ALLANITE FROM BARRINGER HILL, LLANO COUNTY, TEXAS*

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ABSTRACT

Allanite from Barringer Hill, Llano County, Texas, has been analyzed, with especial attention to the "lead-ratio." The resulting value, 0.428, indicates either a large accumulation of "common" lead or extensive alteration. A complete analysis, petrographic studies, and other data are given.

The pegmatites of Barringer Hill, Llano County, Texas, have yielded many specimens of radioactive minerals, a number of which have been analyzed with especial attention to the "lead-ratio." This work has been summarized by A. Holmes (1931) and (1937), so detailed references and discussion need not be given here. It should be pointed out that only one mineral from this locality, an uraninite analyzed by Hillebrand and by Mackintosh, yielded a "lead-ratio" that was completely acceptable to Holmes. Most of the other minerals thus analyzed—mackintoshite, yttrocrasite (from Burnet County), thorogummite, yttrialite and fergusonite,—he considered either to be in the metamict condition or to be alteration products. In the early studies of the "lead-ratio" method of geologic time determination, the varying results obtained from the analyses of Barringer Hill minerals were used to discredit the method temporarily, though, as Holmes has shown, part of the difficulty has since been removed by the discovery of the correct rôle of thorium as a radioactive element in the production of lead. No corrections for "common" lead have been applied to any of the work, as in some cases not enough material for isotope studies was available, and most of the work was done before the need for this correction was realized.

Allanite has been reported from this locality by Dana (1914) (1932), F. L. Hess (1908), and K. K. Landes (1932), but as far as can be ascertained, has not been analyzed. In 1933 the writer received from Dr. A. C. Lane, Chairman of the Committee on Measurement of Geologic Time, a specimen of this mineral, originally furnished by Mr. C. L. Brock, Director of the Houston Museum of Natural History, Houston, Texas. This specimen was collected by Mr. Brock at Barringer Hill on April 20, 1931, on the occasion of a trip made shortly before the locality was to be flooded for reservoir purposes. An account of this trip has appeared in print [C. L. Brock (1932)].

Dr. Lane tested the sample for radioactivity in the spinthariscope,

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* Contribution from the Committee on Measurement of Geologic Time, Division of Geology and Geography, National Research Council.

and reported it to be "about ¼ as active as the kolm of Westergötland, Sweden."[1] As no more minerals would presumably be available for analysis from this locality, the specimen was turned over to the writer. It has been studied in connection with a systematic investigation of allanite as a possible "age-index" mineral.

The sample as received was in one irregular mass, weighing 535 g., showing no crystal nor cleavage faces, but with fresh fracture surfaces. A few fragments of feldspar adhered to it. The outside portions, where the mass had been in contact with other minerals, showed a very thin zone of greyish altered material, a fraction of a mm. thick, which was firmly attached to the unaltered main portion. None of the brown, ochreous alteration products that often accompany allanite were visible.

A flat surface was ground on one side for radiographic examination. On wiping this off with acetone a very faintly visible outer zone, about 2–3 mm. wide, could be seen, suggesting the possibility of slight surface alteration.

An autoradiograph was made, using 23 days exposure. The plate, on development, showed uniform, but exceedingly faint darkening, too faint for reproduction, indicating a very low proportion of radioactive elements, but an apparently uniform distribution.

Material for analysis was taken from a portion of the main mass that showed an apparently uniform appearance. The outer zones mentioned above were carefully avoided. Examination of the coarse fragments under the binocular microscope showed no foreign matter, and this sample was ground to a fine powder, without sieving. The steel muller and agate mortar used were carefully cleaned before use to avoid possible contamination with other minerals, especially those carrying lead.

Several determinations of the lead, thorium, and uranium content were made, as listed in Table 1.

TABLE 1. Pb/Th+U, BARRINGER HILL, TEXAS, ALLANITE

Analysis No.	Weight sample, g.	Weight $PbSO_4$, g.	≈% Pb	Weight ThO_2, g.	≈% Th	Weight U_3O_8, g.	≈% U
1	10.0996	0.0248	0.168	—	—	—	—
2	8.97805	0.01317	0.100	0.07500	0.734	0.00350	0.033
				0.07280	0.713	0.00250	0.024
				0.07140	0.699	0.00450	0.043
4	2.72738	0.00400	0.103	—	—	—	—

Averages: % Pb 0.124
% Th 0.715
% U 0.033

$$\frac{Pb}{U+0.36\ Th}=0.428.$$

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[1] Lane, A. C., Private communication.

Analyses 1 and 4 were lost by accident after completion of the lead determinations. In Analysis 2, lead was determined on the entire sample, thorium and uranium on three aliquots. The value 207.90 was taken for the atomic weight of lead, based roughly upon the relative proportions of uranium and thorium. Little difference, if any, in the computed percentage of lead would result, were the value for "common" lead, 207.21, used instead. In the case of minerals carrying considerable percentages of lead, the proper value for this "constant" must be applied to obtain correct results.

Special precautions were taken, as usual, to ensure that none of the three elements determined above had escaped quantitative determination. The acids, ammonia, and sodium carbonate used in the decomposition of the mineral and in the determination of lead were redistilled, (or re-crystallized), to ensure freedom from traces of lead. Experience has shown thorium and uranium are not present in "C.P." reagents in analytically significant quantities. The mineral was decomposed by repeated evaporation and dehydration with hydrochloric acid, to avoid "loading" the sample with large amounts of sodium carbonate. Silica was removed with hydrofluoric acid, and a small residue brought into solution with acid, followed by fusion with sodium carbonate. Lead was separated as sulfide, purified several times by precipitation as sulfate and sulfide, and weighed as sulfate. Thorium was separated by the peroxynitrate method, then precipitated as oxalate and weighed as oxide. Uranium was separated from iron, etc., by repeated treatment with ammonia and ammonium carbonate, separated from a trace of "heavy metals" by their precipitation with cupferron, finally precipitated with carbonate-free ammonia, and weighed as the mixed oxide, U_3O_8.

The "lead-ratio" of 0.428 derived from these analyses is, obviously, valueless in determining the age of the mineral. Either a large quantity of "common" lead—several times the amount of "radiogenic" lead—is present, or else alteration has progressed to such an extent that thorium and uranium, or one of them, have been extensively leached. Unfortunately the lead sulfate was not recovered from the analytical residues, so that the proportions of the various isotopes cannot be determined by mass spectroscopy. Enough of the analytical sample is available, should it seem desirable to do so in the future.

When we compare this "lead-ratio" with those quoted and discussed by Holmes (*Nat. Res. Counc. Bull.* **80,** p. 333), we find that it is of the same general order as those found by Mackintosh for two samples of fergusonite (analyses H and I), where values of 0.284 and 0.566 were obtained. Holmes suggests that lead may have migrated from mackintoshite (analysis C), "ratio" 0.102, to the fergusonite which accompanies it. He also points out that fergusonite, as a niobate of the rare earths, is likely to be metamict.

The field evidence available offers no evidence as to a possible transfer of lead from some other mineral to this allanite, but the petrographic studies (see below) show that, in all probability, it is in the metamict condition, i.e. the originally anisotropic mineral has become fully isotropic.

Galena or other sulfides, which might possibly carry lead, have not been reported from the pegmatite. However, V. M. Goldschmidt (1938) points out that lead is concentrated in potash feldspars, replacing potassium (p. 93). It may be that the alteration of the allanite has permitted the transfer of lead from the adjacent feldspars. At any rate, transfer of lead from some other mineral is the probable reason for the high "lead-ratio," as there seem to be no secondary alteration products higher in thorium or uranium present. The leaching of these elements may usually be made evident by the occurrence of gummite or gummite-like secondary minerals in cracks and on crystal surfaces.

A small sample of the mineral, in the form of coarse fragments, was sent to Dr. W. D. Urry, then at the Massachusetts Institute of Technology, to see what results could be obtained by the possible application of the helium-radium-thorium ratio. He reports:[2]

"Helium data, Llano County, Texas, allanite.

Date	Weight	Remarks	Result
Feb. 5, 1935	0.070 g.	Fluxed with 7.5 g. Na_2CO_3	1.98×10^{-2} cc. He/g."

Using the analytical data for uranium and thorium given in Table 1, Urry calculates the "helium ratio,"

$$\frac{\text{He}}{\text{U}+0.27\text{Th}}=\frac{1.98\times10^{-2}}{3.3\times10^{-4}+0.27\times7.15\times10^{-3}}=8.76,$$

which is equivalent to a "lead-ratio" of 0.010. This is, of course, far too low for a pre-Cambrian formation. On the basis of the analysis of the uraninites mentioned by Holmes, and on the stratigraphic relationships, the age is at least, pre-Upper Cambrian. The metamict condition of the mineral is presumably responsible for this loss of helium.

A complete analysis of the mineral was also made, to be sure the specimen was indeed allanite, to see if lead, uranium, or thorium had been missed at any point in their determination, and to complete the record as far as possible. Results are in Table 2.

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[2] Private communication.

Table 2. Allanite from Barringer Hill, Texas

Pb	0.12%	Ce_2O_3	10.58	TiO_2	0.89
ThO_2	0.82	La_2O_3, etc.	11.97	SnO_2	0.33
U_3O_8	0.04	Yt_2O_3, etc.	0.81	H_2O (−110°)	0.22
SiO_2	29.89	FeO	8.49	H_2O (+110°)	1.84
CaO	8.48	Fe_2O_3	6.41	K_2O	0.08
SrO	0.00	Al_2O_3	19.09	Na_2O	0.16
MgO	0.15				
				Total	100.37

Density = 3.54 [25°/4°] J. P. Marble, *Analyst.*

The amount of uranium present was so small that determination of both UO_2 and UO_3 was not feasible, especially in the presence of large amounts of FeO and Fe_2O_3. The effect on the total of recalculating to either oxide would be negligible. The rare earths, after removal of cerium, apparently belong almost entirely to the lanthanum sub-group, as is usual in allanite. The presence of tin was confirmed by a qualitative test on the filtrate from the $PbSO_4$ of one of the main analyses. It has been reported also in allanite from Nelson County, Virginia.[3] The analysis in the present paper shows the same general relations of the same oxides as in analyses of allanites from other localities. At any rate, this mineral is much closer chemically to a "typical" allanite than to any other mineral.

The optical properties were most kindly and carefully determined by Miss Jewell J. Glass of the U. S. Geological Survey,[4] as follows:

Allanite from Barringer Hill, Llano County, Texas, U.S.A.
By alteration or inversion this specimen is *isotropic.*
Color: In transmitted light the color is smoky-brownish black, resembling black spinel. Translucent.
Luster: Resinous or pitchy.
Index of refraction: $n = 1.716$.
The specimen is apparently homogeneous, being completely isotropic throughout in all of the five areas observed.

This agrees with the high "lead-ratio," the low helium content, and the considerable water content in suggesting that alteration has taken place to a considerable degree. Apparently a similar fate has overtaken nearly all of the radioactive minerals in this pegmatite, so that the age still rests on the uraninite mentioned at the beginning of this paper.

The net results of this investigation are to add one more to the already

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[3] Dana: System of Mineralogy, 6th Ed., p. 524, analysis 34.

[4] Private communication, Oct. 24, 1939.

large number of allanite analyses on record, to indicate the probability of alteration in the specimen studied, and once more to indicate the urgent need of optical, radiographic, and isotope control in all analyses made for age determination purposes.

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REFERENCES

BROCK, C. L., Rocks and Minerals, June, 54–59 (1932).

DANA, E. S., System of Mineralogy, 6th Ed., Wiley, New York, 522–526 (1914)

———, Text-Book of Mineralogy, 4th Ed., Wiley, New York, 624–625 (1932).

GOLDSCHMIDT, V. M., Geochemische Verteilungsgesetze der Elemente. IX: Die Mengenverhältnisse der Elemente und der Atomarten. *Skrift. Norsk. Vidensk.-Akad. I. Mat.-Naturv. Kl.*, No. 4 (1937). Oslo, 93–94 (1938).

HESS, F. L., *U. S. Geol. Surv. Bull.* **340,** 286–294 (1908).

HOLMES, A., *Bull.* **80,** *Nat. Research Council*, Washington, Chap. IV., esp. 330–334 (1931).

———, The Age of the Earth, Nelson, New York, 204–206 (1937).

LANDES, K. K., *Am. Mineral.* **17,** 381–390 (1932).