Evaluation of the Decay Constant of Uranium 235 from Lead Isotope Ratios[1]

Philip O. Banks

Department of Geology, Western Reserve University, Cleveland, Ohio

Leon T. Silver

Division of Geological Sciences, California Institute of Technology
Pasadena

The decay constant of U^{235} has been evaluated from the radiogenic Pb^{207}/Pb^{206} ratios of several cogenetic fractions of zircon and uranothorite, analyzed by conventional mass spectrometric methods. Variation of the Pb^{206}/U^{238} apparent ages among the mineral fractions demonstrates that some form of isotopic disturbance has occurred during their geologic history. Arguments are presented to show that the method of calculating λ_{235} is relatively insensitive to such disturbance because of the young geologic age of the samples and the probability that zircon and uranothorite experience isotopic disturbance by partial loss of Pb. Inaccuracy in the calculated value is further reduced by deducing, from geologic and isotopic considerations, the most likely limits to the apparent ages to which the Pb^{207}/Pb^{206} ratios should correspond. Although the uncertainties in the method do not permit a unique derivation of the decay constant, the results suggest that the currently accepted value is probably accurate to within 1%, relative to the accepted values for the decay constant of U^{238} and the isotopic composition of natural U.

Currently accepted values for the decay constants and abundance ratio of the naturally occurring unsupported U isotopes are:

$$\lambda_{238} = 1.537 \times 10^{-10} \text{ yr}^{-1} \pm 0.2\%$$

[*Fleming et al.*, 1952]

$$\lambda_{235} = 9.72 \times 10^{-10} \text{ yr}^{-1} \pm 2.2\%$$

[*Fleming et al.*, 1952]

$$U^{238}/U^{235} = 137.96 \pm 0.1\%$$

[*Greene et al.*, 1955]

The relatively large uncertainty in the value of λ_{235} compared with the other constants has occasionally been suggested as contributing to small discrepancies between geologic age determinations made by the U-Pb and other methods. For this reason, as well as intrinsic interest, we have examined isotopic data from a suite of U-bearing mineral samples to investigate whether the accepted value of λ_{235} might actually be as much in error as suggested by the assigned uncertainty.

Ideally, changes in the concentrations of Pb and U in a U-bearing mineral would take place only by radioactive decay. If such closed-system conditions exist, the age T of the mineral sample can be obtained from the ratio of radiogenic Pb^{206} to U^{238} according to the equation

$$T = (1/\lambda_{238}) \ln [Pb^{206}/U^{238} + 1] \quad (1)$$

λ_{235} can then be calculated from the ratio of radiogenic Pb^{207} to radiogenic Pb^{206} by means of the equation

$$\lambda_{235} = \frac{1}{T} \ln \left[k\left(\frac{Pb^{207}}{Pb^{206}}\right)(e^{\lambda_{238}T} - 1) + 1 \right] \quad (2)$$

where k is the abundance ratio of the uranium isotopes.

Alternatively, it is possible to calculate λ_{235} from the ratio of radiogenic Pb^{207} and U^{235} (where $U^{235} = U^{238}/k$):

$$\lambda_{235} = T^{-1} \ln [Pb^{207}/U^{235} + 1] \quad (3)$$

Equation 2, however, has the advantage that errors in measuring the concentrations of Pb and U have a smaller effect on the calculated value.

Of course, neither equation 2 nor 3 provides a truly independent determination of λ_{235}, for any errors in the accepted values of λ_{238} or k will appear in the result. Yet the uncertainties assigned to these constants and the errors in conventional mass spectrometry are small enough so that if minerals were closed systems it would be possible to calculate λ_{235} with a precision considerably better than 2%.

Nier [1939a, b] employed a variation of the methods outlined above with remarkable success in his pioneering applications of modern methods of mass spectrometry. However, subsequent work has shown that natural U-Pb systems seldom behave according to the closed-system model. Commonly the concentration of Pb or U is changed by processes other than radioactive decay, resulting in a variable uncertainty in the calculation of λ_{235} which depends on the geologic age of the sample and the mechanism and degree of isotopic disturbance. This phenomenon is discussed more fully below because the need to minimize the associated uncertainty has governed our choice of samples. Its widespread occurrence in U-bearing minerals has led later workers to rely on independent methods of determining λ_{235}. *Fleming et al.* [1952] obtained the presently accepted value by measuring the specific activity of artificially enriched U^{235}. Their assigned uncertainty of 2.2% was derived after a thorough and conservative consideration of the sources of error, the largest of which was due to the presence of U^{234} in the enriched material. A more precise independent determination will require more efficiently enriched U^{235} and/or improved counting techniques.

Isotopic disturbances of a mineral sample during its geologic history may take place in a number of ways; gain or loss of U, gain or loss of Pb, or gain or loss of intermediate daughter products. Such gains or losses could occur more or less continuously, as by concentration-dependent diffusion, or episodically, as by a short interval of heating or leaching. It is not within the scope of this paper to discuss in detail the possible results of this variety of mechanisms. Some aspects have been discussed by *Wetherill* [1956a, b, 1963], *Russell and Ahrens* [1957], *Tilton* [1960], and *Wasserburg* [1963]. Briefly, the mechanisms can be distinguished by their differential effects on the

apparent ages calculated from the ratios Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{207}/Pb^{206} and the way in which these apparent ages depart from the true age of the mineral.

The true age, though, is seldom known a priori. To investigate the mechanisms of disturbance in real samples, the following operational method may be employed. A suite of mineral samples is obtained from a single rock specimen, so that the entire suite has the same true age and has undergone an identical history. To ensure that the mechanism of disturbance is probably the same for all samples, all members of the suite should consist of the same mineral species, but each should differ from the others in the degree of disturbance that has been experienced (one possible way of accomplishing this is by separating the members on the basis of U content). Each member is isotopically analyzed and the results are plotted on a concordia diagram (Pb^{206}/U^{238} versus Pb^{207}/U^{235} [*Wetherill*, 1956a]). The pattern of analytical points on the diagram will serve to limit the possible mechanisms of disturbance, although it will not usually provide a unique interpretation. Further discussion of the use of cogenetic samples may be found in *Silver* [1963] and *Silver and Deutsch* [1963].

We are especially familiar with a large body of data obtained from analyses of cogenetic fractions of the mineral zircon, in which U occurs as a trace constituent. Samples of widely varying age, U content, and degree of disturbance are represented. In all these data we have never seen any that could not be interpreted in terms of simple partial loss of Pb, either by episodic removal or by some combination of concentration-dependent diffusion and episodic loss. This interpretation is based on the observation that the analytical data for each cogenetic suite of zircons, plotted on the concordia diagram, form a linear array lying on the concave side of the concordia curve. By using zircon analyses in calculating λ_{235}, and accepting the general validity of our observation that Pb loss is the dominant mechanism of disturbance in zircon, it is possible to deduce an important limitation to the *direction* of uncertainty caused by isotopic disturbance. Partial loss of Pb yields the following characteristics (see, for example, *Wetherill* [1956a] for a discussion of the effects of episodic Pb loss):
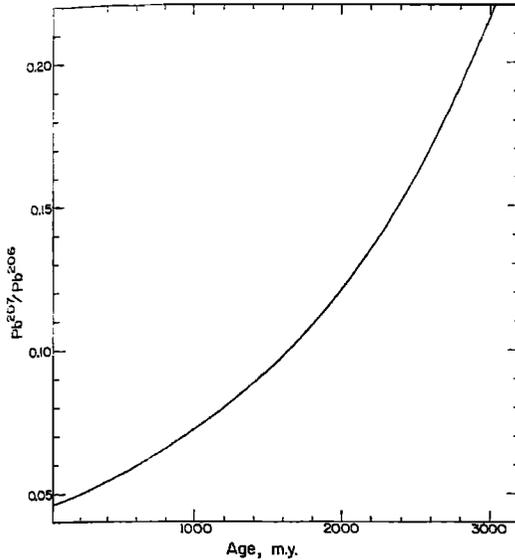
Fig. 1. Relationship between true age and the radiogenic Pb^{207}/Pb^{206} ratio for ideally closed minerals. The smaller slope at younger ages makes the exact age in this region less critical for calculating λ_{235}.

1. The apparent age calculated from the Pb^{206}/U^{238} ratio is always less than the true age.

2. The radiogenic Pb^{207}/Pb^{206} ratio must correspond to an apparent age somewhere between the Pb^{206}/U^{238} apparent age and the true age.

These relationships imply that the direct application of equations 1 and 2 to an analysis of a zircon sample in which Pb loss has occurred will result in a value of λ_{235} that is, in general, too large, because the Pb^{206}/U^{238} ratio corresponds to an apparent age usually lower, but never higher, than the apparent age to which the Pb^{207}/Pb^{206} ratio corresponds.

The *magnitude* of the error introduced by calculating λ_{235} without regard to the possible occurrence of Pb loss cannot be shown in any simple way. The observed isotope ratios for a given sample are a reflection of the correct values of λ_{238} and λ_{235}, the true age of the sample, the amount of isotopic disturbance, and the precise way in which the disturbance has occurred. We assume that λ_{238} is accurately known. It is possible to eliminate, in a general way at least, the uncertainty of how isotopic disturbance has occurred by using cogenetic suites of samples. Only one of the remaining

variables is independent; for example, if the true age is known, the amount of Pb loss, and hence λ_{235}, can be calculated. Unfortunately, none of these variables is known a priori. This is equivalent to saying that there is a family of concordia curves, each curve corresponding to one of the possible values of λ_{235}. A given cogenetic suite defines a unique line of discordance. The upper (older) intersection of this line with each member of the family of concordia curves specifies a particular combination of values for λ_{235} and true age which would produce the observed isotope ratios by an appropriate amount of Pb loss.

For very old minerals the problem has no solution. However, as the true age of the sample decreases, the uncertainty created by a given degree of isotopic disturbance has a diminishing effect on the calculation of λ_{235} because the radiogenic Pb^{207}/Pb^{206} ratio is a more slowly varying function of age for younger ages than for older ages. Figure 1 shows how the Pb isotope ratio changes with age in an ideally closed mineral. In the limiting case of a mineral with zero true age, λ_{235} could be calculated accurately from its Pb isotope composition regardless of any amount or mechanism of partial Pb loss, provided that such a mineral could be analyzed.

To illustrate how the magnitude of uncertainty in the calculated value of λ_{235} is related both to the degree of disturbance and to the true age, it is necessary to assume a particular process of disturbance. We assume that the mineral is isotopically disturbed by losing a portion of its Pb episodically at a very recent time. Analyses of a cogenetic suite of samples so disturbed, when plotted on the concordia diagram, will define a straight line which passes through the origin. In this simple case, the Pb^{207}/Pb^{206} ratio of each member of the suite will correspond to the true age (T) of the suite because there has been no modification of the radiogenic lead by further decay after the disturbance. The Pb^{206}/U^{238} ratio, however, will correspond to an apparent age which is less than the true age by an amount commensurate with the amount of Pb lost. Direct application of equation 1 will yield this apparent age, which is here called the assigned age (T') of the mineral. By substituting the assigned age into equation 2 we obtain a value
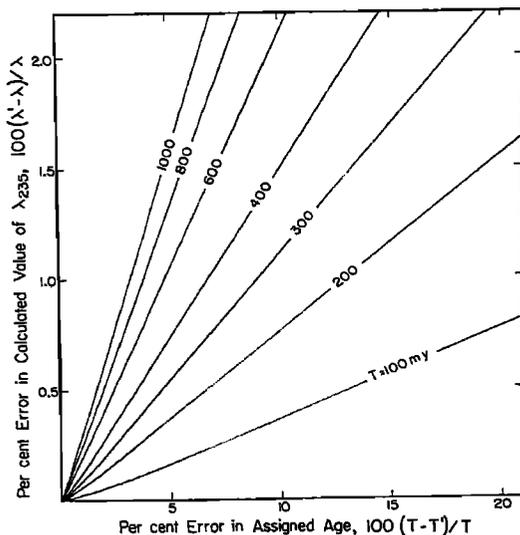
Fig. 2. Per cent error in the value of λ_{235} calculated from the Pb^{207}/Pb^{206} ratio, shown as a function of the error in the assigned age, for the model discussed in the text. Curves are drawn for various values of the true age (T). The assigned age (T') is equivalent to the Pb^{206}/U^{238} apparent age of the sample. It is assumed that the Pb^{207}/Pb^{206} ratio should correspond to the true age, which would be the case if a fraction of the lead was episodically removed from the sample at a recent time.

of λ_{235} that is larger than the correct value by an amount related both to the true age and to the degree of disturbance. Figure 2 shows the error in λ_{235} as a function of the error in the assigned age for this model. Each curve corresponds to a particular value of the true age. Suppose we wish to determine λ_{235} to 1% (exclusive of analytical error). It is readily seen from Figure 2 that an increasingly large degree of disturbance can be tolerated as the age of the sample decreases. A sample with a true age of 100 m.y., for example, may be 20% disturbed, yet the calculation of λ_{235} will be in error by less than 1%. Although this model is not strictly applicable to most real systems, which apparently lose Pb either by continuous diffusion or by episodic loss at some intermediate time in their history, the general conclusion remains valid that the calculation of λ_{235} becomes less sensitive to errors in the assigned age as the true age decreases.

To summarize the foregoing consideration, a reasonably precise evaluation of λ_{235} can be made from mineral samples if a mechanism of disturbance can be postulated which has a known effect on the isotope ratios and if the samples have a sufficiently young true age. To meet the first criterion we have chosen, as previously described, the mineral zircon, which appears to undergo isotopic disturbance by loss of Pb. A few supplementary analyses of the isomorphous mineral uranothorite have also been included. The few data at our disposal on the behavior of uranothorite suggest that it experiences a similar isotopic disturbance to that of zircon. This particular choice of minerals places a practical lower limit of about 100 m.y. on the geologic age of useful samples because zircon seldom contains a sufficiently high content of U to have generated an adequate amount of Pb for analysis during a period significantly less than 100 m.y.

The desired conditions were fulfilled by twelve fractions of zircon and four fractions of uranothorite taken from six samples of the coarse- and fine-grained phases of the Mount Rubidoux leucogranite, Riverside County, California [*Larsen*, 1948]. Geologic evidence indicates that the two phases of granite were emplaced at very nearly the same time; therefore the mineral fractions constitute a cogenetic suite. The following factors render these samples particularly favorable:

1. The Rubidoux granites are part of the Cretaceous batholith of southern California. Their true age is approximately 120 m.y., and, as explained previously, the decay-constant calculation is thus relatively insensitive to small uncertainties in the true age.

2. The Pb^{206}/U^{238} apparent age of each zircon fraction is a function of its U content. It can therefore be recognized that the samples are isotopically disturbed, and a correction can be estimated for this condition which further reduces the error in the calculated value of λ_{235}.

3. The Pb in most samples is markedly radiogenic. In addition, a wide range of Pb^{206}/Pb^{204} values was observed, permitting the derivation of composite radiogenic Pb^{207}/Pb^{206} ratios without the necessity of a specific common Pb correction.

Sample numbers are as follows: SCB-36 and SCB-107 are specimens of fresh coarse granite

TABLE 1. Calibration and Comparison of Mass Spectrometer Operating Characteristics

Experiment	Mass Spectrometer	Collector System	Observed Ratios $\frac{Pb^{206}}{Pb^{204}}$	Observed Ratios $\frac{Pb^{206}}{Pb^{207}}$	Observed Ratios $\frac{Pb^{206}}{Pb^{208}}$	Corr. for Discrimination, $\sqrt{M}$ $\frac{Pb^{206}}{Pb^{204}}$	Corr. for Discrimination, $\sqrt{M}$ $\frac{Pb^{206}}{Pb^{207}}$	Corr. for Discrimination, $\sqrt{M}$ $\frac{Pb^{206}}{Pb^{208}}$	No. of Data Sets
A gravimetrically prepared mixture of nearly pure Pb^{206} and Pb^{208} isotope end members. Atom ratio from gravimetry = 1.0089 ± 0.002. (All data taken from a single load on one filament.)	CIT MS-12-1 (used in this work)	Electron multiplier			1.0123			1.0074	19
	CIT MS-12-2	Electron multiplier			1.0101			1.0053	26
	CIT MS-12-2	Faraday cup			1.0037				22
A radiogenic lead extracted from a zircon and loaded on a single filament for both runs.	CIT MS-12-1	Electron multiplier	1670.	9.100	6.988	1678.	9 078	6.954	17
	CIT MS-12-2	Faraday cup	1670.	9.072	6.939				15
CIT shelf standard lead. Individual loads and runs.	CIT MS-12-1	Electron multiplier	16.658	1.0768	0.4588	16.670	1 0741	0.04564	18
	CIT MS-12-2	Faraday cup	16.640	1.0733	0.4567				15
	NBS-4*	Faraday cup	16 651	1.0733	0.4568				

* *Doe et al.* [1965], average of six runs.

from two different localities. SCB–101C₃ is a specimen of weathered (C zone) coarse granite. SCB–108 is a sample of weathered rind taken from the same residual weathering boulder as SCB–107. SCB–102 and SCB–106 are, respectively, fresh and weathered samples of the fine granite. Mineral separates from each sample were split into two size fractions: −100 + 200 mesh (R200) and −200 mesh (P200). The zircon fractions were washed for

TABLE 2. Analytical Results for Zircon Fractions from the
Coarse- and Fine-Grained Mount Rubidoux Granites
(Sample numbers are explained in the text.)

Sample No.	Size Fraction	Weight, mg	U Concentration, ppm	Pb^{206}/Pb^{204} Observed	Pb^{206}/Pb^{207} Observed	Pb^{206}/U^{238} Apparent Age, m.y.	Pb^{207}/Pb^{206} Radiogenic
SCB-36	R200	383	1882	1786	17.69	114	0.04831
	P200	733	2307	1414	17.05	113	0.04825
SCB-107	R200	452	1765	1826	17.74	110	0.04832
	P200	489	2370	1105	16.25	110	0.04826
SCB-101C₃	R200	454	1937	1367	16.72	105	0.04907
	P200	452	2415	1653	17.49	103	0.04828
SCB-108	R200	502	1771	1711	17.52	108	0.04850
	P200	463	2253	2036	17.85	107	0.04881
SCB-102	R200	351	2639	335	11.19	110	0.04783
	P200	572	3000	892	15.40	108	0.04849
SCB–106	R200	426	2676	1194	16.22	108	0.04937
	P200	295	2990	1230	16.39	108	0.04908

	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
Common lead correction	17.83	15.55	37.62

TABLE 3. Analytical Results for Uranothorite Fractions from the
Coarse-Grained Mount Rubidoux Granite

Sample No.	Description	Weight, mg	U Concentration, %	Pb^{206}/Pb^{204} Observed	Pb^{206}/Pb^{207} Observed	Pb^{206}/U^{238} Apparent Age, m.y.	Pb^{207}/Pb^{206} Radiogenic
SCB-36	Composite R200	8.3	8.16	1634	17.54	97	0.04801
	Composite P200	3.8	8.10	1037	15.95	97	0.04852
	Hand-picked R200A	4.1	10.81	629	14.02	87	0.04797
	Hand-picked R200B	5.7	9.82	498	12.65	111	0.04962

		Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
	Common lead correction	17.83	15.55	37.62

at least 1 hour in hot concentrated HNO_3 before analysis, whereas the uranothorite fractions were untreated beforehand. Concentrations of U and Pb were measured by isotope dilution.

Data were obtained on a 12-inch, 60° sector, single-focusing mass spectrometer equipped with an electron multiplier, a 50% transmission grid, and a dual-pen strip chart recorder. The over-all reproducibility characteristics of this instrument (CIT MS-12-1) have been discussed by *Chow and McKinney* [1958]. *McKinney* [1961] rechecked the calibration of the recorder shunt resistances and has investigated discrimination in the electron multiplier. His results indicate that in the Tl-U region the discrimination closely approximates the theoretical square root of the mass value. The required corrections for mass discrimination and recorder shunts are of the order of a few tenths of 1%, except that in most cases the low intensity of the Pb^{204} peak necessitated a 2% shunt correction for the Pb^{206}/Pb^{204} ratio.

Isotope ratios were measured in sets by scanning once up-mass and once down-mass and averaging the peak heights for each such set. The following table illustrates the average character of the individual Pb composition runs:

One of us (L.T.S.) has made a detailed study of the calibration and operating characteristics of CIT mass spectrometers for Pb isotope analysis. Initial results are shown for comparison in Table 1. This work will be presented in more detail elsewhere.

Analytical results for the twelve zircon fractions are shown in Table 2, and for the uranothorites in Table 3. The variation of Pb^{206}/U^{238} apparent ages among the analyses indicates the existence of isotopic disturbance in these minerals. The apparent ages of the zircon fractions from each rock sample are a function of U content, as illustrated in Figure 3. Also shown in Figure 3 are four repeat concentration analyses of SCB-36 R200 and an analysis of one fraction of SCB-101C_3 for which the Pb composition was not obtained. The composition of the SCB-101C_3 P200 fraction was assumed to apply to this sample. On the basis of the repeat analyses of SCB-36 R200, Pb/U concentration ratios by isotope dilution appear to have an average reproducibility of about 1%; thus the spread in apparent ages is well outside analytical uncertainty.

It is not possible to demonstrate directly that the isotopic disturbance of these samples is compatible with simple loss of Pb because the decay of U during a 100-m.y. interval is almost
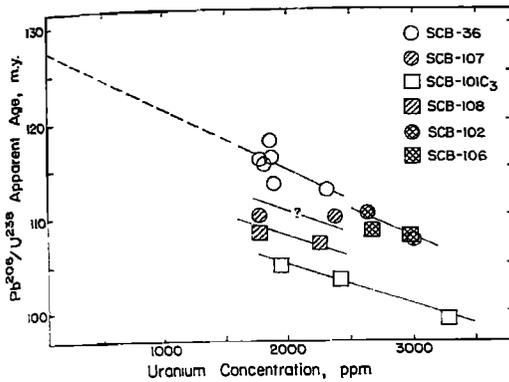
	Pb^{206}/Pb^{204}		Pb^{206}/Pb^{207}	
	No. of Sets	Avg. Deviation from Mean, %	No. of Sets	Avg. Deviation from Mean, %
Zircons	12	1.9	15	0.32
Uranothorites	7	1.0	16	0.26

Fig. 3. Pb^{206}/U^{238} apparent ages of zircon fractions from each rock sample shown to be a function of their U content. Circular symbols are samples of fresh rock; squares are samples of weathered rock. Dashed line indicates possible interpretation of upper limit to the true age by extrapolation to zero uranium content. Cluster of five SCB-36 points at about 1800 ppm U represents one complete analysis and four repeat concentration determinations. Isotopic composition of Pb was not obtained from the most strongly disturbed fraction of SCB-101C$_3$.

linear and the departure of analytical points from the concordia curve is determined as much by analytical error as by the process of disturbance. By analogy with the behavior of older suites of zircon and uranothorite, we believe that Pb loss is the dominant mechanism of disturbance. The only likely mechanism which could seriously alter our conclusions would be preferential loss of intermediate daughter products from one of the decay chains. The simplest form of such loss would be escape of radon (Rn^{222}) from the U^{238} chain. It may be expected that a larger fraction of radon would escape from the uranothorites than from the zircons because of their much higher U content. In such a case, the radiogenic Pb^{207}/Pb^{206} ratios should be systematically higher for the uranothorite samples than for the zircon samples. As will be seen below, the observed situation is opposite to this, which supports our belief that isotopic disturbance has occurred by loss of Pb.

Accepting this conclusion, it follows that the true age of the Rubidoux granites is at least as great as the oldest Pb^{206}/U^{238} apparent age, i.e. 116 m.y. (average of the SCB-36 R200 determinations). An independent lower limit is

set by the age of a dike of pyroxene-bearing granodiorite which crosscuts both phases of the Rubidoux granites. Two fractions of zircon from this dike yielded identical isotope dilution ages of 109 ± 1 m.y. [*Banks*, 1963].

A simple linear extrapolation shown by the dashed line in Figure 3 suggests an upper limit to the true age of about 130 m.y. Although there is no justification at present for this sort of extrapolation, the resulting interval (116–130 m.y.) is compatible with other age determinations in the southern California batholith. In particular, we have obtained ages by isotope dilution on zircons from six other rock types, ranging from 106 to 119 m.y. This work is to be discussed more fully elsewhere. These ages fall within the best-determined stratigraphic interval for batholithic emplacement. *Imlay* [1963] describes Jurassic fossils from the preintrusive Bedford Canyon formation which place an older limit of early middle Callovian age on the batholith of southern California. Upper Cretaceous rocks resting unconformably on the batholith in the Santa Ana Mountains stipulate a younger age limit of middle to upper Turonian [*Popenoe et al.*, 1960]. Elsewhere, in Baja California, batholithic rocks were intruded in the interval from Albian to Maestrichtian [*Silver et al.*, 1963]. These data indicate that most of the batholith is younger than 145 ± 10 m.y. but older than 85 ± 5 m.y. (see, for example, *Kulp* [1961]). It seems likely from all evidence that the true age of the Rubidoux granites is close to 120 m.y.

The radiogenic Pb^{207}/Pb^{206} ratio of each mineral fraction must correspond to an apparent age somewhere between the Pb^{206}/U^{238} apparent age of that fraction and the true age if the

TABLE 4. Isotopic Composition of Common Lead from Various Sources Likely to Contaminate the Radiogenic Lead Analyses

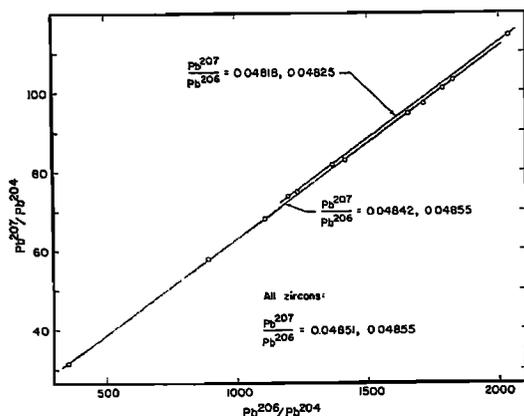| Source of Lead	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$
Borax flux	17.83	15.55	37.62
Ammonium citrate	18.14	15.58	37.93
Acid bath	18.68	15.66	38.22
Mount Rubidoux feldspar	18.95	15.62	38.52

Fig. 4. Composite radiogenic Pb^{207}/Pb^{206} ratios for zircon fractions, derived by least-squares analysis. Upper line is drawn through four samples possibly contaminated with anomalous lead. Dual figures show the result of using each coordinate in turn as the independent variable.

disturbance is caused by Pb loss. Moreover, more strongly disturbed samples should have slightly lower Pb^{207}/Pb^{206} ratios than less strongly disturbed samples. The maximum possible difference between the 'proper' values of this ratio (values which would be obtained if analytical errors were zero) for the least and most disturbed samples is about 1.3%, corresponding to complete loss of Pb from one of the uranothorite samples episodically at 87 m.y. and partial loss from the other samples at the same time. Such a situation is geologically unreasonable, and therefore we believe that the actual spread in proper values is probably considerably less.

The right-hand columns of Tables 2 and 3 show the radiogenic Pb^{207}/Pb^{206} ratio for each mineral fraction, obtained by using the common Pb correction shown at the bottom of each table. A survey was made of the isotopic composition of common Pb in the reagents, in the acid bath used to clean glassware, and in the feldspar of the coarse-grained Mount Rubidoux granite, and the results are given in Table 4. The maximum difference in the radiogenic Pb^{207}/Pb^{206} ratio of any one sample caused by using these different common Pb corrections is less than 0.5%. The range of observed radiogenic ratios is slightly over 3%, which is outside the limits of error caused by an incorrect choice of common Pb, the errors inherent in

mass spectrometry, and the uncertainty in the proper values of the Pb^{207}/Pb^{206} ratios. Another source of difficulty is the possibility of contamination of the samples with 'anomalous' Pb. All other Pb analyzed in this laboratory, consisting of older radiogenic Pb and enriched tracer Pb, have higher Pb^{207}/Pb^{206} ratios than the Rubidoux samples. Very small amounts of some of these leads, especially the tracers, would measurably affect the observed radiogenic ratios. The paths by which contamination might occur are not known, although one possibility is a retention of minute quantities of Pb in the glassware, which until late in the study was used in common for all determinations. It is also possible that occasional zircon grains have cores of older material, although none was seen in mineral separates or grain mounts. These difficulties cannot be quantitatively evaluated, but we believe there is some consequent justification for discounting samples with the highest Pb^{207}/Pb^{206} ratios.

To calculate λ_{235}, the simplifying approximation has been made that the spread in the proper values of the radiogenic Pb^{207}/Pb^{206} ratios for all fractions of a given mineral species is less than the analytical uncertainty. Possible exceptions to this approximation would be those samples which appear to have been contaminated with anomalous Pb. The ob-
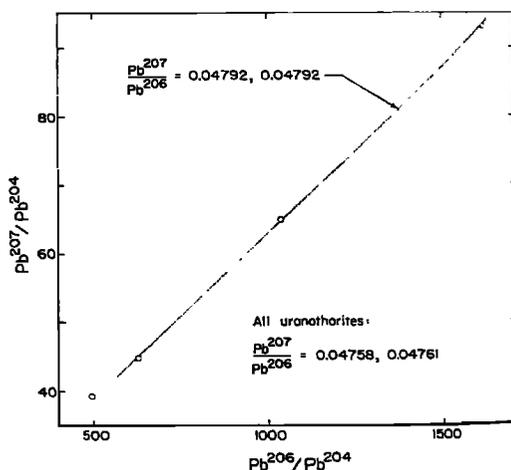

Fig. 5. Composite radiogenic Pb^{207}/Pb^{206} ratios for uranothorite fractions, derived by least-squares analysis. Dual figures show the result of using each coordinate in turn as the independent variable.

served Pb^{207}/Pb^{204} ratios can then be plotted versus the observed Pb^{206}/Pb^{204} ratios, and the slope of a straight line through the data points provides a 'best value' for the average radiogenic Pb^{207}/Pb^{206} ratio of that mineral species. This procedure has the advantage of eliminating from consideration possible errors due to a specific choice of common Pb correction. Figure 4 shows such a plot for the zircon analyses. The data have been divided into two groups, one of which is slightly but consistently richer in Pb^{207}. The four points constituting this group correspond to the four zircon fractions having the highest radiogenic Pb^{207}/Pb^{206} ratios in Table 2. Because of their consistent departure from the rest, these four zircon fractions are interpreted to be slightly contaminated with anomalous Pb. The straight lines in Figure 4 have been fitted by least-squares analysis to the two sets of points. The slope of the lines depends slightly on whether the Pb^{206}/Pb^{204} ratio or the Pb^{207}/Pb^{204} ratio is chosen as the independent variable, so that two values for each slope are given. Also indicated in Figure 4 is the average Pb^{207}/Pb^{206} ratio for all zircon fractions. If anomalous contamination of the four previously mentioned samples has indeed occurred, there is little meaning to the slope of the line drawn through those points and it is shown chiefly to emphasize the nature of their departure.

TABLE 5. Values of λ_{235} in Units of 10^{-10} yr^{-1}, Calculated from All Least-Squares Data Shown in Figures 4 and 5

(The calculations have been carried out by assigning probable minimum and maximum apparent ages to which the Pb^{207}/Pb^{206} ratios should correspond. Lower and upper age limits for the zircons are 115 m.y. and 130 m.y., and for the uranothorites 105 m.y. and 125 m.y.)

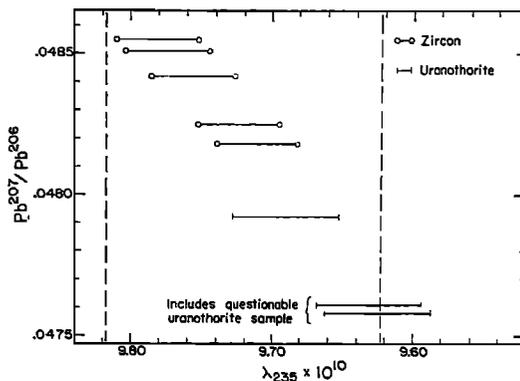| Mineral	$\frac{Pb^{207}}{Pb^{206}}$	λ_{235}, Lower Age Limit	λ_{235}, Upper Age Limit
Zircon	0.04855	9.810	9.752
Zircon	0.04851	9.803	9.744
Zircon	0.04842	9.785	9.727
Zircon	0.04825	9.753	9.695
Zircon	0.04818	9.739	9.682
Uranothorite	0.04792	9.728	9.652
Uranothorite	0.04761	9.668	9.593
Uranothorite	0.04758	9.662	9.587

Fig. 6. Graphical summary of the calculated values of λ_{235} listed in Table 5. Younger age limits correspond to points on the left and older age limits to points on the right. Vertical dashed lines show 1% error limits in the presently accepted value of λ_{235}.

The uranothorite data, which are statistically less reliable than the zircon data, are shown in Figure 5. A straight line has been drawn through three of the points. The remaining point has the highest radiogenic Pb^{207}/Pb^{206} ratio in Table 3 and may, therefore, be contaminated with anomalous Pb. It is also one of the least radiogenic of all samples and hence is susceptible to the largest analytical error. It exerts a noticeable influence on the slope of a line through all the uranothorite data.

The decay constant of U^{235} is calculated from the least-squares slopes by means of equation 2, using the values of λ_{238} and U^{238}/U^{235} listed at the beginning of this paper. On the basis of the arguments presented earlier, the composite radiogenic Pb^{207}/Pb^{206} ratios obtained from the zircons are assumed to correspond to an apparent age greater than 115 m.y. but less than 130 m.y. The uranothorites, being generally more strongly disturbed, have been assigned limits to the Pb^{207}/Pb^{206} apparent age of 105 and 125 m.y.

The results of the calculation for each value of Pb^{207}/Pb^{206} shown in Figures 4 and 5, with the appropriate age limits, are listed in Table 5 and are summarized graphically in Figure 6. All values of λ_{235} so calculated fall within 1% of the presently accepted value, except where the questionable uranothorite sample has been included. Because of the anomalous nature of this sample, we believe it should be rejected from consideration.

These calculations strongly suggest that the presently accepted decay constant of U^{235} cannot be as much as 2% in error, and is very likely accurate to within 1%, relative to the other constants used in the calculation. The uncertainties of the method employed here, and the isotopic disturbance experienced by the samples, do not permit a more precise determination. However, if we assume that our corrections have not introduced any consistent bias, a 'best value' for λ_{235} could be obtained from the data for the eight best zircon samples, using an assigned age of 120 m.y. This yields

$$\lambda_{235} = 9.78_{-0.10}^{+0.04} \times 10^{-10} \text{ yr}^{-1}$$

The uncertainty is assigned on the basis of subjective evaluation of the many complicated sources of error and uncertainty in the entire derivation procedure. Inasmuch as this value is not significantly different from the presently accepted value, and because in our evaluation the most important sources of error are probably unidirectional toward the accepted constant, we believe the current value should continue to be used. Further investigations of this nature, including interlaboratory comparisons, may help to refine the relationship $\lambda_{235}/\lambda_{238}$. At this point, however, it appears that an error in λ_{235} is not adequate to resolve the geochronological discrepancies.

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