed Precambrian age for the granite at Hoppin Hill (Dowse, 1950). A granite sample collected within a few hundred yards of the critical outcrop yielded too little zircon for Pb analysis; the nearest locality for which an age ratio has been determined (225 MY) is three miles distant.

ACKNOWLEDGMENTS

The authors are greatly indebted to L. H. Ahrens and W. H. Dennen for guidance in the spectrographic analysis of lead, and to C. L. Waring of the U. S. Geological Survey for the analysis of selected samples used in calibration. The authors wish to express their grateful thanks to the Office of Naval Research for support of the work and for the instruments used. Reproduction of this article in whole or in part is permitted for any purpose by the United States Government.

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Department of Geology and Geophysics
Massachusetts Institute of Technology
Cambridge, Massachusetts