URANIUM-LEAD ISOTOPIC VARIATIONS IN ZIRCONS: A CASE STUDY[1]

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ABSTRACT

Zircons in a single 250-pound block of Precambrian Johnny Lyon granodiorite from the Dragoon Quadrangle in Cochise County, Arizona, have been concentrated with special attention to yield and nature of impurities. Morphology, zoning, color, inclusions, size distribution, radioactivity, refractive indexes, cell dimensions, and other properties have been compared with the isotopic properties in the U-Pb system (and to a less precise degree in the Th-Pb system). It has been observed: (1) Uranothorite impurities, while less than 1 per cent in abundance, contribute much more than 50 per cent of the activity in conventionally prepared concentrates. The presence of uranothorite drastically affects the apparent ages in the zircons. (2) The uranothorite can be satisfactorily removed by an appropriate acid-washing procedure. (3) The uranothorite-free zircon concentrates are not homogeneous and show systematic variations in radioactivity and various isotopic properties as a function of average crystal size. (4) Individual zircons show internal variation in radioactivity and may differ in specific activity from other individuals by as much as an order of magnitude. (5) It is possible to strip outer layers experimentally from an aggregate of zircons to determine variations in composite internal isotopic properties. (6) The family of uranium-lead systems distinguished in the inhomogeneous zircon suite may be utilized to establish patterns of isotopic ratio variations that yield much more useful geochronological information than any single system. (7) All systems in this rock appear to have formed 1,655 million years ago and to have been profoundly disturbed by an event 90 million years ago. There is no evidence of any type of disturbance other than this simple episodic pattern. (8) While the mechanism of disturbance is not directly established, it is evident that radioactivity and radiation damage strongly influence susceptibility of the systems to disturbance. (9) It is possible to offer reasonable explanations for some of the puzzling discrepancies between uranium-lead and thorium-lead ages determined on a single mineral concentrate. (10) Recognition of the existence of *families of uranium-lead systems* among the variable members of a single mineral species, or in associated mineral species, in a single typical granitic rock provides a powerful tool for investigation of the processes and conditions that have influenced the age-dating systems. (11) The systematic variations in U and Th provide interesting information on the role of some trace elements and accessory minerals in the crystallization history of the rock. (12) The Johnny Lyon granodiorite is the oldest igneous rock dated in Arizona thus far and places a minimum age of 1,655 ± 20 million years on the orogeny called Mazatzal Revolution.

INTRODUCTION

In geochronological investigations of rock systems, methods involving isotope chemistry and mass spectrometry have evolved as precise and useful techniques for analysis of a number of natural radioactivity relationships. A vast body of data on parent-daughter ratios in the systems K^{40}/Ar^{40}, Rb^{87}/Sr^{87}, U^{238}/Pb^{206}, U^{235}/Pb^{207} and Th^{232}/Pb^{208} has been carefully determined by these techniques yielding geochronological information of far-reaching importance to studies of the earth. At the same time, it has become apparent also that numerous factors in the geological setting and history of the analyzed minerals bear directly on the age interpretations made from the carefully measured isotopic relationships. Apparent ages calculated from several minerals in the same host rock commonly have been in significant disagreement. It is to be hoped that some of these contradictory "ages" may be reconciled, in part, by combining careful mineralogical and petrological studies of the analyzed phases with the isotopic measurements to achieve a better understanding of the geological factors. Few such attempts have been made.

Among the several naturally radioactive isotopes used in geochronology, the constant chemical coupling of U^{238} and U^{235} with their chemically similar decay products Pb^{206} and Pb^{207} introduces the fewest assumptions required for a comparison of apparent ages. It is fortunate too that Th^{232}, a similar actinide element commonly associated with uranium,

also decays to a stable lead nuclide, Pb^{208}. Thus it is often possible to compare ages derived from three systems in the same analyses.

Larsen et al. (1952) suggested that one of the most attractive phases in common rock systems for studying these three isotopic decay relations was zircon. They proposed the so-called lead-α method, or Larsen method, a non-isotopic method of age determination. Tilton, Patterson, et al. (1955) and, in particular, Tilton et al. (1957, and numerous
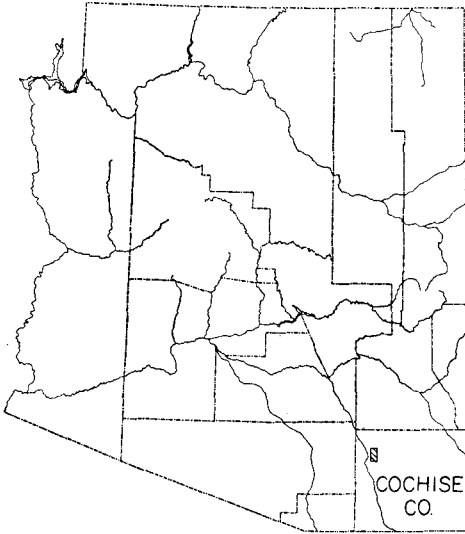

FIG. 1.—Index map of Arizona showing location of Johnny Lyon Hills area in Cochise County.

other publications) demonstrated that precise and significant isotopic measurements could be made on the zircons of many different rocks. Tilton's work more than any other to date has defined the applicability and problems of U-Th-Pb systems in zircons in age-determination studies. The present report is an exploration of some of these problems.

The uranium-lead systems and, with less precision, the thorium-lead systems have been examined in zircon concentrates from a single block of granitic rock. Variations in isotopic properties have been compared with concentrate purity and homogeneity, radio-

activity, size, zoning, and other characteristics. A number of important regularities have been observed. These lead to the conclusion that within these $1\frac{1}{2}$ cubic feet of granite, there exist a large number of uranium-thorium-lead systems which, when studied as a family, can elucidate some types of apparent age contradictions and, indeed, provide some significant additional information on the history of the rock. They also raise some questions about accepted assumptions in age interpretations.

GEOLOGIC SETTING OF THE ROCK

The rock sample was obtained from a large Precambrian granodiorite pluton in the Johnny Lyon Hills in the Dragoon Quadrangle, Cochise County, in southeastern Arizona (figs. 1, 2). Detailed geologic studies have been made of the pluton and its setting by the United States Geological Survey. Preliminary accounts are available (Silver, 1955; Cooper, 1959), and a full report will be published soon (Cooper and Silver, forthcoming). The regional setting is shown on the geologic map of Cochise County (Arizona Bureau of Mines, 1959). The pluton is a post-tectonic intrusive in its Precambrian setting but it has been strongly modified locally by younger deformational, intrusive, and alteration processes, many of which are clearly Mesozoic or Cenozoic. This particular sample (L-312) was selected to be as free as possible from detectable metamorphic effects, as well as from the extensive weathering effects characteristic of this arid region.

The rock is a medium- to coarse-grained, somewhat porphyritic, hornblende-biotite granodiorite. In hand specimen, coarse white plagioclase is set in gray quartz, scattered pink potash feldspar, dark green platy biotite, greenish-black prismatic hornblende and, more rarely, euhedral brown sphene. A few very thin epidote-quartz veinlets, a fraction of a millimeter in thickness, transect the block.

In thin section, the rock is hypidiomorphic-inequigranular with a slightly seriate porphyritic texture. Tabular and zoned

GENERALIZED MAP
OF THE
JOHNNY LYON HILLS

Pal
TQal
U
D
pCpsg
TQal
55
50
A

Pal

L-312

pCj

45

70
65
40

L-609
pCpsg
65
Pal
80
40
64
72
62
Pal
58 66
Pal
50
pCj
35
60
63
D
U
pCpsg 51
65 25
60
65
75
75
18
pCr 75
85
pCr pCr
pCpsg
pCpsg
60
TQal

N

Legend:

TQal
Tertiary and Quaternary alluvium

Pal
Paleozoic or younger rocks

A
Upper pre-Cambrian Apache group with diabase

pCj
Johnny Lyon granodiorite

pCr
Zones of Rhyolite porphyry intrusive sheets

pCpsg
Pinal schist (Slates and graywackes)

Lower pre-Cambrian rocks

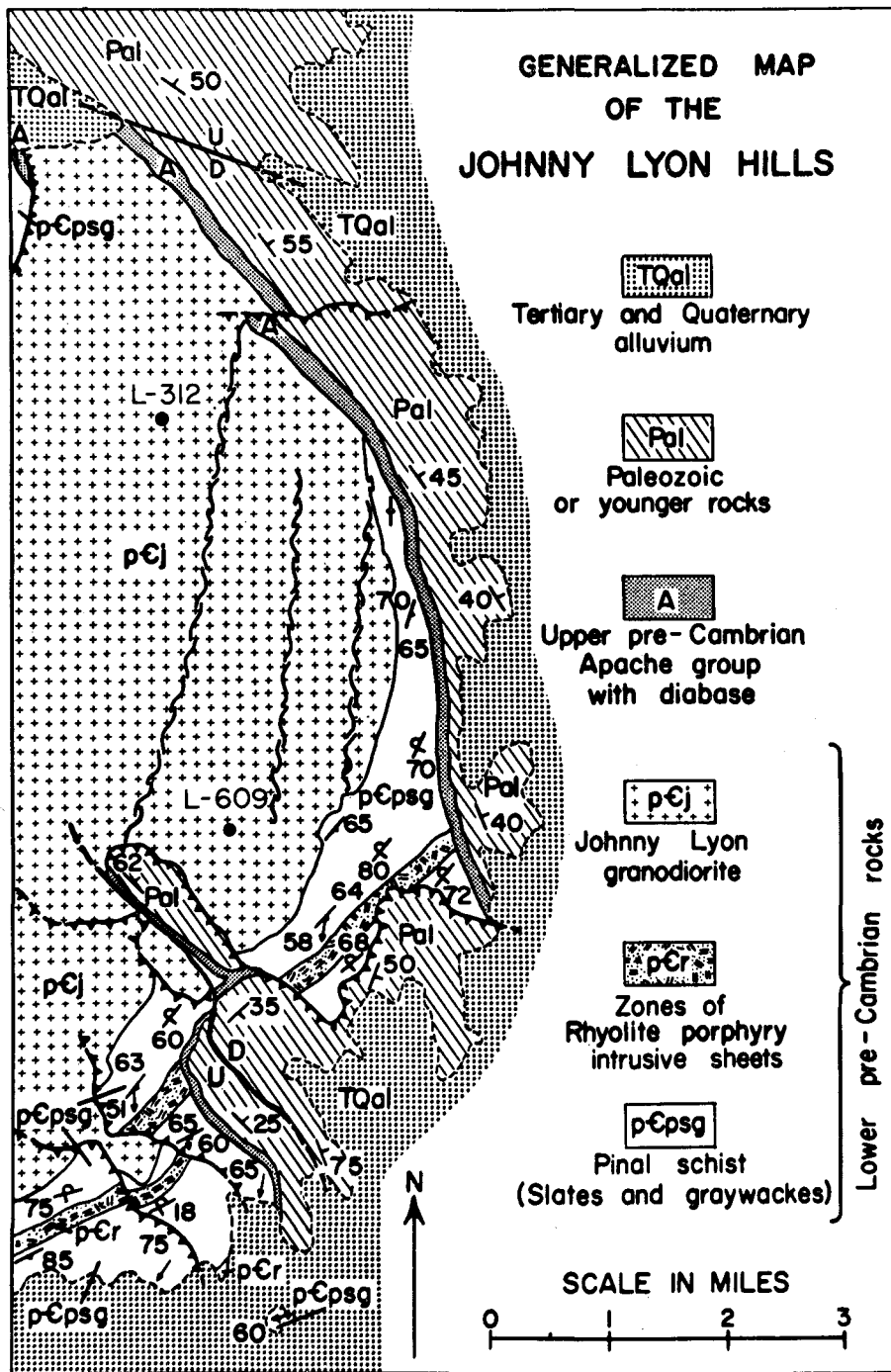SCALE IN MILES
0   1   2   3

FIG. 2.—Generalized geologic map of the Johnny Lyon Hills, showing the stratigraphic and structural relationships of Johnny Lyon granodiorite to both older and younger rocks. Samples L-312 and L-609 were collected to be as free as possible of effects of the three major shear zones and other alteration features in the intrusive.

plagioclase crystals vary in composition from An_{35} at the cores to An_{20} at the rims. Microcline-microperthite is anhedral, texturally late, and bordered by myrmekite fringes on the plagioclase. Quartz is scattered in anhedral aggregates. The biotite and hornblende are subhedral to euhedral. Accessory minerals include magnetite, apatite, sphene, zircon, allanite, and uranothorite in sequence of decreasing abundance. Chemical, normative, and modal analyses are given in table 1. As in every other speci-

TABLE 1A

JOHNNY LYON GRANODIORITE*

CHEMICAL ANALYSIS

	L-312† (Weight Per Cent)	Average of 80 Granodiorites‡ (Weight Per Cent)
SiO_2............	68.89	66.13
TiO_2............	0.45	0.51
Al_2O_3...........	15.02	15.50
Fe_2O_3..........	1.40	1.62
FeO............	1.89	2.70
MnO...........	0.08	0.07
MgO...........	1.43	1.73
CaO...........	3.44	3.70
Na_2O...........	3.84	3.55
K_2O............	3.14	3.17
H_2O comb........	0.88	0.89
P_2O_5...........	0.17	0.17
Others..........	n.d.	0.07
Total.........	100.68	99.90

* (L-312) NE 1/4, SW 1/4, Sec. 20, T. 14 S., R. 21 E.

† W. J. Blake, analyst.

‡ Johannsen, Vol. II (1932), 344.

men of this pluton we have examined, the major minerals show some alteration to sericite, chlorite, and epidote group minerals. Although not shown in the modal analysis, these minerals, principally replacing plagioclase and biotite, constitute about 3–5 per cent of the rock. We have no petrographic criteria for labeling these minerals deuteric or hydrothermal. We have simply accepted them as rather typical attributes of a rock of this composition.

MINERAL SEPARATIONS

The original reservoir of samples collected in the field weighed approximately 250 pounds. Almost all of the zircons used in this study came from a representative 60-pound aliquot of the original sample. It was necessary, however, to process some additional

TABLE 1B

JOHNNY LYON GRANODIORITE

MODAL ANALYSIS

(Point Count)

	L-312* (Weight Per Cent)
Quartz.........	25.84
Plagioclase.....	45.38
Myrmekite.....	1.93
Microcline-perthite......	14.20
Biotite.........	6.44
Hornblende....	4.06
Magnetite......	1.34
Sphene........	0.56
Other accessories	0.25
Total........	100.00
Normative Analysis Salic:	
Quartz........	25.02
Orthoclase.....	18.35
Albite.........	32.49
Anorthite......	14.46
Total........	90.32
Femic:	
Diopside.......	2.22
Hypersthene....	3.99
Magnetite......	2.09
Ilmenite.......	0.91
Total........	9.21
C.I.P.W. Class I, 4, 3, 4	

* Based upon 3,734 points on 13 sq. cm. of thin sections.

rock to replenish supplies of certain size fractions of zircon. Careful comparisons of physical and isotopic chemical characteristics of these new supplies with the old showed no measurable differences between them.

The principal aliquot was crushed in a

Dodge-type jaw crusher and then fed to a Braun UA-type disk pulverizer to produce a product of which more than 95 per cent passed through a 30-mesh sieve. The pulverizer product was carefully sized on a sequence of screens of 30, 50, 100, 200, 300 and 400 mesh.

Each of the size fractions was then processed through heavy liquids of density 2.96 (s-tetrabromoethane) and 3.33 (diiodomethane) at rates controlled to give maximum heavy mineral yields. The heavy min-

and minimum yield efficiency are plotted. *Curve I* shows the weight per cent of total crushed rock in each size fraction. *Curve II* shows the fraction (weight per cent) of the total zircon yield obtained from each size fraction of rock. *Curve III* shows the minimum yield efficiency for the recovery of zircon from each size fraction assuming all of the zirconium in the size fraction to be in the form of zircon.

From a comparison of *Curves I* and *II*, it is apparent that a large fraction of the zircon
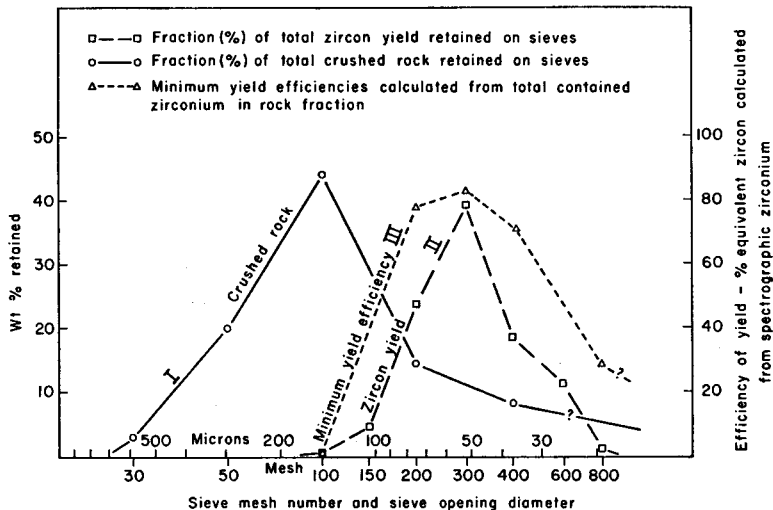

FIG. 3.—Curves relating zircon yields and yield efficiencies to over-all size distribution and sized fractions of crushed Johnny Lyon granodiorite sample L-312.

eral suites were then processed on a Frantz "Isodynamic" electromagnetic separator with emphasis given to maximum yields of zircons.

To measure the efficiency of the zircon extractions, the zirconium content of each of the size fractions of the rock was determined by emission spectroscopy prior to the mineral separations. A maximum possible value of zircon, liberated and unliberated, present in the size fraction was calculated, recognizing that some zirconium is to be found in other phases than zircon.

In figure 3, three curves relating crushed particle size distribution, zircon recovery,

in the rock tends to be liberated before the rock is completely reduced to particles of the average zircon grain size. This is fortunate, inasmuch as the zircon generally is freed in its characteristic original grain shape, and this tendency facilitates the recovery of a more representative sample of the zircon in the rock. Examination of *Curve III*, however, indicates that while extraction efficiency for liberated zircons is quite high (as in the retained 200-, 300-, and 400-mesh size fractions), a considerable part of the zirconium is tied up in material coarser than 100 mesh. All of this coarse material was reground to pass 100 mesh. It was then proc-

essed to recover the zircons as before. Although this involved reprocessing nearly 70 per cent of the total material, the over-all yield was increased by less than 10 per cent. It is concluded that the zircon size fractions used for this study (excepting the passed 400-mesh material) are reasonably representative of each of their size classes in the original rock sample.

The size classes of zircon to which all subsequent discussions will refer are given in table 2.

TABLE 2

Fraction Retained on Sieve Mesh No.	Prism Diameter Range (μ)	Average Prism (Diameter (μ)
R200............	75–150	90
R300............	54–75	64
R400............	37–54	47
Passed 400........	20–37	33

TABLE 3

Mineral	No. of Grains
Zircon................	2,447
Uranothorite..........	17
Quartz and feldspar....	5
Apatite...............	2
Sphene and clinozoisite (?)......	2
	2,473

The zircons coarser than 150 μ are too few for analysis. The zircons finer than 20 μ prism diameter probably are considerably more abundant, but problems of systematic recovery prevented their use.

PHYSICAL PROPERTIES OF THE
ZIRCON CONCENTRATES

Purity.—Each of the zircon concentrates obtained in this study was at least 99 per cent pure. The purity was determined by making permanent grain mounts in a high index mounting medium (Aerochlor no. 4665, $n = 1.65$) of several thousand grains. Grain counts of 2,000 or more grains were then taken. The retained 200-mesh zircon concentrate contained the greatest percentage of non-zircon grains. Table 3 gives the results of a count of nearly 2,500 grains in this size fraction.

The general spectrum of mineral impurities other than zircon was similar for each of the other concentrates, but the relative abundance of uranothorite declined in the finer sizes.

For several different purposes, 100-mg. aliquots of the R200-, R300-, and R400-mesh fractions were hand-picked to observable 99.99+ per cent purity. The removed mineral grains were also mounted and studied. They generally confirmed the mineralogy already determined.

For most of the analytical work, aliquots were not hand-picked. It was determined that a 1-hour wash in hot concentrated nitric acid would effectively remove all uranothorite and apatite. This was employed as a standard preparation procedure and will be discussed in a later section. The remaining impurities were minerals whose concentrations of uranium, thorium, and lead were such that their low abundance in the concentrates could not affect the analytical data within assigned limits of error.

Zircons.—The individual zircon grains are typically euhedral, pale lavender to lavender-brown, visibly zoned, transparent except for minute inclusions of foreign crystals and growth cavities.

Individual grains with excellent euhedral form comprise more than 50 per cent of the over-all zircon population (pls. 1, *e, f,* 2, *e*). It is readily apparent that most of the other grains were broken during the crushing pre-
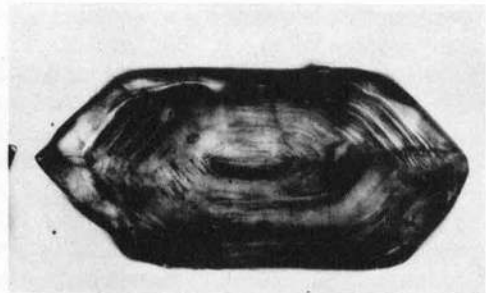

PLATE 1

a–d, R200 fraction zircons displaying characteristic habits, zoning, and inclusions. Linear magnification ×220. *e,* R200 fraction zircons. ×100. *f,* R300 fraction zircons. ×100. *g,* Autoradiograph of R200 fraction of ground zircons, displaying α-particle tracks, zoning, and shadow zone. ×300. *h,* Same as 1, *g.* ×800.
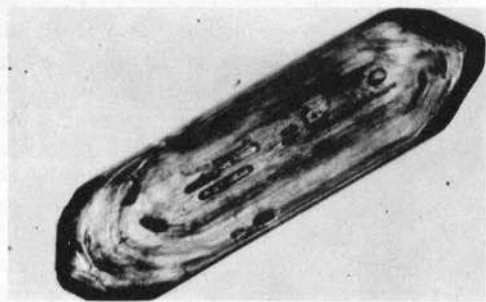
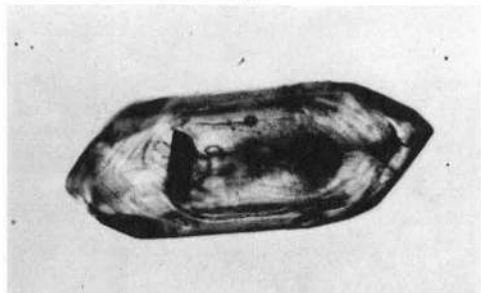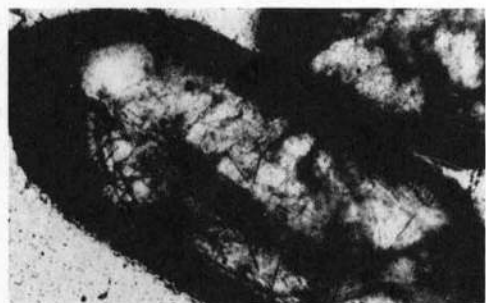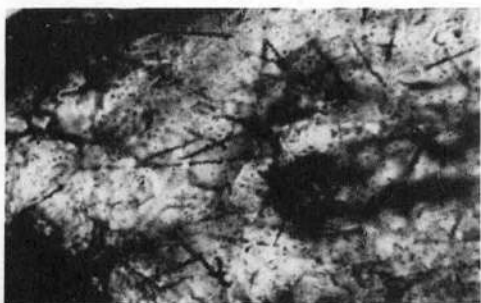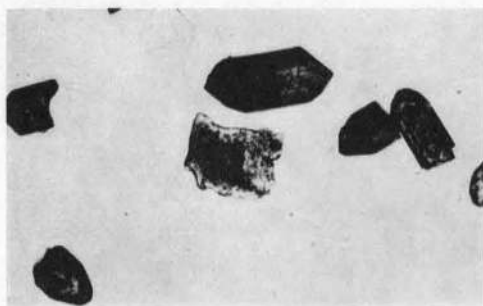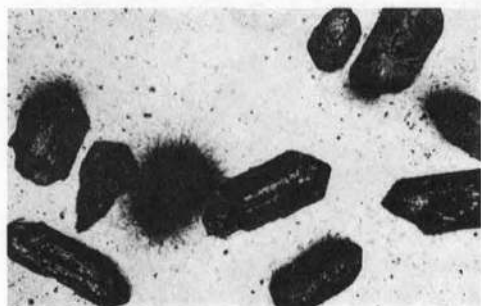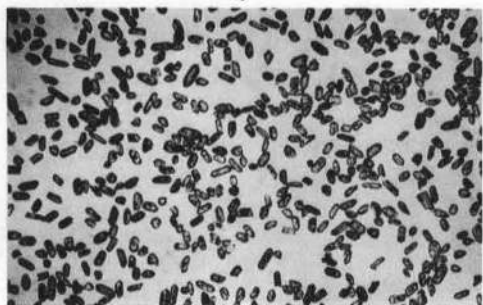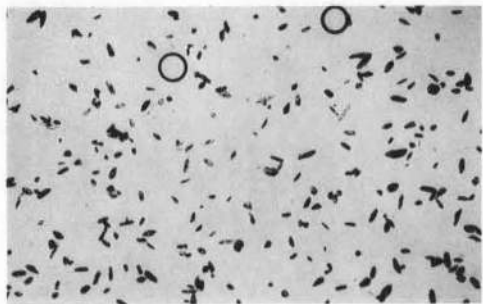R200 fraction zircons displaying characteristic habits, zoning, and inclusions

Photomicrographs showing enlargements of different Zircons

paratory to mineral separation. In general, the percentage of complete grains increases in the finer size fractions to more than 80 per cent of the grains in the passed 400-mesh size. Typically, the crystal forms present include two prominent prisms, a ditetragonal dipyramid and a tetragonal dipyramid (see pl. 1, *a–f*). The basal pinacoid and another dipyramid are more uncommon. The average length-to-width ratio for each fraction is in the range 2.3–2.5.

The color appears to vary in intensity among the grains but does not change appreciably in hue. Individually, lavender with a slight brown tint is predominant; in the aggregate the concentrates generally have a distinct brownish cast. Within a few individual grains there appears to be a slight color zoning with deeper intensities toward the center. This may sometimes be more apparent than real because the abundance of inclusions is usually greatest in the centers, and this may affect the light absorption in this region.

The zircons are distinctly zoned in most cases (see pls. 1, *a–f*, 2, *d*). The zoning is physically apparent under microscopic examination in the form of surfaces of optical discontinuity within the grains. From these surfaces Becke lines are generated that follow, in general, the typical forms of the external crystal faces. The Becke line behavior indicates that the higher index of refraction is more commonly in the crystal interior. In some grains, however, reversals in apparent index of refraction were noted. Some of the zones are marked by fine, dusty, opaque (?) inclusions. Although the external crystal forms are usually represented among the

zone forms, it is not uncommon that the relative development of the forms is changed drastically from within to without.

Only rarely are the individual zircon grains free from some type of inclusion or other imperfection. Inclusions fall into the following categories:

1. Stubby to slender prisms, usually less than 10 μ in diameter, and with length-to-width ratios of 2:12. They are distinctly lower in index than the host zircon with a very low birefringence invariably masked by that of the zircon. These characteristics plus terminations that are characteristically "rounded" basal pinacoids suggest apatite. The prisms may be aligned parallel to the zones or, equally as common, randomly oriented.

2. Equant, anhedral forms with very strong negative relief against the zircon. Indexes are apparently much lower than the grain-mount medium containing the zircon. Low or no birefringence. These may be feldspar or structural cavities. No evidence of a fluid phase was observed.

3. High index, euhedral grains, 1–5 μ in diameter, with indexes very close to that of the host. Forms and length-to-width ratios suggest these are probably other zircon grains. This is much less common than types 1 and 2.

4. Dark-brown zircon grains, 10–40 μ in diameter, with apparently rounded outlines overgrown by typical zoned zircon. Sometimes these zircon inclusions are surrounded by a halo of radiating fractures in the host. Only one or two of these are observed in a grain mount of several thousand grains.

5. Fine, opaque (?) "powder" usually barely resolvable with an oil immersion lens. Rarely this "powder" completely clouds a zircon core.

6. Red-brown plates, 1–5 μ in diameter. These

PLATE 2

a, Fragment of uranothorite in unwashed zircon concentrate. ×100. *b*, Autoradiograph of unwashed concentrate showing dense cloud of α-tracks over a uranothorite grain. ×100. *c*, Zircon residual (R200 fraction) from which outer 55 per cent of volume has been stripped by partial fusion. ×100. *d*, Zircon crystal aliquot (R200f raction) used for stripping experiment. Compare forms with 2, *c*, and 2,*f*. ×100. *e*, Zircon concentrate (R300 fraction) showing typical form and purity. ×8. *f*, Zircon residues of same experiment as 2, *c*. Compare residual form with internal zoning and with forms in 2, *d*. *g*, Residue of aliquot of zircon concentrate in 2, *e*, from which 99.7 per cent has been dissolved. Note common prismatic form. ×8. *h*, Enlargement of several grains from residue in 2, *g*, showing persistent prismatic forms. ×100.

appear to be an iron oxide of some form. Quite uncommon.

7. Tubes (see pl. 2, *d*), spheres, ellipsoids, isotropic with very strong negative relief, some of which can be clearly observed to be cavities. Most of these are geometrically oriented relative to the host zircon structure. None have been observed to have a fluid phase in them. Rarely these may have diameters equal to one-third that of the host.

8. Black, opaque, anhedral to subhedral, magnetic inclusions 1–3 μ in diameter.

9. Fractures radiating from nuclei of type 4 or more commonly from what appear to be simply darker zonal cores. Occasionally a brown film is observed coating some of these fractures. This type of fracture is observed in much less than 1 per cent of the zircons.

Types 1, 2, and 7 are by far the commonest types of inclusions. In considering these

TABLE 4

Grain Size Fraction	a_o	c_o
R200............	6.607 ± 0.002	6.009 ± 0.002
R300............	$6.608 \pm .002$	$6.012 \pm .002$
R400............	$6.608 \pm .002$	$6.012 \pm .002$
P400............	$6.610 \pm .002$	$6.010 \pm .002$
R200 (fusion residue)*......	6.604 ± 0.002	6.006 ± 0.005

* This sample was held in sodium tetraborate flux for one hour at 1100° C.

zircons as chemical systems, the inclusions cannot be ignored. They will be discussed again in the section on nuclear emulsion studies.

Index of refraction measurements were made on all size fractions of zircon. High-index liquids prepared by R. P. Cargille Laboratories after the descriptions of Meyerowitz and Larsen (1951) were used with a sodium light source. The oils were checked for stability by comparison with standard zircons of known indexes.

In all size fractions, a range of index properties was observed. This range is almost identical for all size fractions with $n_o = 1.900$–1.920 (± 0.005) and $n_e = 1.950$–1.970 (± 0.005). In general, most of the zircons fall into the range $n_o = 1.910$–1.920

and $n_e = 1.955$–1.970 with a few darker individuals showing the lowest values. Observations of indexes of zoned fragments indicated slight variations. The intervals in the refractive indexes of immersion oils did not permit a refined determination of these differences.

Comparison of these index determinations with the range of published values (n_o from 1.920 down to 1.810) for zircon indexes indicates only minor reduction of the indexes as a result of radiation damage.

X-ray powder diffraction studies were made on several of the size fractions of the zircon. A Norelco X-ray source equipped with goniometer spectrometer was employed. Using filtered Cu radiation ($K\alpha = 1.5405$Å), uniformly ground powders of zircon mixed with NaCl for an internal standard were scanned at 1/8° per minute speed. Peaks used for the determination of cell dimensions were {200}, {400}, {112}, {312}, {321}, and {331}. Peak shapes were all well defined. A very slight suggestion of asymmetry toward lower 2θ values is the only indication of peak broadening. The multiple solutions for cell dimensions agreed within the indicated limits of error in table 4. The c_o/a_o ratio is distinctly larger than those reported by Holland and Gottfried (1955, p. 294) for both Ceylon gem zircons and granitic accessory zircons. It is clear, however, that the cell dimensions are not unusually expanded by radiation damage. Within the limits of assigned error the c_o values of all unheated zircon fractions are the same. Using the curves of Holland and Gottfried (1955) or Fairbairn and Hurley (1957), the c_0 value indicates a modest radiation dosage of about 1.0×10^{15} α-particles/mg.

The heated sample of the retained 200 fraction is apparently a partly or completely annealed zircon with distinctly reduced cell dimensions, but it preserves the distinctively larger c_o/a_o. This suggests that this ratio may be an original characteristic for these zircons. The application of existing curves for c_0 versus radiation damage thus may give

unduly large values for the radiation damage retained by these crystals.

An explanation of this unusual c_o/a_o ratio possibly may be found in the zirconium/hafnium ratio. X-ray fluorescence comparisons of peak intensity ratios for Zr and Hf indicate the Johnny Lyon granodiorite zircons have the lowest Zr/Hf ratio of a dozen granitic zircons examined. These are preliminary results which have not been calibrated on an absolute basis.

Uranothorite.—The most abundant mineral impurity in the zircon concentration is uranothorite (see pl. 2, *a*, *b*). Although its abundance ranges from only 0.3 to 0.7 per cent in the various size fractions, the contribution by uranothorite to the radioactivity of each size fraction is as great or greater than that of the zircon. Its physical properties are quite variable. The individual particles show no crystal faces and are bounded by conchoidal to irregular fracture surfaces. It ranges in color from yellow to orange to red to brown and black even within single grains. Generally translucent, it may contain a disseminated opaque dust. The luster varies from glossy to dull. It is optically isotropic and index of refraction measurements yielded a number of values ranging from 1.702 to 1.720 for the sodium D line. The specific gravity appears to range between 5 and 6 and averages 5.3.

X-ray diffraction powder photographs yielded no reflections. After heating to about 600° C. in a reducing flame of a Bunsen burner, an aggregate of about twenty grains yielded a weak diffraction pattern most readily interpreted as a mixture of huttonite and thorite reflections.

One milligram of hand-picked uranothorite grains was mixed in a matrix of 25 mg. mixed ferric and aluminum oxide, and examined by emission spectroscopy. Thorium, 1–2 per cent, uranium, 0.2 per cent, silicon about 1 per cent, and traces of zirconium and lead were the only elements observed in addition to those of the matrix. This recalculates to about 25–50 per cent Th, 5 per cent uranium, about 25 per cent silicon, and

the results confirm an approximate composition of a member of the thorite family.

It is quite possible that in addition to thorite or uranothorite, which is clearly in a highly metamict state, related and equally metamict materials, such as thorogummite and huttonite, may be present among the grains assigned to this mineral in the concentrates.

Other impurities.—Quartz and the feldspars, epidote group minerals, apatite, and sphene may also be present as impurities. Apatite is removed in the hot-acid-wash treatment along with the uranothorite. The other minerals have been examined for their concentrations of uranium, thorium, and lead. It is clear that their combined contributions to the concentrates at their abundance levels is negligible, compared to other sources of error.

α-PARTICLE ACTIVITY STUDIES

Two types of α-particle activity measurements have been made on the zircon concentrates. A scintillation counter employing a zinc-sulfide phosphor and RCA 5819 photomultiplier tube was used to measure specific activity values for thick source samples of the various concentrates. In addition, individual zircon grain activities were measured by means of nuclear emulsions.

Scintillation counter measurements.—The contributions of the uranothorite to the total α-activities of the unwashed concentrates are readily observed with the scintillation counter. In figure 4, the specific activity in parts per million of equivalent equilibrium uranium is given for each of the size fractions before and after acid-washing treatment. In addition, the specific activity of aliquots of R200- and R300-mesh zircon fractions, hand-picked free of other minerals, is shown. All of these measurements have a statistical reproducibility of ±2 per cent.

Uranothorite makes the greatest contribution to the activity of the coarser fractions, and even in the passed 400-mesh fraction the uranothorite is more radioactive than all of the zircon in the aliquot. It is also

clear that mechanical purification by hand-picking and chemical purification by acid-washing produced essentially the same reductions of the levels of radioactivity.

Nuclear emulsion study.—The preparation of the zircons for the nuclear emulsion consisted of imbedding several hundred unwashed zircon grains of retained 200-mesh size fraction in a cold-setting high-strength

☐ Unwashed uranothorite-bearing concentrate

△ Acid-washed concentrate

⊙ Hand-picked uranothorite – free concentrate
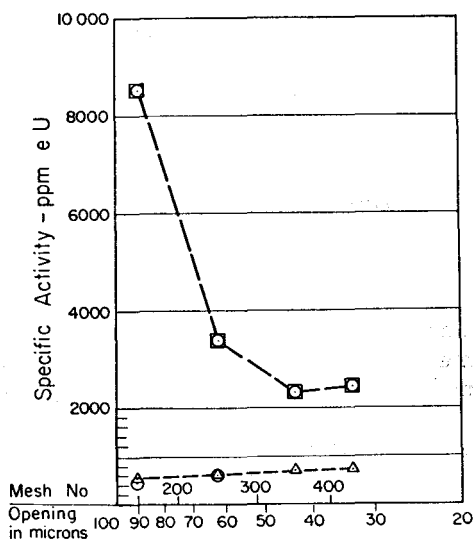

FIG. 4.—Comparison of α-particle specific activities measured by scintillation counter for unwashed, acid-washed, and hand-picked zircon concentrates of different size fractions.
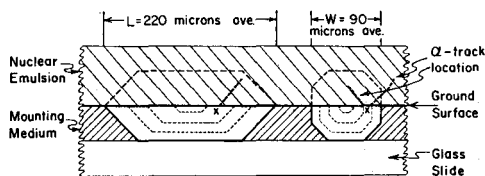

FIG. 5.—Method of preparation of zircons for nuclear emulsion study. Diagrammatic representation of a ground zircon grain mount covered with Kodak NTA nuclear emulsion for autoradiographic exposure to measure α-particle activity distribution in individual zircon grains.

plastic on a glass slide. The zircons lie, in general, on prism faces with c-axes parallel to the slide surface. The grains were ground with very fine abrasive to about a 40–50-μ thickness, which is about half their original thickness. They are thus sectioned longitudinally with a surface that transects most, if not all, of the internal zones. After careful cleaning with xylene, the slide was allowed to dry thoroughly. A layer of liquid nuclear emulsion (Kodak NTA) approximately 100 μ thick was applied to the entire grain mount. Figure 5 illustrates a prepared autoradiograph of this type. The emulsions were exposed for 3 months in a nitrogen atmosphere in a heavy steel tank at 0° C.

When developed, the emulsion and grain mount were carefully examined to select grains of complete crystal form, appropriate orientation, and successful α-track development (pl. 1, *g, h*). Photomicrographs of these grains were enlarged with a linear magnification of 300✕. The grains and superimposed emulsion were then examined under a microscopic magnification of 1,000✕. The point of emergence of each α-track originating in a given grain was plotted as a point on the enlarged photograph of the grain. By this procedure a "photomap" was constructed of the points of emergence of all α-particles on the ground surface. Figure 6 illustrates these maps. Specific activities may be determined for the various areas of the zircon, provided the thickness of the α-emitting source is constant. For zircons we have considered a 20-μ thickness to be an infinitely thick source.

Under ideal conditions this sytem should provide an accurate means of determining the relative specific activities of the various parts of a zircon grain. Several factors may interfere. These are (1) inappropriate orientation of the zircon and its cut surface (to various degrees), (2) departure of the ground zircon from infinite thickness at the dipyramidal terminations, (3) fading of the α-tracks, (4) shadow zones at the interface between zircon and the mounting medium that may conceal overlying α-tracks from observation; (5) obtaining adequate statis-

tics within a single grain with a surface area of 0.015–0.020 mm².

The first factor was eliminated by selecting from the total zircon population those of optimum morphology and orientation. The second factor may be compensated for by a geometrical calculation that provides a correction for the zircon volume missing from underneath that part of the crystal terminations less than 20 μ thick. This can be considered only approximate, being dependent

grain) has been solved with only moderate success. The shadow zone is the product of the index of refraction difference between the zircon and mounting medium. The invariable existence of a second-order prism face and complex pyramidal forms also contributes to critical reflection in the border zone. A substage condenser of large angular aperture on the observer's microscope increased the illumination in this area. Comparison of three observers' independent
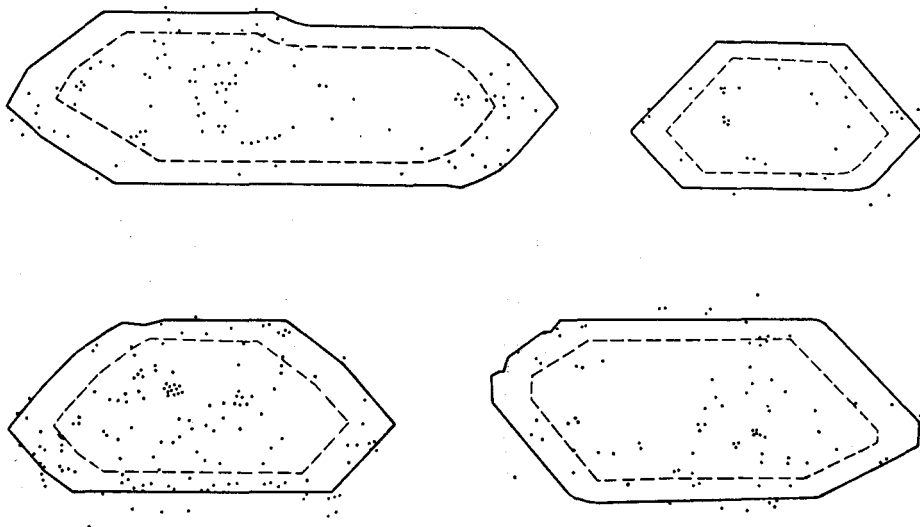

Fig. 6.—Alpha-particle track origins in several zircons, R-200 mesh fraction, Johnny Lyon granodiorite (zoned for a core of 45 per cent of total volume). Outline maps of four zircons showing the distribution of origin points for α-particle tracks observed in the adjacent emulsion. Note the lack of unusual concentrations of points indicating absence of particulate localization of activity within the zircons.

upon interpretation of the zircon terminal morphology and upon the mean α-particle range in the zircon which will in turn depend upon the U:Th ratio. One model calculation requires a 20 per cent increase over the number of α-tracks observed in the outer 20 μ of each zircon termination. The fading of the α-tracks is a random phenomenon that should not bias the relative data. It does make more difficult the discrimination of individual tracks in areas of high activity.

The problem of track observation in the shadow zone (which constitutes a significant fraction of the ground surface area of each

work on individual grains shows an over-all reproducibility of better than 5 per cent. Almost all discrepancies, however, occurred in observing tracks in the border shadow zone. It is possible that perhaps as many as several tracks per grain have been overlooked along the shadow zone. This tends to be a consistent source of error for most of the grains observed and should not seriously affect the relative activities of the various grains studied. The effect must be considered to be more serious in analyzing the zonal distribution of activity.

The final problem of obtaining adequate

TABLE 5

NUCLEAR EMULSION OBSERVATIONS OF TOTAL AND SPECIFIC ACTIVITIES OF INDIVIDUAL ZIRCONS

Grain Number	Total α-Particles	Observed Whole-Grain Specific Activity (10^5 α's/cm²)	Observed Inner-Zone Specific Activity (10^5 α's/cm²)	Observed Outer-Zone Specific Activity (10^5 α's/cm²)	Corrected Outer-Zone Specific Activity (10^5 α's/cm²)
A-3-1	227	6.82	6.42	7.38	7.64
A-7-1	35	1.51	1.02	2.25	2.29
A-8-1	140	6.41	6.19	6.71	6.87
A-8-2	55	3.70	3.43	4.14	4.50
A-11-1	77	3.82	4.35	3.06	3.18
A-13-1	98	5.00	5.43	4.34	4.45
A-13-2	42	3.30	2.50	4.41	4.41
A-14-1	124	7.09	7.53	6.45	6.70
A-15-1	72	3.98	4.57	3.12	3.25
A-18-1	72	4.23	4.38	4.04	4.24
A-21-1	12	1.20	0.86	1.73	1.78
A-22-1	76	5.25	5.85	4.35	4.50
A-22-2	50	5.03	5.62	4.20	4.25
A-24-1	77	6.36	6.66	5.86	6.10
A-24-2	41	3.52	3.49	3.58	3.64
A-26-1	110	9.48	10.71	7.70	7.85
A-26-2	37	3.73	3.42	4.23	4.38
A-26-3	27	2.04	2.04	2.04	2.16
A-28-1	71	6.11	6.67	5.28	5.39
A-28-2	103	4.48	4.80	4.00	4.02
A-29-1	81	5.40	4.51	6.69	7.02
A-29-2	47	2.41	1.45	3.77	3.94
B-5-1	107	3.49	3.73	3.12	3.23
B-6-1	31	3.24	3.02	3.64	4.05
B-7-1	24	1.64	1.73	1.51	1.65
B-8-1	58	5.34	5.74	4.75	4.80
B-10-1	35	2.81	2.44	3.36	3.46
B-14-1	90	5.03	4.91	5.22	5.25
B-17-1	140	9.81	8.14	12.01	12.35
B-18-1	49	3.43	3.43	3.43	3.56
A-5-1	73	5.52	5.61	5.37	5.44
A-24-3	132	9.72	10.30	8.95	9.30
A-6-1	145	14.48	11.45	18.89	19.64
A-9-1	97	5.80	4.63	7.47	7.76
A-20-1	51	9.44	9.07	10.03	11.28
A-27-1	89	8.67	7.41	10.52	11.17
A-27-2	132	9.81	10.47	9.37	9.43
A-27-3	176	9.69	10.22	8.92	9.13
A-27-4	113	9.88	11.94	6.85	7.40
B-1-1	160	8.67	7.93	9.69	9.81
B-1-2	138	6.17	5.12	7.69	7.87
B-2-1	115	5.68	5.40	6.08	6.39
B-16-1	204	10.65	7.22	14.30	14.70
Total: 43 grains	3,833	....	....	....	....
Averages	....	5.67	5.50	5.89	6.14

statistics per grain is limited by the moderate activity of these zircons and their minute size. More prolonged exposure times are indicated, but even this may be limited by the problems of track fading.

In table 5, total observed α-tracks and specific activities are listed for forty-three grains on whose surfaces a total of 3,833 tracks were observed and plotted. Approximately 87 tracks were observed per grain, but the number of tracks per individual ranged from 12 to 227. The specific activity, presented in units of 10^5 α-particles/cm^2/ exposure time, averaged 5.67 per grain, but ranged from 1.51 to 14.48, that is, nearly an order of magnitude variation among invidual crystals.

For comparison with experiments described later, the plotted α-particle distribution of each mapped grain was divided into totals for a central core with similar form but dimensions 77 per cent of those of the over-all crystal, and an outer zone consisting of the rest of the crystal. This dimension was chosen to represent an inner volume of 44.5 per cent of the total crystal. For the inner zone an average specific activity of 5.50 ($\times$ 10^5 α's/cm^2/exposure) was measured, for the outer zone an average apparent specific activity of 5.89 ($\times$ 10^5 α's/cm^2/exposure). To the latter, an approximate correction based upon a geometric solution for less than infinite thickness at each pyramidal termination was made for each grain observed. The correction increased the outer zone activity to 6.14 ($\times$ 10^5 α's/cm^2/exposure).

The following observations on the results of the nuclear emulsion study seem pertinent.

It is quite clear that within the assemblage of morphologically homogeneous zircons of the retained 200 fraction a wide range of individual activities exists. The total of forty-three grains does not provide very good statistics, but a plot of the frequency distribution of specific activities is given in figure 7. There is an indication of a bimodal distribution with a major concen-

tration at about 5 ($\times$ 10^5 α's/cm^2/exposure) and a secondary peak at 9 or 10.

The more radioactive grains tend to have darker colors, perhaps with this emphasized in the cores. They are otherwise similar in crystal form, in degree of zoning, and in the abundance and nature of inclusions. A significant characteristic of the distribution of activity within the grains is that despite the abundance and variety of inclusions, very little of the activity seems particularly lo-

Frequency Distribution of
Individual Zircon Specific Activity
From R200 Autoradiograph
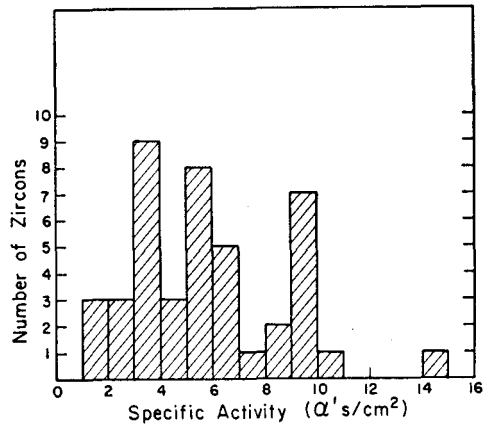
FIG. 7.—Histogram showing frequency distribution of specific activity in individual zircons. Activity units are relative and each unit represents 10^5 α-particles/cm^2 observed.

calized. This is true not only for the forty-three mapped grains but also for about 200 additional grains that were inspected qualitatively. About the only indications of localization are found in a few grains in which five or ten tracks appear to emanate from the vicinity of a fracture.

In contrast, the few grains of uranothorite present in the unwashed concentrate used for this autoradiograph give intense opaque patterns of α-tracks (pl. 2, b). It is clear that the only important contributions of activity from impurities came from such external sources as the uranothorite.

The evidence for zoning of radioactivity within the zircon is modest. The data were derived from a small sample population. A number of problems in observation and analysis of the data are not completely solved. The direction of the two most important sources of error, however, is probably such as to understate the importance of radioactivity in the outer zones of the crystals. For this reason, we believe that the suggestion of a 10 per cent increase in α-activity in the outer 55.5 per cent of the *average* crystals is probably both real and minimal.

ISOTOPIC STUDIES

The uranium-lead isotope relationships in the zircon concentrates have been studied in considerable detail. It would have been appropriate to determine thorium in the same procedure, but problems involving the use of thorium[230] tracer with the available equipment have interfered. The following experimental descriptions will be divided into two parts: (1) uranium and lead in the zircon concentrates as a function of zircon size and uranothorite content; (2) an approach to the study of internal isotopic relations within zircons.

ANALYTICAL PROCEDURE

The chemical procedures followed in the isotopic analysis of the mineral separates are generally similar to those developed by Tilton and Patterson (Tilton *et al.*, 1955; Tilton *et al.*, 1957). The specific procedure is described in Silver, McKinney, Deutsch, and Bolinger (1963). Aliquots of zircon concentrate were washed in 100 mls. of hot (80° C.) concentrated HNO_3. The acid and three subsequent rinses of quadruple distilled water were decanted into a clean Pyrex container and set aside (for separate analysis, where necessary). The uranium and lead concentrations were determined by isotope dilution measurements. To an approximate degree, the scintillation counter measurements of α-activity have permitted calculation of an "equivalent thorium content." It must be emphasized that, aside from assumptions concerning equilibrium and self-absorption

characteristics, this calculation places the combined errors of counting and isotope-dilution uranium determination into the thorium value.

Isotopic analyses were performed on a 12-inch radius, 60° sector, single-focusing mass spectrometer modified and constructed by C. R. McKinney at the California Institute of Technology from a design by M. G. Inghram of the University of Chicago. Chow and McKinney (1958) and Chow and Patterson (1959) have reported on the reproducibility of data from this instrument using common leads for analysis. On most of the data reported here, the assigned mass spectrometric error is somewhat higher, reflecting ratios in radiogenic leads which depart further from unity. In general for most runs our data show reproducibility errors of 0.5–1.5 per cent for Pb^{206}/Pb^{204}, 0.3 per cent for Pb^{206}/Pb^{207}, 0.3 per cent for Pb^{206}/Pb^{208}. Uranium aliquots are spiked generally so that the U^{235}/U^{238} mixtures are close to unity and results obtained are reproducible within ± 0.5 per cent. Somewhat larger errors assigned in the data (table 6) include errors in spike aliquoting, chemistry losses, and uncertainties in corrections for common lead.

For correction of common lead, we have used a single composition chosen because a number of experiments have indicated that most of the common lead observed in our samples is from our reagents and glassware. We have analyzed lead extracted from our reagents during their purification and have adopted a common lead composition of $Pb^{204}:Pb^{206}:Pb^{207}:Pb^{208}$ of 1:18.70:15.50:38.20. It appears possible to treat the entire body of analyses for selection of a more precisely compatible correction. The general results and conclusions would not be changed, however.

SAMPLE REPRODUCIBILITY

In table 6, three analyses of separate aliquots of R300 zircons are listed for evidence of reproducibility. The conditions are not quite comparable in that there was 0.3 per cent residue of undissolved zircon in sample

II and a 3.0 per cent residue in sample III. This rules out the use of concentration figures from sample III, but the effects on sample II values are negligible. It should be noted also that the concentrates used for samples II and III were separated from a different aliquot of the original rock sample than that from which sample I was derived.

The importance of the acid-wash treatment in removing the uranothorite contribution from the zircon is illustrated in table 7. Three sets of comparative analyses illustrate several points.

nizable difference, it is also apparent that the two analyses are sufficiently similar so that the acid-washing treatment has no profound effect on the zircon itself.

In the second set, B, a pair of R300-mesh zircon aliquots with different acid-wash treatments indicate the necessity of arriving at an adequate acid treatment to remove the uranothorite completely. Again, the two analyses are similar but with perceptible evidence of a slight uranothorite residue in the zircon washed in dilute acid for a shorter term.

TABLE 6

REPRODUCIBILITY OF ANALYSES ON ACID-WASHED RETAINED 300-MESH ZIRCONS

	WEIGHT (GM.)	OBSERVED ISOTOPIC RATIOS			RADIOGENIC LEAD COMPOSITION (ATOM PER CENT)		
		Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{206}/Pb^{208}	Pb^{206}	Pb^{207}	Pb^{208}
R300 I......	0.2523	894.5	8.840	4.359	77.60	7.59	14.81
R300 II.....	0.5159	1149	9.054	4.493	77.48	7.63	14.89
R300 III....	0.3486	1012	8.939	4.420	77.49	7.62	14.89

	WEIGHT (GM.)	CONCENTRATIONS (P.P.M.)			ATOM RATIOS	
		Pb^r*	U	eTh†	Pb^{207r}/Pb^{206r}	Pb^{208r}/Pb^{206r}
R300 I.....	0.2523	103.1	542	245	0.0978	0.191
R300 II....	0.5159	101.8	534	260	0.0986	0.192
R300 III...	0.3486	....	....	....	0.0986	0.192

*Pb^r = Radiogenic Pb.

‡ eTh = Equivalent thorium calculated from specific α-activity and uranium concentration.

In set A, 90 mg. of unwashed R200-mesh zircon, painstakingly hand-picked free from all visible uranothorite grains, were compared with similar zircons from which uranothorite had been removed by a standard 1-hour bath in concentrated HNO_3 at 80° C. It is clear that the hand-picked sample has a measurably higher radiogenic lead concentration and a distinctly more Pb^{208}-rich lead composition. The increase in U concentration is barely outside the limits of error but is probably real. These differences are all compatible with a very small uranothorite residue, indicating a hand-picking efficiency of more than 95 per cent. Despite the recog-

Finally in set C, a pair of P400-mesh zircon aliquots were treated with the same acid, one for the standard 1-hour treatment, the other for 14 hours in about three times as much acid, and with a temperature that reached the boiling point, 86° C., for at least half that time. The similarity in the data is clear. The slight apparent drop in concentrations verges on the error limits. There is no significant difference in the Pb^{208}/Pb^{206} indicating that uranothorite probably is not contributing to either aliquot. It may be concluded therefore that the standard wash treatment is effective in removing all activity soluble in acid.

Two fractions of retained 300-mesh zircon, separated independently from different aliquots of the original rock samples, were acid-washed under different conditions. The acid washings were analyzed in each case, and the results are reported in table 8 in the form of yield per gram of zircon washed. The

It is interesting to note that the acid washes contained 80 per cent as much uranium as the residual zircon concentrate and about ten times more thorium. The radiogenic lead content in the wash is only 40 per cent of that in the zircon, however. It appears, therefore, that in terms of U-Pb equilibrium (and also implied for the Th-Pb

TABLE 7

INVESTIGATION OF EFFECTS OF ACID-WASH TREATMENT ON ZIRCONS

SAMPLE	TREATMENT (ACID-WASHED AT 80°C.)	WEIGHT (GM.)	OBSERVED RATIOS			RADIOGENIC LEAD COMP. (ATOM PER CENT)		
			Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{206}/Pb^{208}	Pb^{206r}	Pb^{207r}	Pb^{208r}
A								
R200 ...	Hand-picked	0.0900	505.9	7.898	3.599	76.33	7.60	16.06
R200 ...	HNO_3 (conc.) 1 hr.	0.2123	861.5	8.714	4.495	78.06	7.72	14.23
B								
R300 ...	HNO_3 (2N) ½ hr.	0.3573	736.9	8.549	3.933	76.55	7.53	15.91
R300 ...	HNO_3 (conc.) 1 hr.	0.2523	894.5	8.840	4.395	77.60	7.59	14.81
C								
P400	HNO_3 (conc.) 1 hr.	0.2472	1139.0	9.100	4.325	76.98	7.53	15.48
P400	HNO_3 (conc.) 14 hrs.	0.1661	248.6	6.474	2.937	76.84	7.64	15.53

			CONCENTRATIONS (P.P.M.)		Pb^{208r}/Pb^{206r}
			Pb^r	U	
A					
R200 ...	Hand-picked		103.0±1.0	520±5	0.210
R200 ...	HNO_3 (conc.) 1 hr.		100.3±1.0	510±5	0.182
B					
R300 ...	HNO_3 (2N) ½ hr.		108.2±1.0	571±5	0.208
R300 ...	HNO_3 (conc.) 1 hr.		103.1±1.0	542±5	0.191
C					
P400	HNO_3 (conc.) 1 hr.		106.7±1.0	579±5	0.201
P400	HNO_3 (conc.) 14 hrs.		105.9±1.0	567±5	0.202

two sets of data are impressively similar considering the different history of each sample in terms of mineral concentration and wash preparation.

The isotopic composition of the lead and the implied U/eTh ratio confirm the composition of the soluble material as a uranothorite. Weight losses during acid washing were so small as to prevent calculation of an actual gravimetric composition, but a composition of about $Th_{0.85} U_{0.15} SiO_4$ is suggested.

equilibrium), the uranothorite is a very different system than the zircon.

Apparent ages calculated for the uranothorite systems are in profound discordance.

ISOTOPIC PROPERTIES AS A FUNCTION OF ZIRCON GRAIN SIZE

The isotopic analyses of the four principal size fractions of zircon are given in table 9. It is important to bear in mind that the properties discussed are composite characteristics of concentrates containing 10^4 to

TABLE 8

Isotopic Analyses of Uranothorite Wash Solutions

	Wash Solution	Time	Temp.	Weight Zircon (Gm.)	Conc.	Observed Isotopic Ratios			Radiogenic Lead Comp. (Atom Per Cent)		
						Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{206}/Pb^{208}	Pb^{206}	Pb^{207}	Pb^{208}
R300 #1.....	HNO$_3$ (dil.)	½ hr.	80° C	0.3573	g	141.4±1.0	5.529±0.02	0.4542±0.002	30.2	2.48	67.3
R300 #2.....	HNO$_3$ (conc.)	1 hr.	80° C	0.8474	g	65.9±0.6	3.394±0.01	0.4416±0.002	29.1	2.41	68.5

	Concentrations*			Atom Ratios					Apparent Ages (Millions of Years)			
	Pb^r	U	eTh	Pb^{207r}/Pb^{206r}	Pb^{208r}/Pb^{206r}	Pb^{206r}/U^{238}	Pb^{207r}/U^{235}	Pb^{208r}/Th^{232}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}	Pb^{208}/Th^{232}
R300 #1.....	41.7±0.5	409±4	(2610)†	0.0820	2.227	0.0355	0.402	0.01204	227±30	348±40	1267±40	(245)±100
R300 #2.....	42.1±0.5	390±4	2610†	0.0830	2.353	0.0363	0.414	0.01237	232±30	356±40	1291±70	(250)±100

* g/g zircon washed.

† eTh determined from scintillation radiometry measurements on concentrates before and after acid washing.

TABLE 9

JOHNNY LYON GRANODIORITE ZIRCONS

SIZE FRACTION (PRISM DIAM.)	SAMPLE WEIGHT (GM.)	OBSERVED ATOM RATIO			RADIOGENIC LEAD COMP. (Pb^r) ATOM PER CENT			CONCENTRATIONS (P.P.M.)		
		Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{206}/Pb^{208}	Pb^{206}	Pb^{207}	Pb^{208}	Pb^r*	U	$eTh†$
R200 mesh (150–75 microns)............	0.2123	862±6	8.71±.04	4.495±.02	78.06	7.72	14.23	100.3±1.0	510±5	190±40
R300 mesh (75–52 microns)............	.2523	894±6	8.84±.03	4.359±.02	77.60	7.59	14.81	103.1±1.0	542±5	245±50
R400 mesh (52–37 microns)............	.2404	1113±8	9.04±.04	4.448±.02	77.38	7.61	15.00	103.1±1.0	569±5	285±60
P400 mesh (37–20 microns)............	0.2472	1139±8	9.10±.04	4.325±.02	76.98	7.53	15.48	106.7±1.0	579±5	335±70

	ATOM RATIOS						APPARENT AGES‡ (MILLIONS OF YEARS)			
	eTh/U	Pb^{207r}/Pb^{206r}	Pb^{208r}/Pb^{206r}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{208}/eTh^{232}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}	Pb^{208}/eTh^{232}
R200 mesh.............	0.38	0.0989	0.182	0.1784	2.430	0.0845	1070±20§	1270±20	1630±20	(1660±400)
R300 mesh.............	.46	.0978	.191	.1716	2.311	.0701	1030±20	1230±20	1610±20	(1390±300)
R400 mesh.............	.51	.0984	.196	.1630	2.207	.0610	980±20	1200±20	1620±20	(1210±250)
P400 mesh.............	0.59	0.0979	0.201	0.1649	2.221	0.0554	995±20	1205±20	1610±20	(1100±250)

* Pb^r = radiogenic lead.
† eTh = radiometric equivalent thorium.

‡ Calculated with the following constants:
$U^{235}/U^{238} = 1/137.8$, U^{238}, $= 1.537 \times 10^{-10}$/yr.
U^{235}, $= 9.72 \times 10^{-10}$/yr. Th^{232}, $= 4.99 \times 10^{-11}$/yr.
§ Error assignments for ages are precision errors only.

10^6 individual grains. All of these aliquots were given the standard acid-wash treatment.

A number of systematic variations in isotopic properties are apparent (fig. 8). The zircon concentrates show a progressive increase in the radiogenic lead, uranium, and equivalent thorium concentrations with progressive decrease in size fraction. The lead isotopic composition shows a marked increase in the Pb^{208}/Pb^{206} ratio with decreasing size. This is parallel with the change in eTh/U. The Pb^{207}/Pb^{206} ratio has a range of variation so limited that the apparent decrease with decreasing size falls almost within assignable error limits and may not be real. The ratios Pb^{206}/U^{238}, Pb^{207}/U^{235} and Pb^{208}/Th^{232} all appear to decrease with decreasing size, although the R400 and P400 fractions appear to be very similar in several instances.

The nature of the systematic variations may be explained by one of the following interpretations: (a) There is a progressive increase in the content of residual undissolved uranothorite with decreasing size of the concentrate. (b) There are discrete radioactive inclusions in the zircon of appropriate U/Th and U/Pb ratios which vary systematically in abundance and/or composition with the zircon grain size. (c) There are systematic variations in the concentrations of U and Th (as well as radiogenic products) in the zircon lattice structure which can be related to variation in grain size.

The possibility of residual uranothorite must be considered first, of course. A number of experiments have been described already which indicate that an adequate acid-bath step has been devised to remove all exposed uranothorite. In addition, the comparison of washed and unwashed concentrates illustrated in figure 4 strongly suggests that, if residual uranothorite existed among the washed zircons, it should be more abundant in the coarser fractions. This would be expected not only from original abundances but from the longer dissolution times required by coarser grain size. The observed trend is not compatible, therefore,

with such an interpretation. Further, several of the trends in the isotopic ratios, while suggestively enriched in Pb^{208} or eTh, do not fall on simple mixture curves with the analyzed uranothorites. It seems reasonable to dismiss this possibility.

Johnny Lyon granodiorite, L-312
Isotopic variations in Zircon
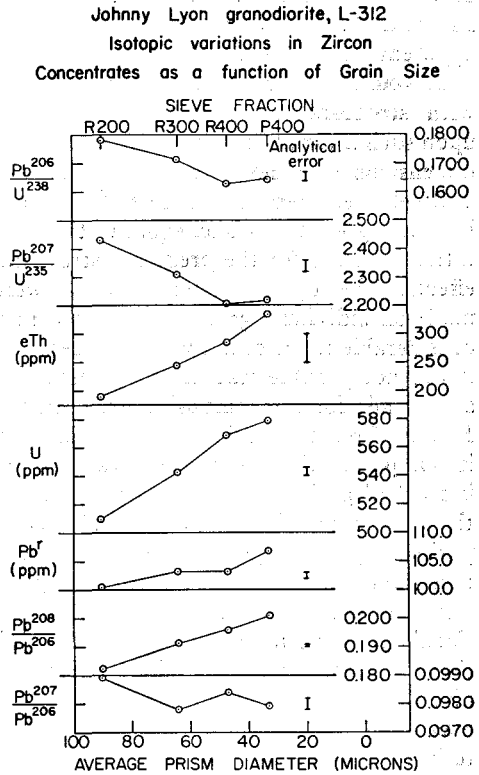Concentrates as a function of Grain Size

FIG. 8.—Columnar graph showing significant isotopic parameters in the U-Th-Pb systems of the L-312 zircons as a function of the average prism diameter of each sieve fraction. Precision errors are scaled on the right side of each graph.

The possibility of radioactive inclusions within the zircons, and therefore not available to the acid wash, is also considered unlikely. This conclusion is based upon the observation of several hundred grains in the nuclear emulsion study of α-particle activity already discussed. No evidence of particulate localization of the radioactivity was observed. Further, if intergrowth of uranothorite (or some other mineral) with zircon is stipulated, this is not in keeping with nu-

merous thin-section observations of the textural occurrence of the zircons. It is also not apparent why inclusion abundance and composition would vary so systematically with grain size.

The final alternative of real changes in uranium and thorium concentrations in the zirconium lattice site in the zircon structure apparently must be accepted.

It would be desirable to support this view with structural characteristics dependent upon such a variation, for example, unit-cell dimensions or indexes of refractions. The unit-cell measurements made so far do not have a degree of precision equal to the resolution required for the predicted structural effects. The optical determinations were made on individual grain fragments with a considerable range of individual values, and it was not possible statistically to establish any trends for the composite concentrates. Finally, from the nuclear emulsion studies, it is apparent that the range of variation of individual grain α-activities is much larger than the range for the various size composites. Thus the general trends observed must be considered as reflections of population trends rather than individual trends. Considering the range of individual activities observed, population shifts of the magnitude reported for the size fractions are reasonable. Indeed, they are small compared to internal variations within zircons as indicated in the next experiments described.

INTERNAL ISOTOPIC PROPERTIES OF THE ZIRCON

The trends of isotopic variation as a function of external grain size raise the question of what variations may exist as a function of location within an individual zircon. The coarsest zircon separate, the retained 200-mesh fraction, has individuals that average 220 μ in length and 90 μ in prism diameter. This corresponds to a weight of about 5×10^{-6} gm. with a content of 2.5×10^{-9} gm. of uranium and 5×10^{-10} gm. of radiogenic lead. Present techniques preclude complete isotopic analysis on such individuals.

We have attempted, therefore, to treat an aggregate of retained 200-mesh grains as a composite "crystal" and have proceeded to try to peel this "crystal" chemically.

An adequate stripping procedure must remove the layers of zircon in a determinable fashion, removing all uranium, thorium, and lead that existed together in radioactive relationship before the laboratory disturbance of the zircon, but it must not disturb the radioactive systems in the rest of the zircon. In other words each increment removal must preserve as closed systems for U, Th, and Pb, both the removed increment and the residual zircon. Recognizing the consistent zoned quality of these zircons, we have attempted to strip zircons parallel to their zones.

Procedure.—The method employed partial fusions of parallel aliquots of the same size zircon, with careful control of temperature and fusion duration. Initial experiments were only partly successful. On two retained 300-mesh aliquots, 2 hours at 1,150° C. and $\frac{1}{2}$ hour at 1,125° C. dissolved the samples nearly completely, leaving zircon residues weighing 0.3 per cent and 3 per cent, respectively. (These are the analyses R300 II and R300 III in table 6.) These experiments did indicate two important points: (1) the ease with which the outer part of the zircon is initially attacked by the flux and (2) the physical nature of the residue. Qualitatively it was apparent that the zircons generally did not disintegrate into fine fragments but remained as residuals with prismatic forms similar to the original shapes but much reduced in over-all dimensions. Plate 2, *g, h,* are photomicrographs of grains in a 1.2-mg. residue of an original 516-mg. sample. Plate 2, *e,* is a photomicrograph of the original zircon.

Using retained 200-mesh zircons, two two-stage dissolutions were completed. After the first fusion step, the contents of the crucible were removed by dissolution of the glass in dilute HCl. The products consisted of three parts: solution, gelatinous silica, and undissolved zircons. The solution and most of the lightweight gel were decanted from the zircons. The zircon residue was rinsed three times with quadruple distilled

water, each rinsing plus more gel being added to the total solution. The residue, consisting predominantly of zircon with some silica gel, was dried by rinsing several times with clean acetone. This was an unsatisfactory drying method, as will be discussed subsequently. The dry gel was mechanically loosened from the zircon by sieving several times through fine bolting cloth. The gel was then separated by flotation in clean s-tetrabromoethane with an eventual recovery of about 98 per cent.

The solution, after centrifugation of the silica gel, was analyzed for composition and

in uranium. The discrepancies are attributed to the treatment separating the decomposition products of the first dissolution step from the zircon residue. The siliceous residues were examined by X-ray powder diffraction and emission spectroscopy. A distinct powder pattern for zirconium oxide was observed in both cases. Zirconium was observed as a major constituent spectrographically. The presence of the zirconium oxide suggests incomplete washing of the siliceous residue and co-precipitation of uranium with the zirconium hydroxide to account for the significant content of urani-

TABLE 10

INITIAL FUSION CONDITIONS	EXPERIMENT A (20 Minutes 1050° C.)			EXPERIMENT B (20 Minutes 1080° C.)		
	Percentage Dissolved	Pb 10^{-6} gm.	U 10^{-6} gm.	Percentage Dissolved	Pb 10^{-6} gm.	U 10^{-6} gm.
Step I......................	37.5			55.5		
Solution.................		12.55	45.5		18.50	65.9
Silica gel...............		0.08	5.8		0.39	11.8
Step II.....................	62.5			44.5		
Residual zircon..........		17.05	76.0		11.4	54.5
Total...............		29.7	127.3		30.3	132.2
Predicted from total sample discrepancy..............		29.8 −0.1	151.5 −24.2		30.3 0.0	153.7 −21.5

concentration of lead and concentration of uranium. The combined silica, except for a small representative aliquot reserved for X-ray and spectrographic analysis, was digested in HF and $HClO_4$ and was analyzed for uranium and lead concentration, using the lead composition determined for the solution. The residual zircon, except for a representative aliquot reserved for X-ray and microscopic examination, was treated as a new sample and submitted to complete fusion and analysis.

Table 10 lists the conditions and results for each of the two experiments. The yields are corrected for aliquots removed for various purposes.

The lead balance is excellent in the two experiments, but there is a clear deficiency

um in the silica. It does not, however, explain in itself the deficiency in uranium. We suspect loss of uranium from the silica during dehydration of siliceous residue by acetone.

In table 11, the isotopic data are given for both experiments. In experiment A, the isotopic composition of lead and the concentrations of lead and uranium were determined for both steps. A calculation of the material balance from the data of the two steps is given for comparison with values for the total sample of retained 200 mesh. The agreement of the lead isotopic compositions and the lead concentrations is better than limits assigned for reasonable mass spectrometric errors. Because of the clear deficiency in total uranium, the value given in paren-

TABLE 11

CHEMICAL STRIPPING EXPERIMENTS ON RETAINED 200-MESH ZIRCON L-312

EXPERIMENT	PERCENTAGE DISSOLVED	SAMPLE WEIGHT (GM.)	OBSERVED ATOM RATIO			RADIOGENIC LEAD COMP. (Pb^r) ATOM PER CENT			CONCENTRATIONS (P.P.M.)		
			Pb^{206}/Pb^{204}	Pb^{206}/Pb^{207}	Pb^{206}/Pb^{208}	Pb^{206}	Pb^{207}	Pb^{208}	Pb^{r}*	U	eTh†
R200 mesh											
Total sample....	100.0	0.2123	862±6	8.71±.04	4.495±.02	78.06	7.72	14.23	100.3±1.0	510±5	190±40
Experiment A											
1st part........	37.5	.1115	575±4	8.25±.04	4.595±.02	79.76	7.77	12.48	113.5±1.5	460±?	n.d.‡
										(676)§	(255)§
2d part.........	62.5	.1855	676±5	8.31±.03	3.857±.02	76.39	7.65	15.94	91.2±1.0	410±4	150±40
Composite A....		.2970				77.84	7.70	14.46	99.7	430	
Experiment B											
1st part........	55.5	.1675	789±6	8.67±.03	4.820±.02	79.30	7.78	12.92	112.9±1.0	464±?	n.d.
										(593)	(220)
2d part.........	44.5	.1339	n.d.	n.d.	n.d.	(76.52)§	(7.64)	(15.84)	84.9±1.0	407±?	150±40
Composite B....		0.3014							100.4	428	

	ATOM RATIOS‖						APPARENT AGES (MILLIONS OF YEARS)			
	eTh/U	Pb^{207r}/Pb^{206r}	Pb^{208r}/Pb^{206r}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{208}/Th^{232}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}	Pb^{208}/Th^{232}
R200 mesh										
Total sample....	0.38	0.0989	0.187	0.1784	2.434	0.0845	1070±20	1270±20	1630±20	(1660±400)
Experiment A										
1st part........	.38	.0974	.156	.1557	2.088	.0625	940±40	1160±40	1600±40	(1240±500)
2d part........	.38	.1000	.202	.1974	2.722	.1090	1170±20	1350±30	1655±20	(2120±500)
Experiment B										
1st part........	.38	.0981	.163	.1755	2.370	.0746	1050±30	1250±40	1620±20	(1470±500)
2d part........	0.38	0.0998	0.207	0.1852	2.508	0.1027	1100±20	1290±20	1650±20	(2000±500)

* Radiogenic lead.

† Equivalent thorium calculated from specific α-activity and measured U concentrations.

‡ Not determined experimentally.

§ Values in parentheses are calculated from material balance.

‖ Pb^{206r}, Pb^{207r}, Pb^{208r} = radiogenic lead.

theses is calculated from material balance consideration.

In experiment B, the isotopic composition of lead in the second step was not determined experimentally because of the small size of the sample. A value determined by difference between the first stage and the total sample is given in parentheses. There is, however, a good agreement in the lead-concentration balance, and, of course, the deficiency in the uranium balance appears here.

The method of obtaining approximate data on thorium concentrations precluded any calculation of material balance for this

of former zones. The principal change simply has been a reduction in over-all dimensions.

Grain mounts of several hundred grains each of the zircon residues of experiments A and B were made for comparison with the original zircon. Measurements were made of the number of whole grains, grains with one broken termination, and grains with two broken terminations. In addition, the average length-to-width ratio and average width for over 200 grains was determined. The results are given in table 12. It is significant that not only do the grain shapes stay con-

TABLE 12

R200 MESH-ZIRCON SHAPES BEFORE AND AFTER PARTIAL DISSOLUTION

| | No. Grains Measured | EXTERNAL FORM | | | | | | |
| | | Per Cent | | | Average L/W Unbroken | Average Width (μ) | Per Cent of Original Volume | |
		Whole	One Broken Termination	More than One Break			Calculated	Measured
Original.......	272	52	40	8	2.46	90.3	100	100.0
Residue A.....	244	45	48	7	2.20	82.5	66	62.5
Residue B.....	240	50	38	12	2.47	69.7	46	44.5

element. The values shown for eTh are calculated from an assumed material balance.

EFFECTS OF THE STRIPPING EXPERIMENTS ON THE ZIRCON

The general physical properties of the untreated zircons have already been described. The residual zircons are remarkably similar in gross morphology to their original forms. They are still prominently prismatic (as already illustrated for an extreme case in pl. 2, g, h). The terminations are not very sharply defined but are still recognizable. The zircons shown in plate 2, c, f, are residues of original zircons represented in plates 1, e, f, and 2, d. The internal zoning is clearly visible. Colors are much paler except where iron oxide "dust" is still visible. A few remnants of siliceous gel adhere to the surfaces in forms, suggesting that they are residuals

stant, but also that the ratio of broken and unbroken grains is similar, indicating that shrinkage does not take place by disintegration. That the population shifts by reduction of the diameter of all grains is indicated by the frequency plot of prism diameters in all three zircon fractions shown in figure 9.

It is apparent that at least part of the interior zones are available to early attack at fracture surfaces. However, calculations based on the morphology indicate that between 90 and 95 per cent of the total original surface area exposed is euhedral surface. The similar values of weight loss as indicated by weight of residues, and volume shrinkage as indicated by the size measurements is striking. From the physical point of view, we feel compelled to interpret our partial dissolution results as true peeling or stripping parallel to the original forms and internal zones.

The data of each of the experiments reported in table 11 may be considered as representing the outer zone and inner core of a composite zircon. The values obtained from material balance may be used for the uranium in the initial stages, and for the isotopic composition of the lead in the residual zircon of experiment B.

The general similarities between the residues of both experiments, and the similar trends from the cores to the outer layers, are striking. We have, therefore, combined the data of both experiments to set up a single composite model of the retained 200-mesh
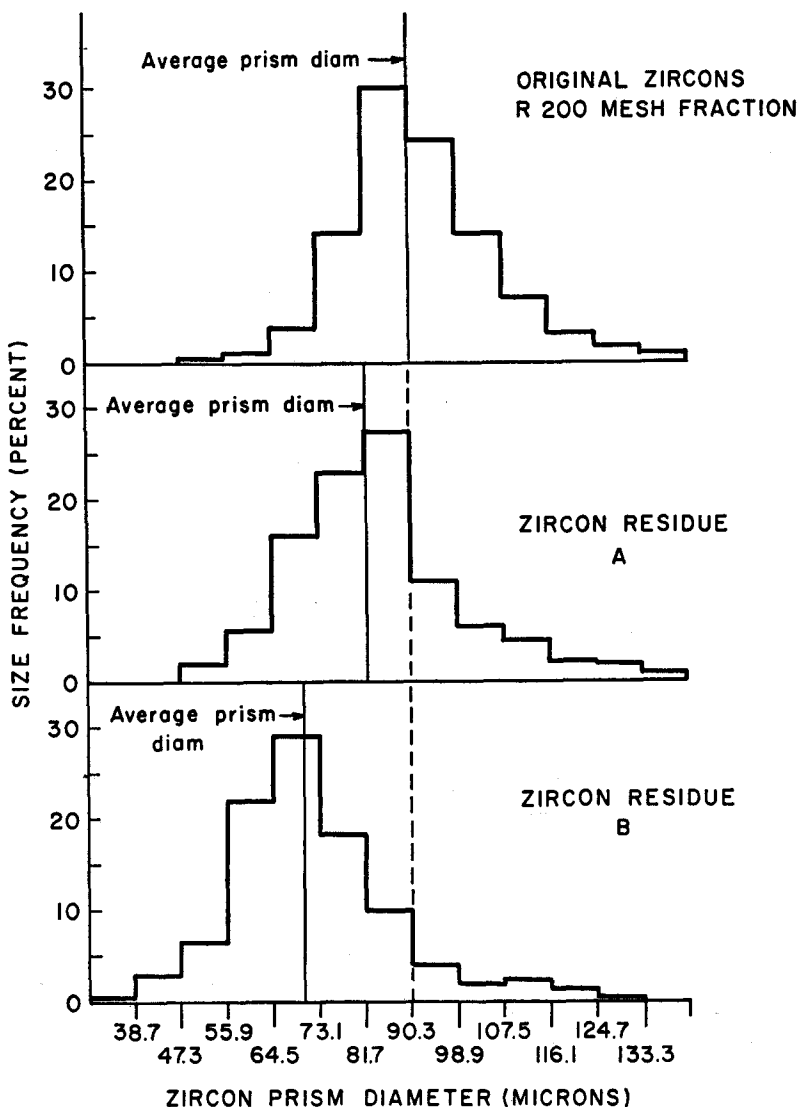
FIG. 9.—Size frequency distribution histograms of original R200 size fraction zircons and the residual zircons of stripping experiments A (37.5 per cent dissolved) and B (55.5 per cent dissolved). The average prism diameters shown are arithmetic mean of 200 or more grains in each sample.

zircon. This model has a core representing 44.5 per cent of the total sample with the characteristics of step II of experiment B. It has an outer shell representing 37.5 per cent of the sample with data obtained in step I of experiment A. The model also has

an intermediate layer or zone representing 18 per cent of the total weight with isotopic characteristics determined from combinations of the data of both experiments A and B. In figure 10 the model is shown with isotopic data plotted against radial distance
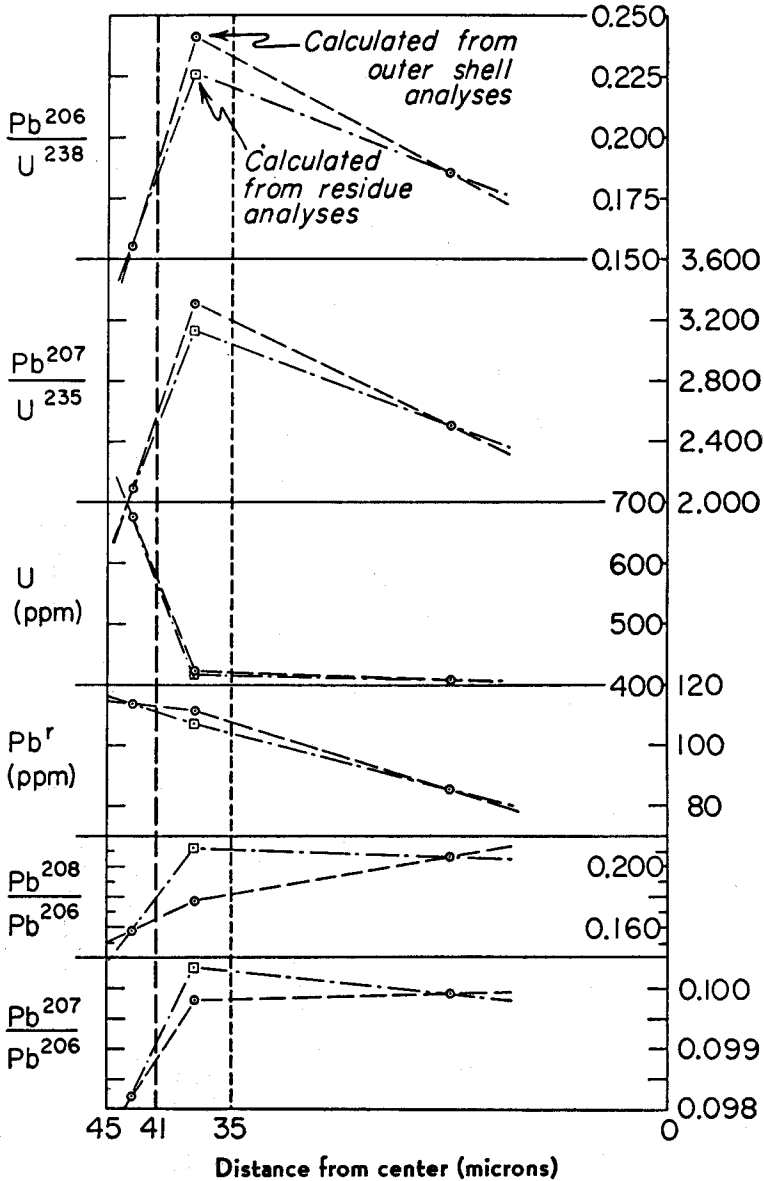
FIG. 10.—Variation of significant isotopic parameters in the U-Pb systems of a model R200-mesh zircon, based upon stripping experiments on composites of 10^4–10^5 grains. Parameters are plotted as a function of radial distance normal to the axis of the prism zone.

from the crystallographic c-axis of the zircon. The outer zone is 4 μ thick, the intermediate zone is 6 μ thick, and the inner core has a radius of 35 μ.

It will be noted that there are two curves shown for every parameter. They reflect the fact that two alternate solutions may be made for the isotopic concentrations ($c_{int.}$) of the intermediate zone. The weight fraction (f) and concentration (c) data from steps (I) of experiments A and B may be used in the expressions

$$f_{AI} \times c_{AI} + f_{int.} \times c_{int.} = f_{BI} \times c_{BI} \, ,$$

where the weight fraction of the intermediate zone $(f_{int.}) = (f_{BI}) - (f_{AI})$. Similarly,

TABLE 13

	Solutions Based on Step I Data, A and B	Solutions Based on Step II Data, A and B	Per Cent Difference
Pb²⁰⁶r......	4.23×10^{-7}	3.94×10^{-7}	−6.9
Pb²⁰⁷r......	4.22×10^{-8}	3.97×10^{-8}	−5.9
Pb²⁰⁸r......	7.50×10^{-8}	8.35×10^{-8}	11.1
U..........	1.764×10^{-6}	1.756×10^{-6}	−0.5
Pbr........	5.41×10^{-7}	5.17×10^{-7}	−4.4

the weight fraction and concentration data from the residual zircons (step II) of experiments A and B may be used to solve for the intermediate zone values.

The extent to which the two solutions agree reflects (1) whether or not the two original aliquots were identical, (2) whether the dissolution processes proceeded in similar manner although to different degrees, and (3) whether the analytical precision was sufficient for this purpose. Complete agreement would also be an argument against differential chemical behavior of the uranium in comparison to the lead during fusion and would support the interpretation of successful chemical as well as physical stripping.

The concentrations in moles per gram in the intermediate zone are given in table 13. The uranium agreement is good. The lead data show disagreement several times larger than normal limits of error assignable to isotope-dilution data. However, in each of

the calculations, the errors of two concentration and two composition analyses are introduced. In addition, the errors of the weight fractions in each experiment (possibly as much as 1–2 per cent) are introduced. We conclude that the lead balance is at least moderately good and that the apparent discrepancies probably are combinations of analytical errors. These data suggest that the fusion stripping preserved the integrity of the uranium-lead systems to a high degree. In the following discussion, a set of average values for the intermediate zone isotopic character of the composite zircon will be used.

THE COMPOSITE 200-MESH ZIRCON

The isotopic composition of lead and the uranium concentration appears to be nearly or completely uniform over 90 per cent of the radius of the zircon. The lead concentration and consequently the ratios Pb^{206}/U^{238} and Pb^{207}/U^{235} rise significantly over the same radial distance.

In the outer zone, 4 μ thick, the uranium concentration increases by 60 per cent. In the same zone, the Pb^{208}/Pb^{206} ratio is 25 per cent lower than in the core, probably reflecting a basic change in Th/U ratio, which in turn reflects the uranium increase. The measured eTh/U ratios do not appear to show this change. However, the large assigned errors to the eTh values more than cover the ratio change suggested here. The Pb^{207}/Pb^{206} ratio drops by 2.5 per cent relative to the core. While this is a small decrease, it is indicated in both experiments and is several times larger than assigned experimental error. The lead concentration appears to be somewhat higher than in the intermediate zone, but does not reflect the sharp increase shown by the uranium. It is this difference that is responsible for the very sharp drops in both Pb^{206}/U^{238} and Pb^{207}/U^{235} in the outer zone.

In summary, it is apparent that the most drastic changes in isotopic character occur in the outer 4-μ shell of the zircons. Since our method only provides an *average* for this zone it is possible, indeed even probable,

that much more drastic changes might be observed in a thinner shell, for example, 1–2 μ.

This change in the outer shell reflects at least two different kinds of phenomena. First, the uranium data and the Pb^{208}/Pb^{206} ratios reflect variations of U and Th concentrations of major magnitude during the growth of the zircon. Second, the daughter-parent relations apparently have had a drastic modification near and in the outer shell. However, the U-Pb equilibria throughout the entire model zircon are strongly disturbed, and it is now desirable to consider the character of these equilibria for all of the concentrates, acid washes, and zircon zones analyzed.

URANIUM-LEAD EQUILIBRIA IN THE ZIRCONS AND URANOTHORITE

The daughter-parent atom ratios, Pb^{206}/U^{238} and Pb^{207}/U^{235}, have been calculated for all of the zircon size fractions. In addition to appearing in the tables, they are presented in a series of daughter-parent diagrams (figs. 11, 12) of the type proposed and mathematically justified by Wetherill (1956). Pb^{206}/U^{238} is plotted relative to Pb^{207}/U^{235} for each system. The graphs show the well-known "Concordia" curve which is the locus for all values of these ratios that give a Pb^{206}/U^{238} age in agreement with the Pb^{207}/U^{235} age in the same system. The ages (T_{238}, T_{235}) are calculated from the relations

$$T_{238} = \frac{1}{\lambda U^{238}} \ln \left(\frac{Pb^{206}}{U^{238}} + 1 \right)$$

$$T_{235} = \frac{1}{\lambda U^{235}} \ln \left(\frac{Pb^{207}}{U^{235}} + 1 \right).$$

If $T_{238} = T_{235}$ in any system, it is called a concordant system; if they are unequal it is called discordant.

Aldrich and Wetherill have stated (1958, p. 267, 268) that the two ages of a mineral system must be in agreement within 3 per cent if either age is to be accepted as the true age. This implies that analytical accuracy must meet these limits to successfully establish truly concordant natural systems. Iso-

tope-dilution techniques are capable of this accuracy on many favorable natural systems. In general, we feel the accuracy of our results meets such requirements, and the observed departures from equilibria are genuine natural relations rather than laboratory-induced effects.

In figure 11, the data from the four zircon size fractions and the two uranothorite washes are plotted. It is possible to draw a straight line through these points in which no point deviates from the line by more than 0.4 per cent of its value. None of the points fall on the Concordia curve, however. The line generated by them intersects the Concordia curve at points corresponding to ages of about 90 and 1,655 million years.

Mass spectrometric errors do not allow us to expect a better fit to a straight line. However, because the line passes so near to the origin of the graph, it is pertinent to make the following observation. Any analytical errors in the uranium or lead concentrations will move the plotted points along lines passing through their true position and the origin of the graph. It is clear that small shifts in the reported concentration values would not move the points very far from the chord. Therefore this fit in itself is no test of analytical precision. However, profound concentration errors would be required to disturb this apparent relationship seriously, or to move points from some distinctly different position into this chord.

Errors of position on the Concordia plot may be introduced in the determination of lead isotopic composition. These may be the result of mass spectrometric errors, or incorrect compensation of Pb^{206} and Pb^{207} introduced into the system with Pb^{204} by non-radioactive processes. Measurement errors in observed Pb^{206}/Pb^{207} are about 0.3 per cent in this data. This in itself is negligible. Further, these errors, if random, would have no systematic effect on a family of points. The method of correction for non-radiogenic Pb^{206} and Pb^{207} in these systems has already been described. In most cases, the samples have had a sufficiently high Pb^{206}/Pb^{204} ratio so that almost any normal error in the

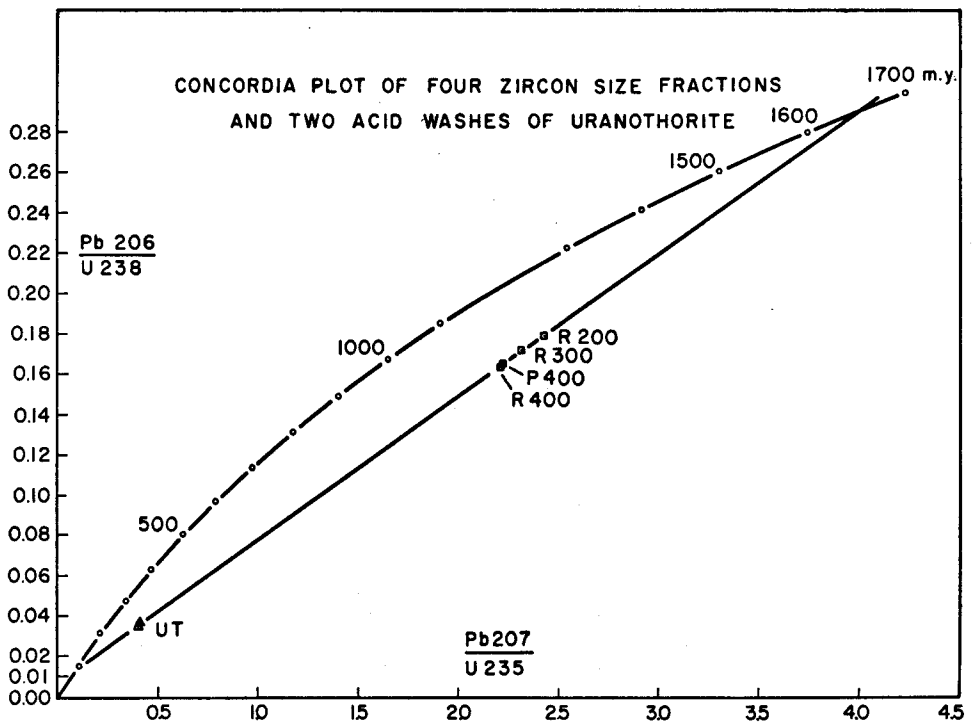FIG. 11.—Graph of Pb^{206}/U^{238} vs. $Pb^{207}/U235$ for the four zircon size fractions and two uranothorite washes (UT) showing chordlike relation to the "Concordia" curve.

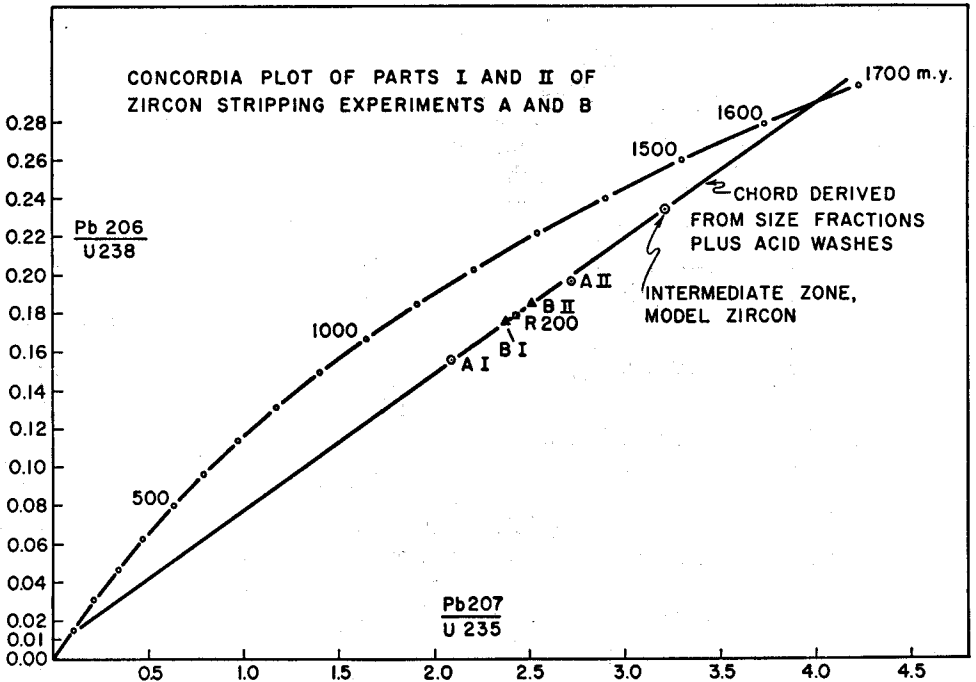FIG. 12.—Graph Pb^{206}/U^{238} vs. Pb^{207}/U^{235} for the R200 zircon fraction and the several zones of this fraction isolated in the stripping experiments. Chord shown was transferred from fig. 11.

selection of an appropriate common lead would have an effect less than the mass spectrometry error. This is apparent in the very small range of variation observed in the Pb^{207r}/Pb^{206r} ratio for all zircon samples. The uranothorite washes have the lowest Pb^{206}/Pb^{204} values and these must be more suspect. The only argument offered here is that considering the two drastically different values ($Pb^{206}/Pb^{204} = 141.4$ and 65.9) and the size of the necessary corrections, their agreement is excellent. Finally, it must be suggested that a family of U-Pb systems that is not initially concordant and that is disturbed by handling generally would not provide a straight line distribution.

Figure 12 is a similar Concordia plot to which has been transferred the chord derived from figure 11. The only point duplicated is that representing the total R200-mesh zircon. The points obtained from the steps I and II of stripping-experiment A appear on opposite sides of this point, but still on or very near the chord. The two steps of experiment B plot on either side of the total zircon point, and also fall on the chord. The larger spread of the experiment A points reflects the greater degree of isolation of the highly discordant outer zone in step A-I.

Also plotted on this curve is an average value for the intermediate zone of R200-mesh zircon model. This is apparently most concordant U-Pb system found in this group of experiments. It falls on the general chord.

Accepting the rectilinear quality of the data, and excepting analytical precision, common lead corrections, and decay constants from the remaining discussion, we may inquire into its origin and significance. Wetherill (1956) derived and Aldrich and Wetherill (1958) have discussed hypothetical models for data yielding such chords. For systems in the region of the Concordia plot where we observe these samples, it could be hypothesized that (1) the group originated 1,655 million years free of radiogenic lead; (2) its evolving uranium-lead systems were essentially undisturbed until 90 million years ago; (3) an episode of profound disturbance characterized by loss of lead and/or gain of uranium occurred in a brief interval of geologic time 90 million years ago; (4) the uranium-lead systems subsequently have not been disturbed further. Aldrich and Wetherill (1958) also observed that a similar chord could be obtained from minerals originating at a younger point in time, which incorporated a characteristic older radiogenic lead from external sources. We have dismissed the latter possibility in this case on the grounds that it is quite improbable that such a radiogenic lead would be attracted to these minerals in such systematic relation to other properties such as grain size, uranium concentration, and eTh/U ratio. Further, there is no evidence of such a primary radiogenic lead in some of the non-radioactive minerals in the host rock.

Each intersection of the chord with the Concordia curve represents the characteristic daughter-parent ratios of systems evolved without disturbance from the indicated point in time until the present. The chord between may be generated by any process which could mix the modern products of two such systems prior to analysis. Wetherill's rigorous proof, for example, may be represented as follows: (1) an original uranium system originating free of radiogenic lead at T_1 is allowed to evolve without disturbance until T_2. At T_2, a fraction of the radiogenic lead is lost, leaving a similar fraction of residual uranium, U_n, with no accumulated daughter. The lead, Pb_o, attributed to the other fraction of residual uranium, U_o, is still undisturbed. (Or, at T_2, a new fraction of uranium, U_n, is added to the system, which has no accumulated daughter, while the indigenous uranium, U_o, has its entire accumulated radiogenic lead, Pb_o, undisturbed.) From T_2 to the time of analysis both fractional systems are undisturbed and uranium continues to decay to radiogenic lead. Pb_o/U_o' now represents the fractional system evolved from time T_1 to the present (the older intersection on Concordia) while Pb_n'/U_n' represents the present nature of the younger system initiated at time T_2 (the younger intersection). In

analysis, of course, it is the total mixture of these two systems, Pb'_o/U'_o and Pb'_n/U'_n, that is measured. The chord is the locus of mixtures of two such systems where the present ratio $Pb'_o/U'_o/Pb'_n/U'_n$ varies from zero to infinity. Indeed, we may define a fraction of concordance (F) for a mixture Pb_x/U_x, which we analyze

$$F = \frac{Pb_x/U_x - Pb'_n/U'_n}{Pb'_o/U'_o - Pb'_n/U'_n}$$

for both uranium-lead isotope ratios. The "fraction of concordance" is a useful parameter for comparing disequilibrium relations in the family of systems. It may be obtained readily from the graphical parameters on the Concordia diagram.

If one considers each analyzed sample as a mineral concentrate (zircon) instead of a hypothetical mineral as in the Wetherill model treatment, then it is apparent that there are a number of additional situations which might provide a linear chord similar to the one we have obtained. Some geologically feasible concentrates might include:

1. Inherited, undisturbed zircon xenocrysts, 1,655 million years old, in a 90-million-year-old granite mixed with undisturbed zircons of the later generation. The mixing may be as old nuclei with overgrowths or as two distinct families of zircons.
2. A similar geologic setting where either the older or younger end members are not zircons, but impurities of minor relative abundance, but with major uranium and lead contribution (e.g., thorite, uraninite, xenotime, etc.).
3. A Precambrian granite that has an original generation of undisturbed (1,655-million-year-old) zircons mixed with a new generation of zircons originating from a metamorphic event (90 million years old).
4. A situation similar to 3 in which either one of the end members is a small but significant impurity in the concentrate.
5. Mixtures of two uranium-lead phases, either dissimilar zircons or zircons and impurities, whose different isotopic characters are determined solely by the same combination of older and younger events but which in neither case lie on the Concordia curve. In-

deed, any number of phases limited to sharing one or both parts of the same two-event history may be mixed to give analytical values that fall on a straight line between the extreme end members.

The previous list represents only some of many geologic possibilities. To these, of course, may be added non-geological "accidents," that is, the laboratory mixing of two unrelated uranium-lead systems. This is unlikely and unnecessary, but unfortunately, occasionally possible. We feel we have eliminated this consideration in this case.

Returning to the listed geological possibilities, the first two cases can be eliminated for the Johnny Lyon granodiorite on the grounds that clear-cut field relations demonstrate the Precambrian age of the intrusive (see fig. 2).

The third case is considered to be eliminated because of (1) the generally homogeneous physical characteristics of the zircon, (2) the lack of evidence of a significant metamorphic episode imposed on this sample of granite, (3) the evidence of the stripping experiments for disturbance throughout the zircon, as well as limiting the presence of 90-million-year overgrowth to something considerably less than 4 μ thick.

The fourth case is eliminated on the argument that the only significant radioactive impurity recognized in the autoradiographs of the unwashed zircon concentrates is uranothorite. The lead isotopic composition of the latter clearly labels it as an old system.

The fifth case might well apply to unwashed or inadequately washed mixtures of Johnny Lyon zircon and uranothorite. We have already presented our data on the acid elimination of uranothorite in our size-fraction samples. The stripping experiments show the pervasive discordant character *within* the zircon, where there is an inverse relation between degree of discordance and the Pb^{208}/Pb^{206} ratio (which we would expect to reflect the presence of the discordant uranothorite).

As long as the samples consist of large

populations of grains, they are composite with respect to certain variable zircon characteristics. For example, the specific activity of individual grains in the same size fraction has been shown to range over an order of magnitude. Despite our inability to state whether a range or several distinct classes of Pb/U ratios exist within these zircon individuals, we consider it probable that each fraction we have analyzed as a whole, or stripped in stages, is a composite mixture in its isotopic character. To a considerable extent, the distribution of points along the linear chord must be derived from this mixing phenomenon. This does not alter the unique time significance of the chord intersections pointed out by Wetherill.

Recently, Tilton (1960) has revived a model of volume diffusion as a mechanism for discordant uranium-lead ages. Lead diffusion is considered continuous throughout the history of the radioactive crystals at rates governed by diffusion coefficients, effective crystal radii, and concentration gradients. This model had been invoked earlier by Nicolaysen (1957) in an interesting attempt at resolving discrepancies in the U-Pb ages of individual minerals. Nicolaysen recognized the value of testing continuous diffusion as a *possible* cause of disagreement on several samples from the same locality but did not cite any experimental investigations. Tilton's renewed interest, however, was directed toward the explanation of some patterns of discordant ages in assemblages of minerals with regional to intercontinental distributions. Using Nicolaysen's tables, Tilton calculated and presented curves on the Concordia plot that are the loci of Pb^{206}/U^{238} and Pb^{207}/U^{235} values, generated with diffusion loss, for families of uranium-lead systems. Members of each family originated at the same time and represent all values of D/a^2 for lead loss. No suites of analyses for minerals that were demonstrably cogenetic were presented, but Tilton suggested this mechanism might be generally applicable.

In figure 13, four curves representing the calculated loci of diffusion systems originat-

ing 1,600, 1,700, 1,800, and 1,900 million years ago are plotted. The complete suite of analytical data from the Johnny Lyon granodiorite L-312 sample is shown and the familiar chord is redrawn. In addition, the two points labeled L-609 represent two zircon fractions from an independent sample locality in the Johnny Lyon granodiorite about three miles away from L-312 (see fig. 2).

The L-312 zircon points in the inset have been enlarge five times to show the regularity of their fit to the chord. This set of data shows no obvious effects of continuous lead diffusion, despite the near parallelism of the curves in this region of the diagram. The L-609 points analyzed for an extended study (in preparation) of the same intrusive body simply confirm, by their positions on the chord, that they have been exposed to a similar episodic history.

EVIDENCE ON THE NATURE OF THE DISTURBANCE MECHANISMS

The recognition that there is a differential rather than a uniform response to a disturbing episode among various uranium-lead systems in the same rock is of great importance. It provides a basis for establishing informative isotopic patterns for rocks in many geologic situations. It suggests the possibilities of investigating the nature of disturbing processes as well as being utilized in the establishment of chronologies.

In this suite of data, one of the most significant clues to the mechanisms of disturbance lies in the general observation that the Pb^{206}/U^{238} ratio decreases as the U, eTh, and total radioactivity concentrations increase in the various fractions. This is shown in table 9 for the four size fractions and in table 11 for the stripping experiments. The only apparent exception to this is found in the calculated intermediate zone of the R200 composite zircon. The Pb^{206}/U^{238} ratio is an index of discordance when compared to the value of 0.2900 for Pb^{206}/U^{238} for a concordant 1,655-million-year-old system. In figure 14, Pb^{206}/U^{238} is plotted against equivalent uranium measured by α-particle scintillome-
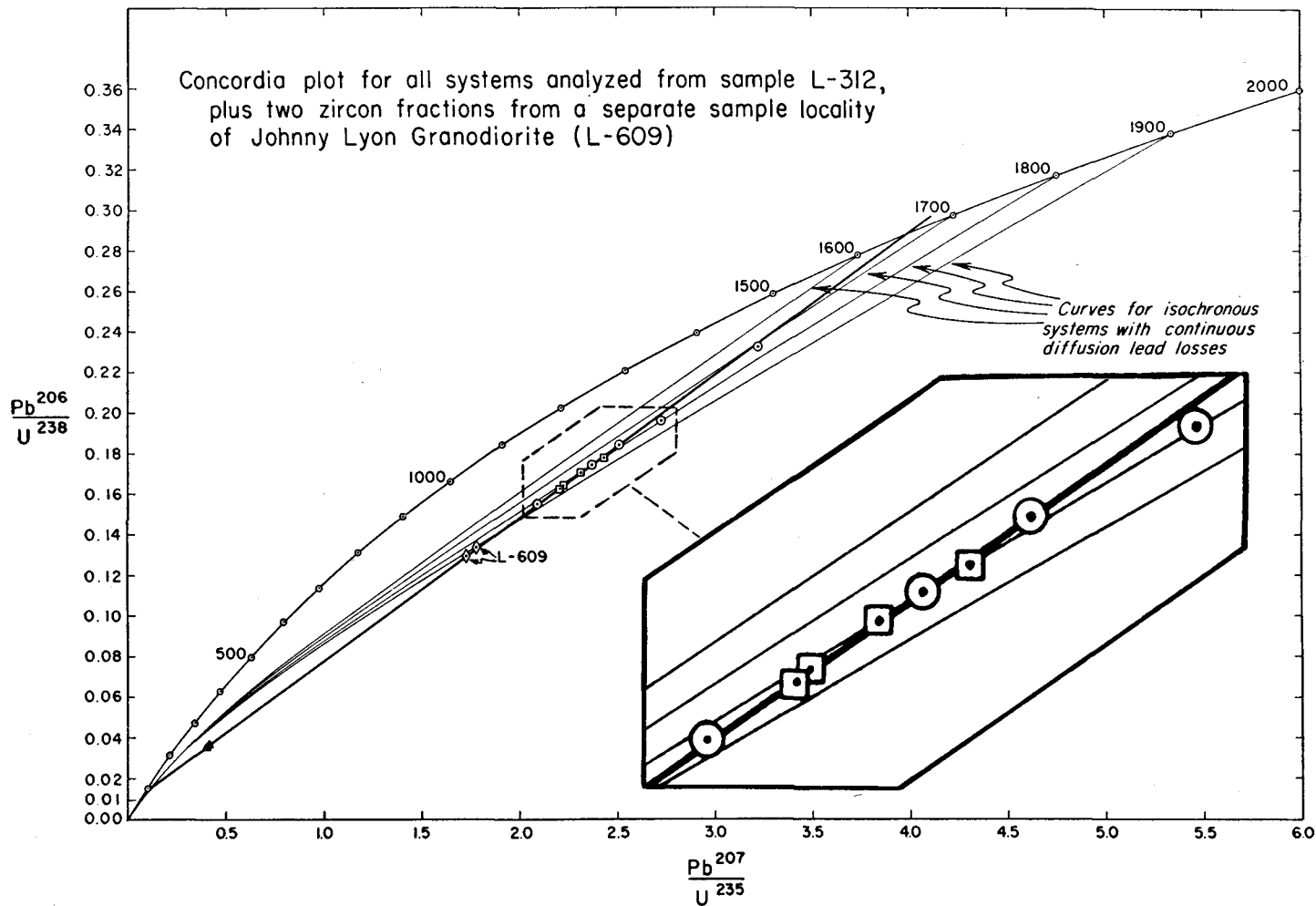
FIG. 13.—Concordia plot for all of the U-Pb systems analyzed from L-312 sample and for two zircon fractions from a locality, L-609, 3 miles south of L-312 in Johnny Lyon granodiorite (see fig. 2). Photographic enlargement (5×) shows the close fit of the data.

try. (Uranium contributes 75–90 per cent of this activity, hence the similar correlation.) The coupling of the trend of increasing discordance with increasing radioactivity strongly suggests that the greater the total radiation flux in the history of these zircons, the greater their vulnerability to disturbance. It is worth noting that both L-609 samples are 50 per cent more radioactive (1,150 p.p.m. eU) and are significantly more discordant than any of the fractions in L-312. The L-312 uranothorite is 500 times

turbance would explain some of the relations that have discouraged the use of radiation damage as a simple measure of age.

Several lines of evidence suggest that lead loss rather than uranium gain is the important change occurring in these disturbances. The positive correlation between radiogenic lead concentration and uranium concentration occurs in almost all fractions in increments several times too large to be explained by the accumulation of lead since a postulated gain of uranium 90 million years
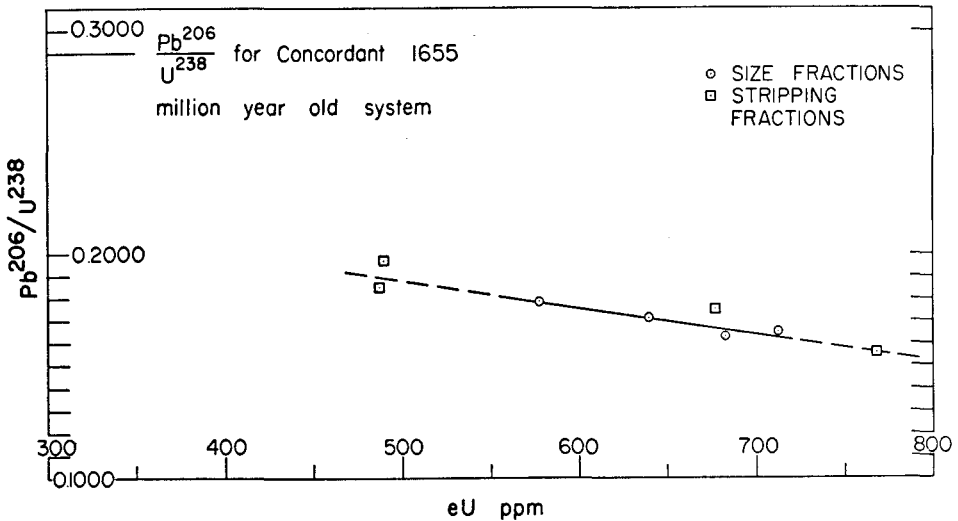
FIG. 14.—Variation of Pb^{206}/U^{238} as a function of total radioactivity of each fraction (eU = equivalent Uranium measured by α-particle scintillometer). Increasing departure from the concordant value of 0.2900 is a measure of increasing discordance in age with increasing radioactivity.

more radioactive than the most radioactive zircon and is the most discordant system in the suite, although as a different mineral species its response to disturbance may not be directly analogous to that of the zircons. Surprisingly, the X-ray and index of refraction measurements have shown that the L-312 zircons now display the radiation damage to be expected in a young rock perhaps 100 million years old (Holland and Gottfried, 1955; Fairbairn and Hurley, 1957). Apparently, annealing of the zircon structure accompanied or followed the disturbance of the contained lead-uranium systems. The coupling of annealing and dis-

ago. It is difficult to accept the hypothesis that the uranium gain would be greatest where the lead concentrations were already highest, but this would be required by the greater discordances within the more radioactive systems. Mobility of lead during the 90-million-year-old episode is the only ready explanation (other than analytical error) that we have for the maximum in Pb^{206}/U^{238} ratio in the intermediate zone of the R200 composite zircon (fig. 10). The accumulated radiogenic lead attained a maximum concentration in the more radioactive outer parts of the zoned crystals prior to the disturbance. During the disturbing episode, diffu-

sion of lead probably was partly influenced by the concentration gradients in the overall crystal system. For this reason, the maximum concentration, while being reduced, may also have broadened by diffusion both outward and toward the center. It may also have shifted laterally as well. Thus, despite a pervasive loss of lead throughout the composite zircon, the intermediate zone lost less lead relatively than the neighboring zones.

Although we have not determined thorium precisely in these experiments, it is possible to draw some conclusions that have an important bearing on the commonly observed discrepancies between U-Pb and Th-Pb ages in the same mineral. The iso-

characteristic in the minerals used in age dating, then the age discrepancies are not at all surprising.

Of course, some discrepancies between the U/Pb and Th/Pb ages simply represent the effect of minute quantities of highly discordant thorium-rich or uranium-rich impurities, such as thorite or uranite mixed with concentrates of more concordant zircons. A mixture of systems with distinctly different Th/U ratios and different degrees of disturbance will always give apparent ages in disagreement. This is illustrated by the data in table 14 on the R300 unwashed composite of zircon and uranothorite compared with the analyses of zircon and uranothorite separately. We have very little basis

TABLE 14

SAMPLE	APPARENT AGES (MILLIONS OF YEARS)				AGE RATIO
	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}	Pb^{208}/Th^{232}	$(Pb^{206}/U^{238})/$ (Pb^{208}/Th^{232})
R300 zircon acid-washed.	1,030	1,230	1,610	1,390	0.74
R300 uranothorite wash no. 1................	230	350	1,280	245	0.93
R-300 unwashed ziron and uranothorite composite.	710	950	1,570	360	1.97

topic compositions of radiogenic lead in the stripping experiments show large variations in the Pb^{208}/Pb^{206} ratio in different parts of the composite crystal, while the Pb^{207}/Pb^{206} ratio is nearly uniform. If degree of lead loss is not uniform through the crystal but is systematically higher at the outside, then the lost lead will not have a composition representative of the total lead prior to loss. It has been axiomatic that isotopic fractionation in the mass range of lead does not occur in nature. This process we describe would not produce fractionation of any originally homogeneous lead. It would take an inhomogeneous lead system and separate it into mobile and residual fractions in a non-representative manner. A very special loss process would be required to do otherwise in a system as inhomogeneous as this R200 fraction. If zonation in the Th/U ratio is a common

for understanding the extreme discordance in the uranothorite, other than to point out its characteristic extreme radiation damage as a condition that makes it susceptible to disturbance.

We have observed minerals of the thorite group in ten (about 20 per cent) of the granitic rocks we have recently examined. In mineral separation flow sheets it sometimes follows the zircon, monazite, or sphene, primarily because of variable magnetic susceptibility. It is also variable in color and form. Commonly, acid washing is the only satisfactory method of separating thorite from the other minerals. Its solubility characteristics are also quite variable. The acid-washing experiments reported by Tilton, Patterson, et al. (1955), Starik (1956), and Tilton (1956) frequently have been cited as evidence on the nature of lead-

uranium fractionation from the principal mineral of each concentrate. Unfortunately, documentation on the freedom of the concentrates from minor soluble minerals such as thorite is difficult to obtain, and certainly was not provided in these papers (see, e.g., Tilton, 1956, p. 230). We strongly suspect, on the basis of mineral separations on a similar sample from the same locality, that thorite may have been present in the sphene and zircon fractions of the Tory Hill, Essonville, granite cited by Tilton. We prefer to interpret the principal results of these older acid-wash studies on zircons as bearing as much on the nature of the minor minerals in the concentrates as upon the stability of the uranium-lead systems in the zircon, monazite, and other mineral species. More definitive studies of the acid mobility phenomenon in the light of the complete mineralogy of the mineral concentrates must be awaited.

Another suggested mechanism of discordance is the loss of intermediate daughter products, particularly radon (Giletti and Kulp, 1955). Loss of radon (Em^{222}) would provide a sequence of apparent ages $Pb^{206}/U^{238} < Pb^{207}/U^{235} < Pb^{207}/Pb^{206}$, which is the pattern we observe for our individual mineral concentrates. However, this mechanism operating by itself would require that in our different size fractions the Pb^{207}/Pb^{206} ages progressively rise as the Pb^{206}/U^{238} ages decrease. This is not the observed situation. The P400 zircon size fraction and the outer zone of the R200 composite crystal have the highest radioactivities and greatest surface areas. They could be expected to suffer greatest relative radon loss. The Pb^{207}/Pb^{206} ratios, although nearly constant, are, if anything, somewhat lower than in other samples. Even the extremely metamict uranothorite fails to confirm the pattern for radon loss. Thus, although the effect cannot be dismissed as entirely absent, radon loss alone cannot explain the major age patterns of the L-312 zircons. If continuous intermediate daughter loss is responsible for the linear patterns on Concordia it must involve isotopes in *both* decay chains, and must be

governed by a special set of limiting conditions for which we can offer no ready phenomenological explanation at present.

The role of crystal size in influencing the mechanism of disturbance is not completely clear principally because more important factors, such as distribution of radioactivity and isotopic composition, are variable with grain size. However, the stripping experiments clearly showed striking isotopic differences in the outer 4-μ shell compared to the interior of the R200 zircon. One can explain many of the characteristics of the other size fractions with a similar 4-μ shell over relatively smaller cores. Thus some of the isotopic properties may vary nearly as a function of the ratio of surface area to mass, providing a dependence on grain size. To the extent that the surface "film" is most seriously discordant, it would appear that the rate effects for the disturbance mechanism are controlled to some degree by available surface area.

Russell and Ahrens (1957) have suggested loss of daughters by recoil of disintegrating atoms as a general mechanism of disturbance. A surface film would certainly be the site for maximum effect of such a phenomenon. It is possible, therefore that at least some of the depression of the Pb^{206}/U^{238} and Pb^{207}/U^{235} ratios in the outer zone reflects loss by recoil. The slight drop in Pb^{207}/Pb^{206} ratio in that zone is also compatible with greater loss of Pb^{207} because of the greater cumulative recoil energies (hence total range) of the U^{235} series over the U^{238} series. On the other hand, the directions of these effects are not unique to the recoil hypothesis. It is difficult to understand how a more general application of the recoil hypothesis alone would explain the correlation of disturbance with radioactivity in all of our fractions.

The pervasive disturbance throughout the R200 composite crystal and the evidence for the operation of lead loss must require some process of internal lead diffusion to have operated during the disturbing episode. The present lead concentration gradient in the crystal is well defined. The gradient be-

fore the 90-million-year event must have been similar in sign and much more strongly developed. Since the data indicates that the lead concentration reached a maximum near the outer margin, it is clear that diffusion controlled by this gradient alone could not have produced the extensive internal losses that have occurred. We conclude that smaller elements of structure within the crystal (in part, perhaps, defined by the radiation damage) were the effective domains with local concentration gradients in which conditions for diffusion were controlled.

It may be possible to make further deductions on the nature of a possible disturbance mechanism in the zircon crystals. In a broader study (in preparation) of zircons in the Johnny Lyon granodiorite, and associated Precambrian rocks, some geologic environmental factors can be introduced to provide some limits on conditions prevailing during the disturbance. Independent evidence is needed on the conditions prevailing in the alteration history of the Johnny Lyon granodiorite during late Mesozoic and early Cenozoic times.

SOME PETROLOGIC AND GEOLOGIC CONSIDERATIONS

Several results of this study have implications for our understanding of minor and trace element behavior in a crystallizing granitic melt. It is universally assumed in studies of accessory minerals in rocks that any given separate is both homogeneous and adequately representative of the respective mineral species in the rock. This is, of course, aside from the question of mineral concentrate purity. It is clear from this study that the zircons in the Johnny Lyon granodiorite are not homogeneous. Nor can we state, despite considerable painstaking efforts, that they are fully representative of all of the zircons in the rock. The basis of prism size that we have employed to fractionate arbitrarily the over-all zircon concentrate is not necessarily the most fundamental parameter to be used for this purpose, but it was convenient. We have found systematic trends in the zircon populations that strongly suggest that trace element variation in solid-solu-

tion-forming minor minerals is governed by the same petrological factors which influence major and minor element variations in the major minerals. In this instance, it appears that, on the average, zircons started to crystallize relatively early in the history of the melt and *grew over a very significant part of the total crystallization history.* As the residual melt was reduced in volume, U and Th were concentrated by exclusion from the major crystallizing phases. The partition coefficients between the zircons and their growth environment may also have changed but, in any event, the outer zones and finer sizes (later nucleation?) were markedly enriched in U and Th. That this is not a phenomenon unique to the Johnny Lyon granodiorite or to zircons will be documented in another paper (in preparation) on the distribution of uranium and thorium in igneous rocks. We see no reason to believe that such effects would be limited to uranium and thorium.

The evidence of profound disturbance in the uranium-thorium-lead systems has led us to re-examine the petrography and geologic setting of the sample for independent evidence of such an episode. We are faced with the question of whether the later chlorite-epidote-"sericite" alteration assemblage is a superimposed metamorphic (hydrothermal) effect or merely a deuteric suite. No obvious independent answer is available.

We have observed one condition that is suggestive. There is a surprisingly sparse development of pleochroic halos around zircons in the biotites of the L-312 sample. Deutsch *et al.* (1957) have shown that the optical density of a pleochroic halo is a function of the total radiation flux and the sensitivity of the biotite to irradiation. By comparing the pleochroic halos and radioactive sources in a rock of unknown age with those in an unaltered rock with similar biotites of known age, it is possible to estimate the age of the pleochroic halos.

Deutsch (1960) and Picciotto and Deutsch (1963) have evidence that the pleochroic halos are quite sensitive to metamorphic effects.

We measured the optical density $\bar{D}$ of the halos in the L-312 biotite and the specific activity of the corresponding inclusions. In figure 15 the points are plotted on logarithmic plot of $\bar{D}$ as a function of specific a-activity measured by autoradiography. Also shown are three "isochrones" corresponding to the best-fitting line for data of the Elbe granite (30 million years old), the La Bresse granite (320 million years old), and a hypothetical granite of 1,000 million years age with biotite of similar sensitivity to that of the Elbe. Of six zircon inclusions observed in the biotite, four had no halos. Two zircons had very light halos with a mean density of 4 (in a range of 3 to 7 represented by the arrow). The data suggest an apparent age for the halos of 100 ± 100 million years. If the biotite has a normal sensitivity to radiation, it would appear that original pleochroic halos as radiation damage effects were completely erased by the younger event 90 million years ago. A more extensive study is required to evaluate the specific effects in this rock, but the method provides an interesting correlation with the evidence of annealing observed in the zircon crystal structures.

The application of this data to the regional geochronology has already been discussed in a preliminary report presented at the symposium, "Geochronology of Rock Systems," held by the New York Academy of Sciences in March, 1960 (Silver and Deutsch, 1961). The Johnny Lyon granodiorite is a post-tectonic intrusive whose age of crystallization places a younger limit on a major Precambrian orogenic event recorded in the rocks of the Dragoon Quadrangle (Cooper and Silver, 1954). The 1,655-million-year-old age of crystallization indicated in our analytical data is, therefore, a younger limit for this orogeny that has been correlated with the "Mazatzal Revolution" of southern and central Arizona. The recent paper by Giletti and Damon (1961, p. 642), placed the Mazatzal Revolution at somewhere between 1,200–1,550 million years based on a series of Rb^{87}–Sr^{87} dates from scattered exposures of Precambrian rocks in

Arizona. Unfortunately, none of the work represented extended investigations at any one locality. Inasmuch as the authors have also recognized evidence of younger disturbances in their samples from the region, we believe that their data can only be interpreted as placing minimum limits on the age of their rock samples.

The evidence for a major younger event (or events) sometime after the deposition of the Bisbee group (early to middle Creta-
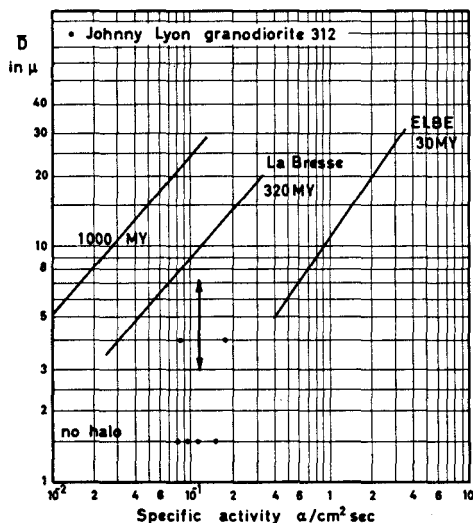

FIG. 15.—Graph showing optical density of pleochroic halos in biotite around zircon inclusions as a function of specific activity. Four zircons show no halo and two show halos to be expected in a 100-million-year granite when compared with effects in biotites of unaltered granites of known age (Deutsch et al., 1957).

ceous in age) is well documented in studies of the Dragoon Quadrangle and Cochise County. We are reluctant to interpret from our data that a single point in time covers all of the important events that occurred in the late Mesozoic and in much of the Cenozoic history of the region. We only conclude that some episode about 90 million years ago (late Cretaceous time) profoundly affected the mineral systems we have investigated. In subsequent work, we will report on broader manifestations of this younger event superimposed on Precambrian rocks.

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