method employed made use of the knowledge that the uranium and actinium series end ultimately as isotopes of lead having the masses 206 and 207, respectively. From the isotopic analysis of the lead found in a uranium mineral of known age, the relative activities of the actinium and uranium series at the present time and the decay constant of U_I, it was possible to find the decay constant of AcU. As the result of calculations of this sort, Rutherford[15] arrived at the value $T(\mathrm{AcU}) = 4.2\times 10^8$ yr.; Kovarik,[16] 2.7×10^8 yr.; v. Grosse,[17] 4×10^8 yr.; Western and Ruark,[18] 4.45×10^8 yr.; Meyer,[19] 7.0 and 6.3×10^8 yr.

From the relative abundances of the uranium isotopes it is possible to obtain this quantity by a quite independent method requiring only as additional information a knowledge of the decay constant of U_I and the present activity ratio of the actinium and uranium series. The careful investigation of large number of radiogenic lead samples indicates[8] that the actinium series is 4.6 percent as active as the uranium series. This fact is conveniently expressed by means of Eq. (2). Making the necessary substitution one finds $\lambda(\mathrm{AcU}) = 9.72\times 10^{-10}$

$$0.046 = \lambda(\mathrm{AcU})N(\mathrm{AcU})/\lambda(U_I)N(U_I), \qquad (2)$$

yr.$^{-1}$ or $T(\mathrm{AcU}) = 7.13\times 10^8$ yr.

Acknowledgments

The writer wishes to express his appreciation to Professor Kenneth T. Bainbridge who suggested the problem. The prosecution of the work was possible only through the cooperation of Professor G. P. Baxter of the Department of Chemistry, Harvard University, who very kindly prepared and supplied the uranium compounds used.

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[15] Lord Rutherford, Nature **123**, 313 (1929).

[16] A. F. Kovarik, Phys. Rev. **35**, 1432 (1930).

[17] A. v. Grosse, Phys. Rev. **42**, 565 (1932); J. Phys. Chem. **38**, 487 (1934).

[18] F. Western and A. E. Ruark, Phys. Rev. **44**, 675 (1933); **45**, 628 (1934).

[19] S. Meyer, Wien Ber. IIa, **146**, 175 (1937); **146**, 581 (1937).

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The Isotopic Constitution of Radiogenic Leads and the Measurement of Geological Time. II

Alfred O. Nier*
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

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The isotopic constitution of 21 samples of radiogenic lead has been determined with a mass spectrometer and the results have been correlated with mineral analysis data available for the specimens from which the leads were extracted. The common lead contamination in the samples was found, on the whole, to agree closely with that estimated from earlier atomic weight determinations. The AcD/RaG ratios ($\mathrm{Pb}^{207}/\mathrm{Pb}^{206}$ ratios corrected for common lead contamination) appear to be in better agreement with a value 4.6 percent for the present day ratio of the activity of the actinium series to that of the uranium series than with the directly determined and commonly accepted value 4.0 percent. The results indicate that AcU was not nearly as abundant in the early days of the earth as was at one time believed.

The measurement of geologic age from AcD/RaG ratios is discussed and it is shown that in the event of mineral alteration the ages obtained are more reliable than those found from the Pb/U ratios.

The relatively small amount of Pb^{204} present in samples containing a large amount of thorium indicates that it is extremely unlikely that Pb^{208} decays to Pb^{204}.

IT IS a well-known fact that the natural disintegration of uranium results in the ultimate formation of two stable isotopes of lead, Pb^{206}(RaG) and Pb^{207}(AcD), while the

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* This work was done while the writer was a National Research Fellow at Harvard University. Present address, Department of Physics, University of Minnesota, Minneapolis, Minnesota.

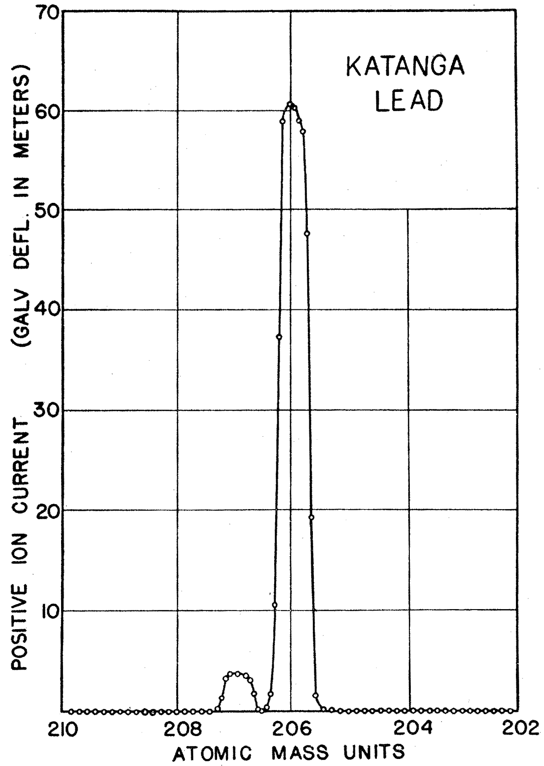

FIG. 1. Mass spectrum showing isotopes of uranium lead. The experimental points are obtained by plotting positive ion current passing through the exit slit of the analyzer as a function of the energy of the ions while the magnetic field is held constant. As there is a definite relation between the energy and the mass of the ions collected, namely, energy ×mass = a constant, the voltage scale can be readily changed to a mass scale, as was done in the figure. The width of the peak is, of course, caused by the finite width of the slits used and the imperfections in focusing.

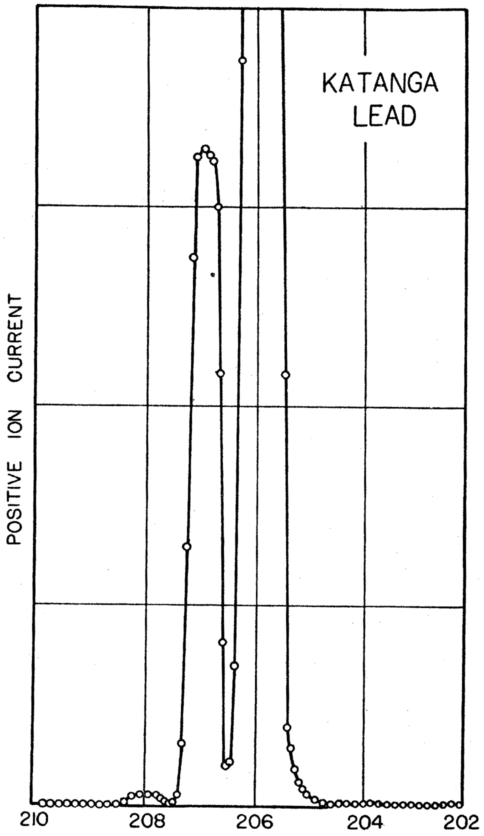

FIG. 2. Figure 1 drawn with an enlarged ordinate scale. The peak at 208 is caused by a trace of ordinary lead impurity.

disintegration of thorium leads to the single isotope Pb^{208}(ThD). Thus it can be seen that from the known decay constants of uranium and thorium, together with the so-called Pb/U and Pb/Th ratios for a radioactive mineral, it is possible to compute the mineral's age, provided one knows the amount of common lead impurity present. As the atomic weight of common lead, 207.21, differs considerably from that of either uranium lead, approximately 206.03, or thorium lead, approximately 207.98, the amount of contamination can usually be found from the atomic weight of the lead in question. An isotopic analysis gives one the same information, and, in addition, in the case of uranium minerals, provides important data on the rate of disintegration of the actinium series—data which, as will be seen, furnishes an important check on the mineral's age as computed from the Pb/U ratio.

In the present work, the relative abundances of the isotopes of a number of radiogenic leads were determined. The results obtained are especially interesting, as most of the samples are the identical ones for which mineral analysis data are available. Moreover, chemical atomic weight determinations have been made on many of the samples.

APPARATUS AND PROCEDURE

The mass spectrometer differed from that described in the previous paper only in that it did not contain the small internal furnace used to volatilize the substance studied. It was the same one as was used in some earlier work.[1] The particular technique developed for the study of

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[1] A. O. Nier, Phys. Rev. 52, 933 (1937).

lead has been described elsewhere.[2] Briefly, it may be stated that lead ions are produced by the bombardment of lead iodide vapor with electrons, that an analysis can be obtained in less than two days, and less than six mg of lead are consumed in the process.

The complete absence of water or grease vapor in the apparatus, together with the extreme purity of the samples, entirely eliminates any difficulties with impurities, especially hydrides.

As the ion currents are measured with an electrometer-tube amplifier, it is possible to obtain accurate relative abundances merely by determining galvanometer deflections. The quantitative measurement of ion currents with electrical instruments is certainly to be preferred to the method generally employed in mass spectrographs in which the magnitude of the ion current is determined from the blackening of photographic plates.

The iodine used in preparing the lead iodide was especially purified, since $Br^{79}I^{127}$ and $Br^{81}I^{127}$ have molecular weights 206 and 208, the same as two of the isotopes of lead.

RESULTS

The isotopes of uranium lead, Pb^{206} and Pb^{207}, are clearly seen in Fig. 1, which is a mass spectrum obtained for a specimen of Katanga pitchblende, sample 6 of Table I. That this particular specimen is remarkably free from ordinary lead contamination may be concluded from Fig. 2, in which the lower portion of Fig. 1 is drawn with a greatly enlarged ordinate scale. It is to be recalled that in common lead, Pb^{208} is more than twice as abundant as any of the other isotopes, Pb^{207}, Pb^{206} and Pb^{204}. As a contrast to Fig. 1 is shown Fig. 3, a spectrum obtained for some St. Joachimsthal pitchblende, sample 1 of Table I. This specimen contains a large proportion of common lead. The spectrum shown in Fig. 4 is for Norwegian thorite, sample 20 of Table I, a specimen containing $ThD(Pb^{208})$ contaminated by small amounts of common and uranium leads.

In Table I are given, together with other information, the relative abundances of the isotopes in 21 samples of radiogenic lead. The bulk of these leads were extracted from uranium minerals

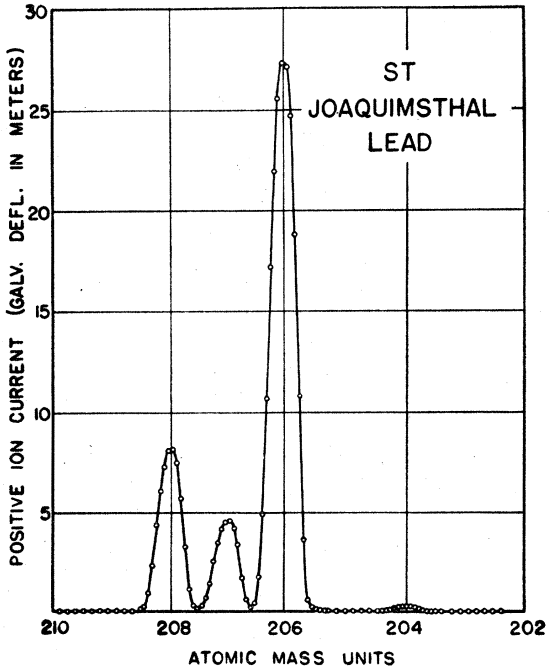

FIG. 3. Mass spectrum for lead extracted from St. Joachimsthal pitchblende. Both common and uranium leads are present here.

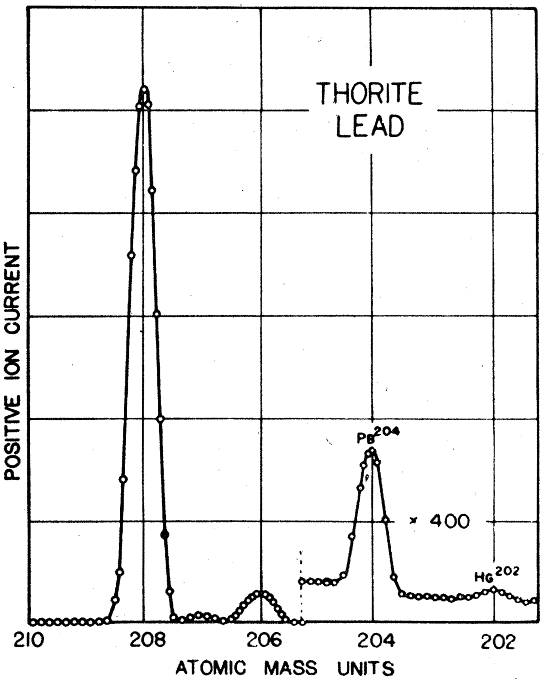

FIG. 4. Mass spectrum for lead extracted from Norwegian thorite. The thorium lead is contaminated by small amounts of common and uranium lead in this case. The ordinate scale in the 204 to 202 region has been increased by a factor of 400.

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[2] A. O. Nier, J. Am. Chem. Soc. **60**, 1571 (1938).

containing essentially no thorium. A few, numbers 13, 14, 15, 17 and 18, contained some thorium, while in two only, numbers 16 and 20, did the amount of thorium exceed the uranium.

The isotope abundances (relative to the most abundant isotope in each sample) are all believed to be correct to *within at least one percent* unless otherwise noted. An idea of the ability of the apparatus to reproduce results is gained from an examination of the data for samples 2, 6, 8, 10 and 13, where two separate analyses were made. It should be emphasized that the two analyses in each case were obtained at totally different times and that at least one other sample had been in the apparatus between the two analyses. In several cases, months passed and many samples, including some of common lead, were investigated between the two analyses.

The atomic weights were computed from the abundances by first calculating the mean mass number and converting this by assuming the packing fraction of lead to be +1.55, and the conversion factor in going from the physical to the chemical scale to be 1.000275. The choice of +1.55 as the packing fraction is quite arbitrary. It happened to be the value which the writer found would bring the chemically and physically determined atomic weights of common lead[2] into the best agreement. Possibly the value 2.0–2.3 deduced from Dempster's[3] data would be a better one to use.

Although the physically and chemically determined atomic weights do not agree exactly in all cases, the agreement is on the whole extremely gratifying. Samples 8, 11, 12 and 19 were given as "unknowns" to the writer to analyze. The close agreement in the case of sample 8, the Katanga curite, is especially interesting as the two chemical atomic weight determinations on this sample had previously been made *independently* in two different laboratories.

The AcD/RaG ratio is determined by correcting the measured Pb^{207}/Pb^{206} ratio for common lead contamination. As the relative abundances of the isotopes of common lead depend somewhat upon the source of the lead there is some uncertainty as to how the correction should be made. Fortunately, these variations appear to follow fairly definite rules,[2] and for the samples so far studied the relative abundances fell between rather definite limits. Table II gives the relative abundances for the two extreme samples of common lead so far investigated, numbers 1 and 7 of Table I, reference 2.

In the case of thorium-free radiogenic minerals one should be able to find what type of common lead impurity is present by comparing the Pb^{208}/Pb^{204} ratio with the data of reference 2.

Actually, in 20 of the 21 samples investigated the amount of common lead is so small that one need not take account of the variations in its composition. In a number of samples where the abundance of Pb^{204} was very low no attempt was made to measure the amount of it as the determination would be of no particular value. It is of interest to note that the ability of the apparatus to detect and measure relatively small amounts of Pb^{204} is of considerable value in the study of minerals containing both uranium and thorium. In that case, one may conveniently use Pb^{204} as an accurate measure of the common lead contamination provided, of course, the amount of common lead is small, as is usually the case, so that one need not be concerned with variations in its composition.

Figure 4 gives one a good idea of the ease with which it is possible to measure the abundance of rare isotopes. It is to be noted that the spectrum for the Pb^{204} region and lower has been drawn with an ordinate scale 400 times as great as that for the rest of the spectrum.

Although the apparatus was carefully baked prior to use, and liquid air was used on the traps, very small traces of mercury vapor from the diffusion pumps were sometimes present in the tube. The contribution that Hg^{204} made to the Pb^{204} peak could accurately be determined by merely measuring the height of the Hg^{202} peak (see Fig. 4) and making use of the known isotope abundances for mercury.[1] Hg^{202} is 4.4 times as abundant as Hg^{204}.

Table III gives the isotopic analysis obtained by Aston,[4] Rose and Stranathan,[5] and Mattauch and Hauk[6] for samples taken from the same

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[3] A. J. Dempster, Phys. Rev. **53**, 869 (1938).

[4] F. W. Aston, Proc. Roy. Soc. **A140**, 535 (1933).

[5] J. L. Rose and R. K. Stranathan, Phys. Rev. **50**, 792 (1936).

[6] J. Mattauch and V. Hauk, Naturwiss. **25**, 763 (1937).

regions as were some of the writer's. All percentage abundances have been converted to abundances relative to the most abundant isotope for the sake of comparison. In the case of the Great Bear Lake, Morogoro and thorite material, the *identical* samples were used by the several investigators so that the results are strictly comparable. The discrepancies in the table lie considerably outside of the writer's limits of error.

THE RELATIVE ACTIVITIES OF THE ACTINIUM AND URANIUM SERIES

As the intermediate members of the uranium and actinium series are short lived compared with the ages of the minerals with which we are concerned, it is possible to write the following expressions relating the radiogenic lead and uranium isotopes

$$N(\mathrm{Pb}^{206})=\mathrm{RaG}=N(\mathrm{U_I})(\exp[\lambda(\mathrm{U_I})t]-1), \quad (1)$$

$$N(\mathrm{Pb}^{207})=\mathrm{AcD}$$
$$=N(\mathrm{AcU})(\exp[\lambda(\mathrm{AcU})t]-1), \quad (2)$$

$$\frac{N(\mathrm{Pb}^{207})}{N(\mathrm{Pb}^{206})}=\frac{\mathrm{AcD}}{\mathrm{RaG}}=\frac{N(\mathrm{AcU})}{N(\mathrm{U_I})}\,\frac{\exp[\lambda(\mathrm{AcU})t]-1}{\exp[\lambda(\mathrm{U_I})t]-1}. \quad (3)$$

Eq. (3) predicts the manner in which the $\mathrm{Pb}^{207}/\mathrm{Pb}^{206}$ ratio (corrected for ordinary lead contamination) in a uranium mineral should depend upon the mineral's age. Conversely, if all the constants in the equation have been properly evaluated it should be possible to determine the age from the $\mathrm{Pb}^{207}/\mathrm{Pb}^{206}$ ratio.

If one calls the present day ratio of activities of the actinium and uranium series R, one can write

$$R=\lambda(\mathrm{AcU})N(\mathrm{AcU})/\lambda(\mathrm{U_I})N(\mathrm{U_I}). \quad (4)$$

Solving Eq. (4) for $\lambda(\mathrm{AcU})$, substituting the results in Eq. (3) and replacing $N(\mathrm{U_I})/N(\mathrm{AcU})$ by 139 (see previous paper), one has

$$\frac{N(\mathrm{Pb}^{207})}{N(\mathrm{Pb}^{206})}=\frac{\mathrm{AcD}}{\mathrm{RaG}}=139^{-1}\frac{\exp[139R\lambda(\mathrm{U_I})t]-1}{\exp[\lambda(\mathrm{U_I})t]-1}. \quad (5)$$

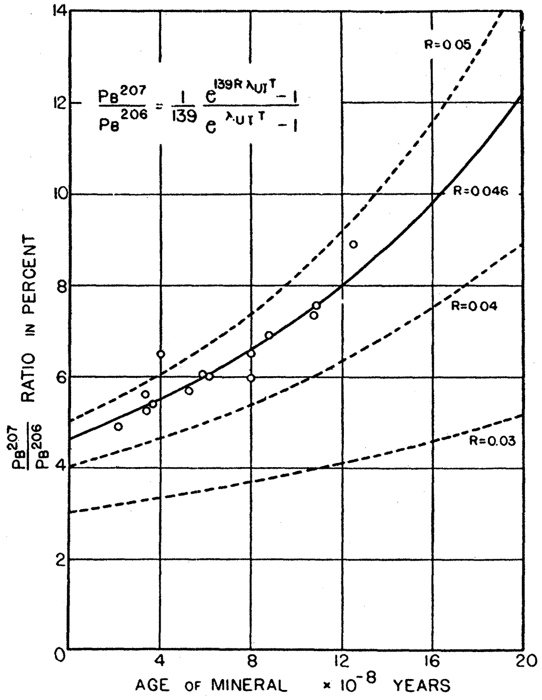

FIG. 5. $\mathrm{Pb}^{207}/\mathrm{Pb}^{206}$ (corrected for common lead impurities) as a function of the age of the mineral from which the lead was extracted. The curves are plotted according to the formula in the diagram for various assumed values of R (the ratio of activities of the actinium and uranium series). The circles are experimentally determined points.

In Fig. 5 is plotted $\mathrm{Pb}^{207}/\mathrm{Pb}^{206}$ *versus* t for various values of R substituted in Eq. (5). The decay constant of $\mathrm{U_I}$ is chosen as 1.520×10^{-10} yr^{-1}.* The experimental points shown in the figure are obtained from the data given in Table I. The ages given in column 16 are computed from Eq. (1), with allowance, of course, for the fact that the equation refers to numbers of atoms, while the Pb/U ratios refer to weights of material. The points corresponding to samples 3, 7, 8, 14 and 20 are not plotted. Samples 3 and 7, Katanga yellow specimens, are definitely known to be alteration products of samples 2 and 6, Katanga black specimens, and hence, not reliable for age determinations. Likewise, 8 and 14, Katanga curite and Manitoba uraninite, respectively, were extracted from minerals which had suffered alteration. Sample 20, Norwegian

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* In a trial computation λ was taken as 1.524×10^{-10} yr.$^{-1}$, a value depending upon the commonly accepted value, 4.0 percent for the ratio of activities of the actinium and uranium series. When it was found that R should be 4.6 rather than 4.0 percent $\lambda(\mathrm{U_I})$ was changed to 1.520 $\times10^{-10}$ to take account of the difference. As $\lambda(\mathrm{U_I})$ depends only very slightly upon the value assumed for R it makes very little difference what exact value one assumes for $\lambda(\mathrm{U_I})$ so far as the discussion which follows is concerned.

Table I. *Relative abundances of the isotopes in 21 samples of radiogenic lead.*

1	2	3	4	5	6	7	8	9
No.	Mineral and Source*	Isotope Abundances 208	207	206	204	Mean Mass Number	Atomic Weight Physical	Chemical
1.	Pitchblende[7] St. Joachimsthal, Bohemia	32.5	17.75	100	0.884 ±3%	206.536 ±0.005	206.511	206.50[7]
2.	Pitchblende[8] Black Component I Katanga, Belgian Congo, Africa	0.042 ±10%	6.03	100		206.058 ±0.001	206.033	206.00[8]
		0.047 ±20%	6.07	100				
3.	Pitchblende[8] Yellow Component I Katanga, Africa	0.51 ±3%	6.27	100	<0.02	206.068 ±0.001	206.043	205.97[8]
4.	Pitchblende[9] Black Component Ia Katanga, Africa	0.092 ±5%	6.04	100		206.059 ±0.001	206.034	
5.	Pitchblende[9] Yellow Component Ia Katanga, Africa	2.09 ±2%	6.96	100		206.102 ±0.001	206.077	
6.	Pitchblende[10] Black Component II Katanga, Africa	0.077 ±10%	6.08	100		206.060 ±0.001	206.035	206.04[10]
		0.076 ±5%	6.08	100	<0.006			
7.	Pitchblende[10] Yellow Component II Katanga, Africa	0.247 ±3%	6.23	100	0.007 ±20%	206.063 ±0.001	206.038	206.05[10]
8.	Curite[12] Katanga, Africa	0.186 ±3%	6.11	100	<0.02	206.061 ±0.001	206.036	206.027[12] 206.03[13]
		0.180 ±3%	6.13	100				
9.	Pitchblende[14] Beaver Lodge Lake, N. W. T., Canada	0.309	6.31	100	0.0557 ±3%	206.113 ±0.001	206.088	206.08[10]
10.	Pitchblende[15] Great Bear Lake, N. W. T., Canada	(a) 2.51	9.76	100	0.063 ±3%	206.130 ±0.001	206.105	206.06[16]
		(b) 2.54	9.73	100	0.061 ±5%			
11.	Cyrtolite[17] II Bedford, N. Y., U. S. A.	2.22	6.07	100	0.0443 ±2%	206.096 ±0.001	206.071	206.07[12]
12.	Cyrtolite[18] I Bedford, N. Y.	4.29	6.89	100	0.095 ±5%	206.139 ±0.002	206.114	205.92[19]
13.	Uraninite[20] Besner, Ont., Canada	1.082 ±2%	6.73	100		206.082 ±0.001	206.057	206.05[12]
		1.06 ±2%	6.73	100	0.0073 ±10%			
14.	Uraninite[21] Huron Claim, Manitoba, Canada	6.51	16.17	100	0.022 ±20%	206.238 ±0.002	206.215	
15.	Uraninite[22] Wilberforce, Canada	6.16	7.49	100	0.011 ±20%	206.174 ±0.002	206.149	206.195[23]
16.	Thorianite[24] Ceylon, India	100.	3.43	59.0	0.006 ±20%	207.252 ±0.01	207.227	207.21[24]
17.	Uraninite[31] Morogoro, Tanganyika Territory, Africa	0.18 ±10%	5.98	100	0.001 ±20%	206.060 ±0.001	206.035	
18.	Cleveite[25] Auselmyren, Holt Aust-Agder, Norway	1.05	7.55	100	0.0006 ±50%	206.089 ±0.001	206.064	
19.	Cleveite[26] Pied des Monts, Quebec, Canada	1.92 ±2%	7.60	100	0.047 ±5%	206.103 ±0.002	206.078	
20.	Thorite[27] Brevig, Norway	100.	1.22 ±2%	5.53	0.061 ±5%	207.883 ±0.001	207.858	207.90[24]
21.	Kolm[28] Güllhögen, Sweden	(a) 1.91 ±2%	7.29	100	0.050 ±20%	206.102 ±0.002	206.077	206.01[29]
		(b) 2.08 ±2%	7.34	100	0.055 ±5%			
		(c) 2.07 ±2%	7.42	100				

TABLE I (*Continued*).

		10	11	12	13	14	15	16	17	18	19
No.	MINERAL AND SOURCE	AcD/RaG %	MINERAL ANALYSIS % U	% Th	% Pb	Pb/U	RaG/U^{238}	AGE FROM RaG/U^{238} IN 10^6 YR.	ThD/Th	AGE FROM ThD/Th IN 10^6 YR.	AGE FROM AcD/RaG IN 10^6 YR.
1.	St. Joachimsthal Pitchblende	4.88	60.24	—	3.22	0.0536	0.0302	227	—	—	140
2.	Katanga Black I Pitchblende	6.00 6.05	74.9	—	6.7	0.089	0.0845	616	—	—	610
3.	Katanga Yellow I Pitchblende	6.07	58.5	—	8.4	0.144	0.1358	973	—	—	635
4.	Katanga Black Ia Pitchblende	6.00									610
5.	Katanga Yellow Ia Pitchblende	6.13									655
6.	Katanga Black II Pitchblende	6.05	77.2	—	6.48	0.0839	0.0797	582	—	—	625
7.	Katanga Yellow II Pitchblende	6.13	68.5	—	6.74	0.0983	0.0930	676	—	—	655
8.	Katanga Curite	6.05	65.3	—	9.7	0.1483	0.1405	995	—	—	625
9.	Beaver Lodge Pitchblende	5.62	51.16	—	2.492	0.0488	0.0447	333	—	—	460
10.	Great Bear Lake Pitchblende	8.88	52.32	—	10.51	0.201	0.180	1251	—	—	1420
11.	Bedford Cyrtolite II	5.41	6.73	—	0.351	0.0522	0.0486	361	—	—	375
12.	Bedford Cyrtolite I	5.23	7.29	—	0.374	0.0513	0.0454	341	—	—	300
13.	Besner Uraninite	6.63	67.6	1.57	7.69	0.114	0.1062	765	0.0359	787	825
14.	Huron Claim Uraninite	15.9	54.14	12.37	15.47	0.285	0.232	1570	0.0579	1252	2200
15.	Wilberforce Uraninite	7.33	53.52	10.37	9.26	0.173	0.1532	1077	0.0452	983	1035
16.	Ceylon Thorianite	5.67	11.8	68.9	2.34	0.198	0.0723	531	0.0209	461	485
17.	Morogoro Uraninite	5.96	70.45	0.2	8.30	0.1177	0.1117	803	—	—	595
18.	Norwegian Cleveite	7.54	67.18	2.76	11.19	0.1666	0.1543	1085	0.0385	840	1090
19.	Pied des Monts Cleveite	6.88	49.25	—	6.67	0.1354	0.1233	882	—	—	905
20.	Norwegian Thorite	6.1 ±30%	0.45	30.10	0.35		0.0324	243	0.016	355	—
21.	Swedish Kolm	6.47	0.462	—	0.026	0.056	0.0517	388	—	—	770

TABLE II. *Isotope abundances in two samples of common lead.*

No.	MINERAL AND SOURCE	ISOTOPE ABUNDANCES 206	207	208	204
1	Galena, Great Bear Lake, Canada	35.3	15.30	15.93	1.000
2	Galena, Joplin, Mo., U. S. A.	40.8	15.88	21.65	1.000

TABLE III. *Comparison of isotope abundances obtained by various investigators.*

MINERAL	INVESTIGATOR	ISOTOPE ABUNDANCES 206	207	208	204	AcD/RaG	MEAN MASS NUMBER
Pitchblende Great Bear Lake	Aston	100	8.8	2.56		7.72	206.125
	R. & S.	100	9.46	3.15		8.24	206.139
	Nier	100	9.75	2.53	0.062	8.88	206.130
Pitchblende Katanga, Africa	Aston	100	7.18	0.02		7.18	206.067
	R. & S.	100	6.74	0.3		6.67	206.069
	M. & H.	100	5.15			5.15	206.049
	Nier No. 6	100	6.08	0.077	0.006	6.05	206.060
Uraninite Wilberforce, Ont., Canada	Aston	100	9.66	6.75		9.67	206.199
	R. & S.	100	8.32	7.17		8.30	206.196
	Nier	100	7.49	6.16	0.011	7.33	206.174
Uraninite Morogoro, Africa	Aston	100	7.42	0.0		7.42	206.069
	Nier	100	5.98	0.18	0.001	5.96	206.060
Thorite Brevig, Norway	Aston	4.88	1.38	100			207.895
	Nier	5.53	1.22	100	0.061		207.883

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* References for this column refer to analyses of minerals appearing in columns 11, 12, and 13.

[7] G. P. Baxter and C. I. Kelley, J. Am. Chem. Soc. **60**, 62 (1938).

[8] G. P. Baxter and C. M. Alter, J. Am. Chem. Soc. **55**, 2785 (1933).

[9] Samples 4 and 5 were fresh extractions from the *same* mineral samples as were samples 2 and 3, respectively.

[10] G. P. Baxter, J. H. Faull, Jr., and F. D. Tuemmler, J. Am. Chem. Soc. **59**, 702 (1937).

[12] G. P. Baxter and C. M. Alter, J. Am. Chem. Soc. **57**, 467 (1935).

[13] O. Honigschmid, unpublished, referred to in reference 12.

[14] G. P. Baxter and M. E. Averill, J. Am. Chem. Soc. **59**, 705 (1937).

[15] J. P. Marble, J. Am. Chem. Soc. **58**, 434 (1936). Sample (a) obtained from J. P. Marble through G. P. Baxter. Sample (b) identical lead as was used by Aston for his isotope analysis and obtained from A. v. Grosse. Both samples were taken from the same original lot. It is interesting to note that in spite of extensive chemical treatment in different laboratories the isotopic analysis for the two samples are in nearly perfect agreement.

[16] J. P. Marble, J. Am. Chem. Soc. **56**, 854 (1934).

[17] O. B. Muench, J. Am. Chem. Soc. **56**, 1536 (1934).

[18] O. B. Muench, Am. J. Sci. **21**, 356 (1931).

[19] G. P. Baxter and C. M. Alter, J. Am. Chem. Soc. **55**, 1445 (1933).

[20] H. V. Ellsworth, Am. Mineral. **16**, 577 (1931).

[21] DeLury and Ellsworth, Am. Mineral. **16**, 569 (1931).

[22] R. C. Wells, appears in *Report of the Committee on the Measurement of Geologic Time*, (1931), No. 7, G. Kirsch and A. C. Lane, Proc. Am. Acad. **66**, 365 (1931).

[23] G. P. Baxter and E. W. Bliss, J. Am. Chem. Soc. **52**, 4851 (1930).

[24] O. Honigschmid, Zeits. f. Electrochem. **25**, 91 (1919).

[25] E. Gleditsch, unpublished.

[26] O. B. Muench, unpublished.

[27] K. Fajans, Zeits. f. Electrochem. **24**, 163 (1918).

[28] R. C. Wells, Appears in *Report of the Committee on the Measurement of Geologic Time*, (1930), No. 6, p. 4. Sample (a) was the identical material used in chemical atomic weight analysis. The material had been converted at one time to $Pb(CH_3)_4$ through a rather complicated chemical process. As used finally by the writer it was in the form of PbI_2. Sample (b) had been through the same chemical treatment as sample (a) had. Sample (c) was a fresh extraction from original mineral.

[29] G. P. Baxter and E. W. Bliss, J. Am. Chem. Soc. **52**, 4848 (1930).

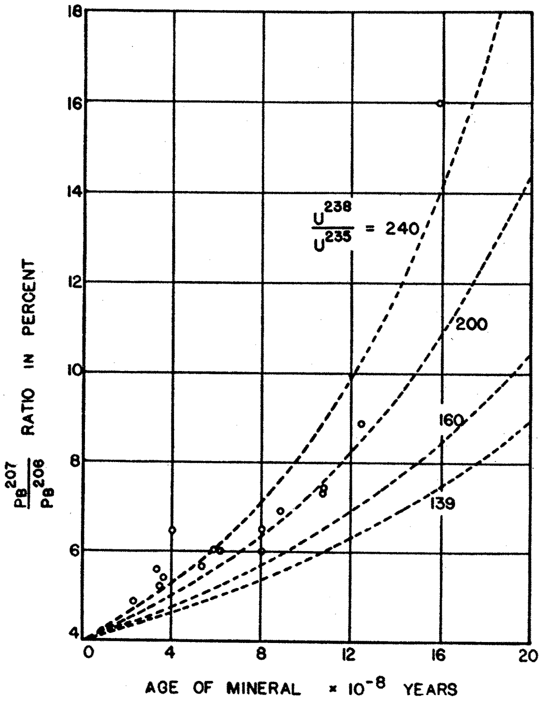

FIG. 6. Pb^{207}/Pb^{206} (corrected for common lead impurities) as a function of the age of the mineral. The curves were plotted for various assumed values for U^{238}/U^{235} on the hypothetical assumption that the actinium series is just 4 percent as active as the uranium. The circles represent the same experimentally obtained points as were plotted in Fig. 5.

thorite, is not included as the accuracy in calculating AcD/RaG was too low. Sample 17, Morogoro uraninite, probably should not have been plotted. Its Pb/U ratio, 0.1177, is much higher than that usually found for the region,[30] and hence indicates that this particular sample has been altered.

The results are seen to be in much better agreement with an assumed $R=4.6\pm0.1$ percent than with the directly determined value 4.0–4.1 percent, as measured by v. Grosse,[31] Gleditsch and Foyn,[32] and Francis and Da Tchang.[33] It is hard to account for the discrepancy. All of the Pb^{207}/Pb^{206} ratios except that for sample 1, the St. Joachimsthal pitchblende, are believed to be correct to about one percent. Because of the large amount of ordinary lead in sample 1, it is difficult to make an accurate correction, and hence, the corrected ratio may be in error by as much as ten percent in this case.

The Pb/U ratios from which the ages of the minerals were calculated certainly could not be in error by an amount large enough to explain the discrepancy, unless the minerals had been altered. If one were to account for the difference in this manner, one would have to assume all of the minerals in question had been altered to about the same extent in the same direction, an extremely artificial hypothesis. Moreover, the alteration would have to be one in which lead rather than uranium had been lost, an occurrence which is just the converse of what is believed usually to happen when uranium minerals suffer alteration.

That the difficulty is caused by an error in the U^{238}/U^{235} ratio seems very unlikely because first of all this ratio was carefully determined and is believed to be correct within a percent, and second, even if this ratio were in error by as much as 10 or 20 percent, it would not explain the large difference in question. At this point one might inquire whether the U^{238}/U^{235} ratio, as measured with a mass spectrometer, is really what enters into the problem; that is to say, could it be possible that not all U^{235} atoms disintegrate, and that the uranium isotope ratio which enters into the equation should thus be greater than 139?. Such a hypothesis does not seem likely, as not only is there no record of the existence of *any* stable isotope of *any* element heavier than bismuth, but moreover, one would have to assume U^{235} to exist in both a stable and an unstable form, an assumption one is reluctant to make on the basis of the evidence presented here. In this connection it seems worth mentioning that even if one admits this possibility and constructs a family of Pb^{207}/Pb^{206} *versus* t curves with U^{238}/U^{235} as a parameter, while R is held fast at 0.04, as was done in Fig. 6, it is not possible to find a curve which fits the experimentally determined points any better than does the chosen curve of Fig. 5. In other words, as far as the isotopic analysis of the leads is concerned there is no reason to believe that the abundance ratio $U^{238}/U^{235}=139$ and the activity

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[30] *Age of the Earth,* National Research Council Bull. 80, p. 369.

[31] A. v. Grosse, Phys. Rev. **42**, 565 (1932); J. Phys. Chem. **38**, 487 (1934).

[32] E. Gleditsch and E. Foyn, Comptes rendus **199**, 412 (1934).

[33] M. Francis and T. Da Tchang, Comptes rendus **198**, 733 (1934); Phil. Mag. **20**, 623 (1935).

ratio $R=0.046$ are not the proper quantities to use in the equation.

The writer's Pb^{207}/Pb^{206} *versus* t curve, solid curve in Fig. 5, rises much less rapidly with the age of the mineral than does the relation usually employed and accepted at the present time. The difference is not surprising when one considers that these older computations involve indirectly determined U^{238}/U^{235} ratios lying between 250 and 330,[31, 34–37] numbers in striking disagreement with the writer's directly determined ratio of 139. The curves commonly accepted belong to the family shown in Fig. 6 and rise even steeper than does the steepest curve shown in that figure, the one for $U^{238}/U^{235}=240$. The recent computations of Meyer gave the values 110[38] and 180.[39] These are the only calculated U^{238}/U^{235} ratios falling even near to the writer's value.

In view of the evidence presented in the previous paragraphs, one is forced to conclude that either (1) the relative activities of the actinium and uranium series is higher than has usually been supposed—close to 4.6 percent rather than 4.0 percent, or (2) that some unknown factor or factors not taken into account in the present theories of the disintegration of the actinium and uranium families are causing the disagreement. Should the former and far more likely hypothesis prove to be correct, it will be necessary to modify the decay constants and half-lives commonly accepted for U_I and AcU. The new values will be $\lambda(U_I)=1.520\times 10^{-10}$ yr.$^{-1}$, $T(U_I)=4.56\times 10^9$ yr., and $\lambda(\text{AcU})=9.72\times 10^{-10}$ yr.$^{-1}$, $T(\text{AcU})=7.13\times 10^8$ yr.

TABLE IV. *Variation of the* U^{238}/U^{235} *ratio with geologic age.*

Number of Years Ago	Ratios Based on Present Work		Ratios Based on Earlier Work	
	$\frac{U^{238}}{U^{235}}$	$\frac{\text{Activity of AcU Series}}{\text{Activity of U Series}}$	$\frac{U^{238}}{U^{235}}$	$\frac{\text{Activity of AcU Series}}{\text{Activity of U Series}}$
0×10^8	139.0	0.046	300	0.04
4	100.2	0.065	153	0.079
8	72.2	0.089	79	0.127
12	52.1	0.123	40.3	0.298
16	37.5	0.171	20.8	0.575
20	26.9	0.238	10.6	1.13

From these new decay constants one may readily calculate the manner in which the U^{238}/U^{235} ratio has varied throughout geological time. In Table IV are given the results of these calculations together with the corresponding ratios of activities of the actinium and uranium series as computed by Eq. (4). In the second half of the table are tabulated the results for the analogous computations based upon older data. The present day U^{238}/U^{235} ratio is here taken as 300 and the present ratio of activities of the series as 0.04. From a comparison of the data one concludes that in the early days of the earth's history U^{235}(AcU) was not nearly as abundant as was at one time thought, and hence, the heat energy released by its decay did not play nearly so important a part in influencing the earth's thermal history as was at one time believed by some.

THE MEASUREMENT OF GEOLOGICAL TIME

The mineral ages as computed from the RaG/U^{238} ratios in the present work are in good agreement with those previously calculated from the Pb/U ratio. In the earlier work the common lead contamination was computed from the atomic weight of the lead and the correction for AcD was made empirically.

In those samples containing both uranium and thorium the isotopic analysis of the lead enables one to make an independent calculation of the mineral's age. This has been done in columns 17 and 18 of Table I. The computations were made by applying an equation analogous to (1) and (2) to the ThD/Th ratio. The recently determined decay constant of thorium,[40] 4.99×10^{-11} yr.$^{-1}$, was employed in the calculations.

TABLE V. *Alteration of* 10^9 *yr.-old mineral by loss of 50 percent of uranium* t_1 *years ago.*

t_1	Approximate Apparent Ages Computed from Pb/U	Approximate Apparent Ages Computed from AcD/RaG
0×10^8 yr.	2.0×10^9 yr.	1.00×10^9 yr.
2	1.8	1.07
4	1.6	1.11
6	1.4	1.15
8	1.2	1.11
10	1.0	1.00

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[34] Lord Rutherford, Nature **123**, 313 (1929).

[35] A. F. Kovarik, Phys. Rev. **35**, 1432 (1930).

[36] F. Western and A. E. Ruark, Phys. Rev. **44**, 675 (1933); **45**, 628 (1934).

[37] A. Holmes, *Age of the Earth* (Nelson Press, 1937), p. 151.

[38] S. Meyer, Wien. Ber. IIa **146**, 175 (1937).

[39] S. Meyer, Wien. Ber. **146**, 581 (1937).

[40] A. F. Kovarik and N. I. Adams, Phys. Rev. **53**, 928 (1938).

Although the uranium and thorium ages are in rough agreement there appear to be some discrepancies. Whether these can be attributed partially to errors in the decay constants and partially to alterations in the minerals or entirely to mineral alterations, one hardly can conclude from the present data. In view of the limited number of minerals investigated the latter hypothesis is to be preferred. The writer does not believe that the differences can be caused by errors in the mineral or isotopic analyses.

An attempt to make age determinations from the AcD/RaG ratio of uranium leads has already been made.[5] The writer believes that the present work demonstrates the practicability of such method provided, of course, the proper decay constant for AcU is employed. The method once well established will, together with the Pb/U analysis of the mineral, give *two completely independent determinations* of age on the same specimen. This fact is especially significant as an alteration of the mineral affects the ages as computed by the two methods in quite different ways. In the case of the alteration of a uranium mineral, uranium rather than lead usually is lost. The age as computed from the Pb/U ratio is thus too high—by an amount depending upon the amount of uranium lost and time at which the loss took place. On the other hand, the age computed from the Pb^{207}/Pb^{206} ratio hardly differs from the true age of the mineral.

This point is perhaps best illustrated by means of an example. Let us consider a uranium mineral 10^9 yr. old which has lost half of its uranium at a time t_1 years ago. Columns 2 and 3 of Table V give the approximate apparent ages of this mineral as computed for various values of t_1 from the present day Pb/U ratio and from the present day AcD/RaG ratio for this mineral. In this case one can clearly see that the AcD/RaG age is far more reliable than that calculated from the Pb/U ratio.

In a similar fashion one may compute the effects of a hypothetical alteration in which lead has been lost. The results shown in Table VI indicate that in this case, too, the age determined from the AcD/RaG ratio is closer to the true age of the mineral than that found from the Pb/U ratio.

TABLE VI. *Alteration of 10^9 yr.-old mineral by loss of 50 percent of accumulated lead t_1 years ago.*

	APPROXIMATE APPARENT AGES COMPUTED FROM	
t_1	Pb/U	AcD/RaG
0×10^8 yr.	5×10^8 yr.	10.0×10^8 yr.
2	6	8.9
4	7	8.5
6	8	8.6
8	9	9.2
10	10	10.0

The calculations indicate the validity of the statement made earlier that the alteration of a mineral affects the ages as computed by the two different methods in different ways. Thus, if one is willing to accept the possibility that the activity of the actinium series is 4.6 percent that of the uranium, as is indicated by Fig. 5, then the close agreement of most of the experimental points in that figure with the solid curve indicates that only a few of the minerals for which data are plotted have suffered serious alteration. In column 19 of Table I are given for comparison the ages as computed from the Pb^{207}/Pb^{206} ratio on the assumption that the solid curve of Fig. 5 properly describes the way in which Pb^{207}/Pb^{206} varies with t.

In discussing alterations of the minerals no mention was made of the possibility that leaching of the intermediate products of the radioactive series might have taken place. Without considering specific examples it would be difficult to predict exactly how such effects might affect the ages as computed by the two methods. In general one might say that a loss of any of the intermediate actinium series products would give a low Pb^{207}/Pb^{206} ratio without appreciably affecting the Pb/U age, while a partial loss of an intermediate product of the uranium series would change both the Pb^{207}/Pb^{206} ratio and the Pb/U ratio, but not in the same amounts. In any event, it appears safe to conclude that with the exception of isolated cases *any* simple alteration will manifest itself in a difference in the ages as computed by the two different methods.

An examination of the figure indicates that only three of the points, those for samples 10, 17 and 21, are in serious disagreement with the curve. The facts concerning sample 17, the

Morogoro uraninite, have been discussed in the third paragraph of the previous section. The discrepancy for samples 10, the Great Bear Lake pitchblende, and 21 can only mean that these samples, too, have suffered alteration of some sort. In the case of sample 21, the Swedish kolm, the discrepancy appears to be particularly serious.

It is of interest to examine the data for samples (3) and (7), the yellow components of the Katanga pitchblende specimens. The Pb^{207}/Pb^{206} ratios indicate the ages must be close to those for the black components while the Pb/U ratios give higher ages, especially in the case of sample (3). The data are thus consistent with the view that the yellow components are alteration products of the corresponding black components and that they have suffered a loss of uranium. This conclusion has been reached quite independently[8] of the present work. The abnormal age obtained for the Katanga curite sample, number 8, from the Pb/U ratio can in all probability be explained by a loss of uranium from the mineral. It is extremely interesting to note that *all* of the Katanga samples have essentially the same AcD/RaG ratio *in spite of* apparent alterations in the minerals.

The data for the uraninite from Manitoba, Canada, sample 14, offer possibilities for speculation. Fortunately, this sample contained very little common lead, as evidenced by the small amount of Pb^{204}, so that one can be reasonably certain that the isotopic analysis is not complicated by the presence of common lead. The uranium and thorium ages for this sample are in definite disagreement, a fact which is not surprising when one considers the alteration processes which this very old mineral has probably suffered.[21, 41] The age as computed from the AcD/RaG ratio is 2.2×10^9 yr., a value greater than the present assumed *age of the earth.* This is especially disturbing, as any alterations by which one might conceivably explain the differences in the ages as computed by the three methods would tend to give a low AcD/RaG ratio. In other words, the true AcD/RaG ratio for the corresponding unaltered mineral would have to be higher than 15.9, and hence, the true age of the mineral would have to be greater than 2.2×10^9 years!

The relatively small amount of Pb^{204} present in the two samples containing the large amount of Th indicates that the opinion advanced by Meyer[38, 42] that Pb^{208} might decay into Pb^{204} is without experimental foundation.

This work was made possible through the very active help and encouragement of Professor G. P. Baxter, Department of Chemistry, Harvard University, who very kindly prepared and furnished most of the lead iodide samples. It is a pleasure to acknowledge the interest taken by Professor Alfred C. Lane, Chairman of the Committee on the Measurement of Geologic Time, through whose efforts a number of the specimens were obtained. Samples 16, 17, 20, and one of the number 10 samples were prepared and supplied by Dr. A. v. Grosse of the University of Chicago.

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[41] A. Holmes, *Age of the Earth* (Nelson Press, 1937), p. 167.

[42] S. Meyer, Wien Ber. IIa, **145**, 577 (1936).