LEAD-URANIUM RATIO AND POSSIBLE GEOLOGIC AGE OF ALLANITE FROM GREENWICH, MASSACHUSETTS[1]

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ABSTRACT

Allanite from a pegmatitic lens in the Monson granodiorite at Greenwich, Massachusetts, contains 0.03% Pb, 1.53% Th, 0.095% U. The results of other studies are outlined, and a maximum possible age of about 390 million years is calculated.

On May 27, 1942 the writer received from Dr. Robert Balk, at that time Chairman of the Department of Geology, Mount Holyoke College, a number of small chips of allanite, containing some small quartz inclusions, marked "Allanite crystals, from pegmatitic lens, in injection gneiss (Emerson's Monson gneiss, *U.S.G.S., Bull. 597*), $\frac{1}{2}$ mile E. of Greenwich Village, Belchertown quadr., Mass. Collected by R. Balk." The material had to be put aside until after the war. In 1946, on learning that the locality was no longer accessible due to the flooding of the Quabbin Reservoir, and that in any event there was no more fresh allanite there, it was decided to undertake examination of the sample, though the small size made it extremely doubtful if enough lead could be extracted for determination of the isotope ratios. So far as is now possible, the work has been completed, and it seems worth while to put the results on record, even though a complete age determination appears impossible.

The allanite was found by Balk in the course of prolonged field studies in the area subsequently flooded. His report is at present in manuscript in the hands of the U. S. Geological Survey. He describes the locality in the following terms (Balk, 1949):

> "Abandoned quarry, west base of hill 751 ft., SE corner of the new $7\frac{1}{2}$-minute Quabbin Reservoir Quadrangle, Massachusetts. This hill is now an island in the reservoir. Before the area was flooded, and the new $7\frac{1}{2}$-minute quadrangles were published, the locality was: W base of hill 760+ft., $\frac{1}{4}$-mile due east of Greenwich village, 15-minute Belchertown Quadrangle, Massachusetts."

The gneiss in which occurs the pegmatitic lens containing the allanite, forms part of the Monson granodiorite of Emerson (1917), who mapped it as late Carboniferous. His age assignment is probably made on the basis of the Carboniferous age given to the Worcester phyllite some 30-odd miles to the east, but this is not specifically stated in the paper. In his earlier work in this area, Emerson (1898) refers to this rock as the Monson gneiss, and lists it as Lower Cambrian, placing it above the supposed

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[1] Contribution from Committee on Measurement of Geologic Time. Division of Geology and Geography, National Research Council.

Algonkian rocks of the western part of the state. In his geological map of this date the area in question is apparently mapped as Cambrian Becket gneiss. On the other hand, Billings (1934, *et seq.*), and Chapman (1948) consider the Oliverian gneisses of New Hampshire as post-Silurian, and it may well be (though but little field work in the intervening areas has been done) that the Monson granodiorite is a southward continuation of the New Hampshire rocks. Knopf (1949) says that the Monson granodiorite has been traced southward into Connecticut and it may be that the Spinelli and Strickland quarries of the Middletown-Portland, Connecticut area are allied to it. Radioactive age determinations on minerals from these quarries (Holmes, 1947, pp. 136–7) yield a figure of approximately 260 million years. This, on the basis of Holmes' latest views (1947), represents the lower Mississippian. The Monson granodiorite is definitely older than the Triassic rocks of the Connecticut Valley to the west. It has been suggested, though the writer can find no references in published works, that the rocks of the Central Massachusetts Upland are very much older than those of the Worcester Trough to the east. Whether or not this "very much older" means pre-Cambrian or early Paleozoic was never made clear, but presumably the latter was meant. There has always been a tendency to call, on first examination, any highly metamorphosed or extremely gneissoid rock of uncertain origin pre-Cambrian until evidence to the contrary is forthcoming. As regards the rocks of this area, this view apparently was not held long enough to get into print.

It thus appears that the field evidence as to the relative age of the Monson granodiorite is somewhat contradictory. The field relations are complex throughout the New England area, and are especially so in the Central Massachusetts Upland. Thus any evidence as to the absolute age, even though incomplete, will be of some interest. As will appear later, the present work has by no means resolved the differences of opinion.

The optical properties of this sample of allanite were studied, in a very preliminary fashion, by the writer, who found virtually all of the fragments examined to be anisotropic. As this looked hopeful—isotropic allanite is metamict, and nearly always gives meaningless lead ratios because of alteration—several randomly selected chips were given to Miss Jewell J. Glass of the U.S. Geological Survey, who reported as follows (1947):

> "Allanite, from Greenwich, Massachusetts. Small fragments of broken crystals or crystalline material. Color jet black with pitchy luster in hand specimen, brownish smoky-gray in thin grains. No cleavage observed. Fuses with swelling. Gelatinizes with hot HCl.
>
> "Optical properties: In grain mounts in immersion oils the crushed powder of a single grain varies from completely isotropic to weakly anisotropic. Isotropic grains smoky gray. Index variable, $n=1.698$–1.702. Anisotropic grains feebly pleochroic brownish gray to

greenish gray. Absorption: $Z>Y>X$. Negative, $2V$ large. Indices variable. Average indices: $\alpha=1.706$, $\beta=1.711$, $\gamma=1.714$. Associated with quartz and biotite."

An autoradiograph of this material, enlarged 5×, made by Dr. Herman Yagoda of the National Institutes of Health, appears as Fig. 1. The chips of allanite, etc., were mounted in bakelite, by the technique usual for making polished sections, and then the surface ground flat. The original exposure was 933 hours. In the print the quartz inclusions appear as small black areas randomly scattered through the allanite. Dr. Yagoda points out (1946) that the seven chips apparently are of very nearly equal radioactivity, and says further that "Microscopic examination of the polished sample reveals the presence of minute white inclusions"—the quartz inclusions noted above—and that "radiocolloid structures are absent from these samples." Radiocolloids are considered to indicate incipient alteration or the interruption of radioactive equilibrium by some outside process.

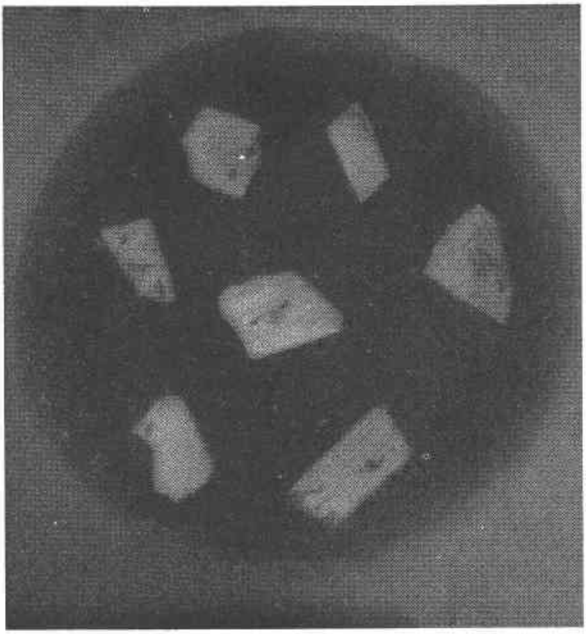

FIG. 1

Dr. Yagoda has calculated the total surface activity, i.e. the activity due to U+Th for each unit of surface, from the writer's analysis,[2] and

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[2] The analytical figures quoted by Yagoda in the reference given, were supplied by the writer on the basis of early calculations based on one analysis. The difference from those given in the present paper is insignificant for the purposes for which Yagoda used them.

also from examination of the autoradiographs (Yagoda, 1949, p. 164). The agreement is as good as for any other material so studied.

All of the available sample, except for the chips used by Miss Glass and by Dr. Yagoda, and three or four deposited as a reference sample in the U.S. National Museum, was used for the analyses. The material was crushed in a clean steel mortar, mulled to a medium powder with a clean steel roller and plate, and the quartz with a few small fragments of biotite separated with fresh, washed bromoform. Separation was aided by the greater brittleness of the allanite, which caused it to be in somewhat finer powder than the light minerals, and so they tended to float. Two treatments produced light and heavy fractions that showed no mutual contamination when examined under the binocular microscope. The allanite fraction was thoroughly washed with acetone, dried on the steam-bath, and then allowed to remain exposed to dust-free air for several days to ensure complete removal of organic matter.

The analyses were carried out by methods outlined by the writer in several previous papers and in several Reports of the Committee on Measurement of Geologic Time. For the "age analyses" redistilled acids and 3× recrystallized Na_2CO_3 were used for the solution of the sample and the determination of lead. The mineral decomposed readily in 1:1 HCl, but as usual, repeated evaporation and retreatment was needed to dehydrate the silica. Lead was first separated as the sulfide, and determined as the sulfate, with examination of all filtrates for possible traces of this element. Thorium was separated from uranium, etc., as the oxalate, separated from rare earths by repeated precipitation as peroxynitrate, and determined as the oxide. Iron, etc., were separated from uranium by precipitation with ammonia and ammonium carbonate, repeated as often as tests showed necessary. A very small "heavy metal" fraction (probably largely $V_2O_5+MoO_3$) was then scavenged with cupferron, uranium precipitated with carbonate-free redistilled ammonia, and weighed as U_3O_8.

Because of the very small total uranium it was not possible to separate it into UO_2 and UO_3 fractions. The large excess of iron, nearly $\frac{2}{3}$ of which is in the ferrous state, would presumably have resulted in the complete oxidation of the uranium. The separation of the rare earths into La and Y groups is approximate only, as usual, based on the relative solubility of their double potassium sulfates. It is felt that no further comments on analytical methods are needed.

As the lead content was small it was necessary to take as large samples as possible to make the accuracy of the determination of this element as great as could be. In Analysis II the combined solutions after the determination of lead were made up to a known volume, and four determina-

TABLE I. "AGE ANALYSIS" OF ALLANITE FROM GREENWICH, MASSACHUSETTS

% Pb	% Th	% U
AGI 0.031	AGI 1.520	AGII (a+b) 0.091
AGII 0.033	AGIIa 1.577	AGII (c+d) 0.098
	AGIIb 1.544	
	AGIIc 1.578	
	AGIId 1.430	
Ave.=0.032	Ave.=1.530	Ave.=0.095

tions of thorium made on aliquot parts thereof. This was done partly for convenience in working with smaller quantities of major constituents, and partly to obtain further checks on the thorium content. After the removal of iron, etc., the first two aliquots were combined and one determination of uranium made on them, and the same procedure was followed for the last two. Due to an accident, the uranium fraction of Analysis I was lost. The above procedure accounts for the varying number of Pb, Th, and U determinations shown in Table I. The complete analysis of the mineral given in Table II is based on from 1 to 5 determinations of each constituent, made during the course of the various "age analyses". One determination of "total rare earths" gave 17.64%, which agrees reasonably well with the sum of Ce, La group, Y group oxides of 18.48%. From the reasonably close agreement of the summation to 100%, it appears that no constituent of importance was missed. In one case, the filtrate from a Pb determination was tested for Cu and other elements precipitated with H_2S in dilute acid solution, but no weighable amount was found. There appear to be no peculiarities of

TABLE II. COMPLETE ANALYSIS OF ALLANITE FROM GREENWICH, MASSACHUSETTS

SiO_2	32.22%	CaO	10.86
Pb	0.03	SrO	0.02
ThO_2	1.74	MgO	1.66
U_3O_8	0.12	Ce_2O_3	3.86
Fe_2O_3	4.87	La_2O_3, etc.	13.92
FeO	9.07	Y_2O_3, etc.	0.70
Al_2O_3	17.89	$MoO_3+V_2O_5$, etc.	0.03
TiO_2	0.29	MnO	0.15
K_2O	0.14	H_2O, +110°	1.81
Na_2O	0.29	H_2O, −110°	0.09
			Total=99.76%

composition to distinguish this material from any other "typical" allanite.

The water content is a little higher than is desirable in such material when used for age determination. This, plus the presence of some isotropic grains reported by Miss Glass, suggests incipient alteration. On the other hand, the high FeO content is reassuring. Tentatively we may classify this as "good grade B" material.

It should be borne in mind that, in summing the analysis of a mineral containing radiogenic lead the lead is substituting for uranium or thorium in an uranium oxide or thorium oxide lattice. Thus the lead is present as the element Pb, and not as the oxide PbO. When the quantity of lead is very small, as in this case, the effect on the summation is negligible, but when it is considerable, as in geologically old pitchblendes, the difference needs to be taken into account. In the calculations in these analyses the atomic weight of the lead was taken as 207.25, based on the Th/U ratio. Any other value in the vicinity of 207.2 would probably have served equally well.

From these analytical data we now come to calculate the approximate age. For a mineral of a high Th/U ratio such as this, the value of the constant "k" in the approximate age equation (Pb/U+kTh) becomes important. This value is still not known with desirable exactness. The usual value given is 0.36, but some workers prefer 0.34. Dr. A. F. Kovarik (letter from A. Knopf to J. P. Marble, October 21, 1949) calculates 0.333 for a mineral of mid-Paleozoic age. As the two isotopes of uranium have different decay rates, the value of this "constant" varies, in theory, with the age of the mineral under consideration. However, as the amount of the isotope U^{235} is so much smaller than that of U^{238}, it probably suffices to use only three different values, for very old, moderately old, and relatively young minerals. Work now in progress on the exact values of the half-lives of U^{235}, U^{238} and Th will presumably clear the matter up. To avoid using these various values, we may take ages from the curves drawn by Wickman (1943), who has constructed graphs converting analytical data into ages, based on the then current values for the radioactive constants. Lopez de Azcona (1948) has constructed similar curves. The various calculations are summarized in Table III.

TABLE III. APPROXIMATE AGE CALCULATIONS, GREENWICH, MASS., ALLANITE

1. Pb/U+0.36 Th×7600 m.y.=0.049×7600 m.y.=c.370 m.y.
2. Pb/U+0.34 Th×7600 m.y.=0.051×7600 m.y.=c.390 m.y.
3. Pb/U+0.333 Th×7600 m.y.=0.053=7600 m.y.=c.400 m.y.
4. Pb/U+Th=0.02; U/U+Th=0.06; age from curve=c.390 m.y.

Average=c.390 million years

As was said earlier, it is extremely unfortunate that it is not at present possible to determine the isotope ratios of the lead extracted from this allanite. The weight of $PbSO_4$ obtained in Analysis I was 0.00040 g., in Analysis II, 0.00263 g., a total of about 3 milligrams. In the process of further purification and conversion to iodide, further losses would occur, and less than 5 milligrams is, at the moment, impossible to use, unless one is willing to take the chance that the first run will come out all right. This material is being saved, and when accurate mass-spectroscopic work can be done on less than 2.5 mg. of lead salt, we hope to be able to work this up into suitable form.

Meanwhile it must be borne in mind that the approximate age derived on the basis of the above calculations simply represents a maximum value. The presence of any "common" lead will reduce the age, and since the percentage of lead is the smallest number in the ratio, the effect of any change in this will be at a maximum.

Based on the tables given by Holmes (1947), which are based on the best available evidence, it appears that 390 million years comes about between the Ordovician and the Silurian. The presence of a comparatively small amount of "common" lead would reduce this figure to one corresponding to a late Silurian age, which would suggest that the views connecting the Monson granodiorite with the Oliverian magma series of New Hampshire were correct. However, a somewhat greater amount of "common" lead, but not an impossibly large quantity thereof, would reduce the age still further, and we might presumably end up with a Lower Carboniferous age. The effect of analytical errors is, of course, unpredictable. With the small amount of material here available it is not possible to make enough analyses to see if there is any trend in the results. The writer can only say that his normal procedures seemed to work without difficulty, and that he tried to take all the needful precautions.

The results make a pre-Cambrian age untenable, and also seem to throw out the Cambrian age given in Emerson's earlier paper. The field evidence is quite clear that these rocks are pre-Triassic. The writer is not willing to go farther than to say that the present, admittedly incomplete, work indicates a middle to lower Paleozoic age for this allanite from the Monson granodiorite.

The writer takes this opportunity to thank Dr. Robert Balk for supplying the material, describing the locality, and assisting in the discussion of the age relations; Miss Jewell J. Glass for making the optical determinations; Dr. Herman Yagoda for making and interpreting the autoradiographs; Dr. Adolph Knopf for assistance in the discussion; and the Secretary of the Smithsonian Institution for making it possible

for the writer to carry out the analyses and other processes in the laboratories of the U. S. National Museum.

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