width of an x-ray emission line is the sum of the widths of the initial and final states of the radiating atom. The full width at half maximum of either line in the $K\alpha$ doublet for Ge (32) is about 3.5[8] volts and for Sr (38) is about 5.8[8] volts, so that the sum of the L and K energy level widths for Br, Rb and Sr should lie between 4 and 6 volts and the widths of the K levels alone must be less than this. The widths of the K edges of Table I, determined as they are by the triangle method, are approximately $\pi/2$ times the actual[1] widths of the K levels involved. It would seem, therefore, that the width values given in this paper are not too low but are in agreement with experimental line width data.

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Geologic Time and Isotopic Constitution of Radiogenic Lead

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The isotopic constitutions of samples of lead from Colorado carnotite, Wilberforce uraninite, and Katanga and Great Bear Lake pitchblendes were found from densitometer measurements of the hyperfine structure of λ5372. The probable geologic ages of these minerals calculated from the Ac D : Ra G ratios agree very well with the ages from Pb : U ratios with the exception of the Great Bear Lake pitchblende in which case leaching or some other method of alteration may have changed the Pb : U ratio.

ACCURATE knowledge of the relative abundance of the lead isotopes, Th D, Ac D, and Ra G (Pb^{208}, Pb^{207}, and Pb^{206}), end products of the thorium, actino-uranium (Ac U), and uranium (U I) families, found in radioactive minerals is very useful in the solutions of certain cosmological problems, especially those of the geologic ages of the minerals[1, 2] and origin of the actinium series.[3–12] Estimates of the isotopic constitutions of radiogenic leads have been made from chemical atomic weights. Mass spectrograph results[11] are available for only a few samples of lead. Both methods of analysis are long and laborious, the mass spectrograph requiring a new discharge tube for each lead examined.

From the hyperfine structure of the lead spectral line λ4245, Rose and Granath[12] were able to observe Ac D in lead from Katanga pitchblende and it was suggested by them that densitometer measurements of certain hyperfine structure patterns might be a very simple and effective method of determining the relative abundance of the isotopes of lead. Recently the present authors,[13] using the structure of λ5372 found this method very satisfactory in obtaining the isotopic constitution of ordinary lead from galena.

ISOTOPIC ANALYSES OF RADIOGENIC LEADS

The spectra of several samples of lead from different uranium bearing minerals have been photographed and variations in the relative

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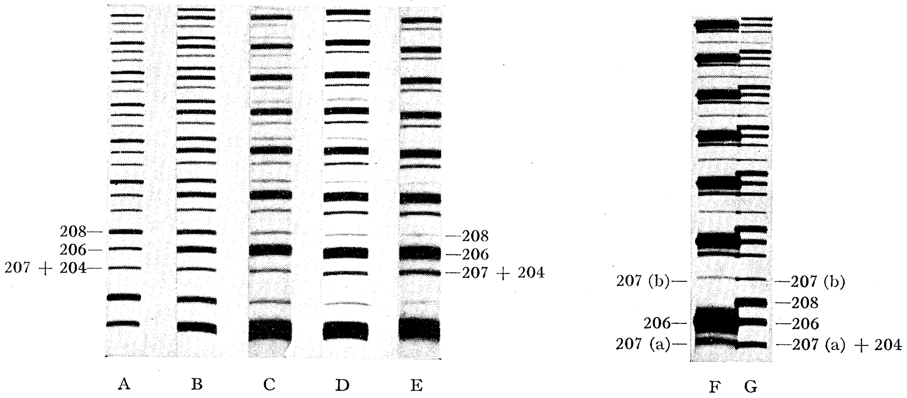

FIG. 1 (left). $\lambda 5372$, etalon spacer 5.194 mm. A. Ordinary lead; B. Colorado carnotite; C. Wilberforce uraninite; D. Great Bear Lake pitchblende (Pb extracted by Riblett); E. Katanga pitchblende. (Right) $\lambda 5372$ etalon spacer 3.561 mm. F. Katanga pitchblende; G. Ordinary lead.

intensities of the hyperfine structure components of the same line show that the proportions of isotopes are not the same. This can be seen from the photographs in Fig. 1 of the patterns of $\lambda 5372$ with a 5.194 mm etalon spacer. All of the densitometer data were obtained from photographs with this spacer, for which the Pb^{204} component and both components of Pb^{207} appear as a single component. Due to the large proportions of Pb^{206} in these leads the wire screens with percentage transmissions from 14.8 to 67.3 which were previously used with ordinary lead could not be used singly in comparing the intensities of the Pb^{206} components with the components due to Pb^{207} and Pb^{208}. Although intensity marks can be made with some success with combinations of two or more screens it was thought better to use the above screens one at a time with a brown glass filter in front of the source. The transmission of the filter was found to be 16.5 percent for $\lambda 5372$. The relative blackenings of the photographic plates from densitometer traces of the Pb^{208} and Pb^{207} components for an exposure of 100 percent transmission of light from the source were compared with an intensity-blackening curve for the Pb^{206} component in the same order of the interference pattern. The curve was obtained from photographs of equal exposure times with the wire screens and glass filter in front of the source. This method of estimating relative intensities is not so accurate as the method used for ordinary lead in which the intensity ratios of the components are not as large and where the average of several values can be found for the ratios from intensity-blackening curves for each of the components. The maximum error, however, in the results in Table I, row 4, should not be more than ∓ 0.3 in the percentage abundance of any isotope.

All of the minerals from which the leads were extracted, with the exception of the Wilberforce uraninite, contain no more than a trace of thorium and therefore the Pb^{208} in these minerals must be due to contamination of ordinary lead. Chemical analyses of the thorium content and petrographic studies indicate that the Pb^{208} in the Wilberforce material is entirely the end product of thorium. With the previous results for the isotopic proportions or ordinary lead and the percentages in Table I it is possible to determine for the above leads the percentages of Pb^{207} and Pb^{206} (Ac D and Ra G), which are the end products of uranium. The ratio of these isotopes as shown in Table I, row 8, appears to vary with the age of the mineral. This is in accordance with the present theory concerning the origin of the actinium series.

ACTINIUM SERIES

It has been known for some time that Pb^{206} is the end product of U^{238} (U I) through the radium series and it was an early view that the actinium series was a branch of the uranium family. Piccard and others[3, 4] later suggested that the actinium series contains one or more

TABLE I.

		1	2	3	4	5	6
1. Mineral		Galena [a]	Carnotite [b]	Uraninite [c]	Pitchblende [d]	Pitchblende [e]	Pitchblende [f]
2. Geographic origin		Missouri, U. S. A.	Colorado, U. S. A.	Wilberforce, Canada	Great Bear Lake, Canada	Great Bear Lake, Canada	Katanga, Belgian Congo
3. Probable age from geologic evidences			Late Cretaceous to Early Tertiary [1]	Middle Pre-Cambrian [1]	(?) Pre-Cambrian [16]	(?) Pre-Cambrian [16]	Upper-Pre-Cambrian [1]
4. Isotopic constitution from hyperfine structure in percent	Pb^{208}	51.5 [13]	32.2 [h]	6.2 [i]	4.7 [h]	2.8 [h]	0.3 [h]
	Pb^{206}	26.3	52.2	86.6	86.2	88.8	93.4
	$Pb^{204}+Pb^{207}$	22.2 [g]	15.6	7.2	9.1	8.4	6.3
5. Mean mass number [j]		207.228	206.785	206.196	206.182	206.139	206.069
Changed to chemical scale [k]		207.20	206.75	206.17	206.15	206.11	206.04
6. Chemical atomic weight of Pb		207.22 [l]	206.59 [m] 207.00	206.195 [n]		206.054 [o] 206.058	206.027 [p] 206.030
7. From hyperfine structure in percent	RaG		35.75	86.6	83.8	87.4	93.2
	Ac D		1.7	7.2	7.1	7.2	6.2
8. Ac D : Ra G ratio in percent			4.75	8.30	8.48	8.24	6.67
9. Age of mineral from Ac D : Ra G ratio in million years							
$\lambda(U\ I)=1.5\times10^{-10}yr^{-1}$	$\frac{\lambda(Ac\ U)}{\lambda(U\ I)}=10$		246	952	977	944	694
	" $=11$		220	860	882	852	622
$\lambda(U\ I)=1.6\times10^{-10}yr^{-1}$	" $=10$		222	900	923	892	650
	" $=11$		207	808	828	800	586
10. Pb : U ratio			0.0013–0.0053 [1]	0.162 [q]	0.114–0.273 [r]	0.201 [15]	0.07–0.084 [1]
11. Age of mineral from Pb : U ratio in million years			60	1050		1323	600
12. Isotopic constitution from mass spectrograph in percent	Pb^{208}	50.1 [s]		5.8 [11]		2.3 [11]	0.02 [11]
	Pb^{206}	28.3		85.9		89.8	93.3
	Pb^{207}	20.1		8.3		7.9	6.7
	Pb^{204}	1.5					
13. Mean mass number [j]		207.173		206.199		206.125	206.067
Changed to chemical scale [k]		207.14		206.17		206.09	206.04
14. Ac D : Ra G ratio in percent				9.67		7.72	7.18
15. Age of mineral from Ac D : Ra G ratio in million years:							
$\lambda(U\ I)=15.\times10^{-10}yr^{-1}$	$\frac{\lambda(Ac\ U)}{\lambda(U\ I)}=10$			1132		870	785
	" $=11$			1016		784	705
$\lambda(U\ I)=1.6\times10^{-10}yr^{-1}$	" $=10$			1054		820	736
	" $=11$			962		754	662

[a] Ordinary lead (test lead, Ag, Bi, etc. free) National Lead Co.

[b] Lead chloride residue from U. S. Radium Corp. Lead purified and reduced to a metal by Dr. E. W. Riblett (1932).

[c] Lead extracted from a single crystal of uraninite by Dr. C. M. Alter, Boston Univ. (1936).

[d] Lead extracted by Dr. Riblett from a portion of a large piece of pitchblende sent by Prof. Alfred C. Lane, Tufts College (1933).

[e] This lead obtained from Dr. J. P. Marble is from the same lot used by Marble, and Baxter and Alter for atomic weight determinations and by Aston for isotopic constitution analysis.

[f] Lead carbonate residue from Union Minière du Haut-Katanga. Purified and reduced to a metal by Dr. Riblett (1932).

[g] Pb^{207}, 21.4 percent; Pb^{204}, 0.8 percent.

[h] Pb^{208} and Pb^{204} from contamination of ordinary lead.

[i] Very little ordinary lead contamination; Pb^{208} probably all Th D.

[j] From above percentages assuming the masses of the isotopes to be integral.

[k] Mean mass number corrected for a packing factor of +1 and then converted to chemical scale; ratio of chemical (O = 16.0000) to the physical scale ($O^{16}=16.0000$) is at least 1.00025.

[l] Present international atomic weight.

[m] 206.59, T. W. Richards and M. E. Lembert, J. Am. Chem. Soc. **36**, 1329 (1914); 207.00, T. W. Richards and C. Wadsworth, ibid. **38**, 2613 (1916).

[n] G. P. Baxter and A. D. Bliss, J. Am. Chem. Soc. **52**, 485 (1930).

[o] Atomic weights from same lot; 206.054, J. P. Marble, J. Am. Chem. Soc. **56**, 854 (1934); 206.058, G. P. Baxter and C. M. Alter, ibid. **57**, 467 (1935).

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[q] Above ratio by R. C. Wells reported in reference n. Other ratios range from 0.150 to 0.172; L. T. Walker, Univ. of Toronto Studies, Geol. Ser. No. 17, 42 (1924); H. V. Ellsworth, Am. Mineral. **15**, 455 (1930); Am. J. Sci. (5) **9**, 127 (1925); 0.1628 by F. Hecht and 0.1646 by E. Kroupa in Munich, reported by A. C. Lane at meeting of Committee on Measurement of Geologic Time, New York, Dec. (1935). For minerals containing thorium the ratio commonly used is Pb : U+0.36 Th.

[r] This range for distinctly altered material to that which contains barite and silver; reference 2, page 3 (1932).

[s] F. W. Aston, Nature **137**, 613 (1936).

uranium isotopes genetically independent of U^{238} and U^{234} (U II). This hypothesis is substantiated by the mass spectrograph studies of Aston[11] and further by the results from hyperfine structure analysis in Table I for the relative abundance of Pb^{207} and Pb^{206} in uranium leads. The percentages of Pb^{207} by both methods are too large for Ac D to be the end product of a branching U I series. Since the end product of the actinium series, Pb^{207}, has an odd atomic weight, it can never arise by branching from an even atomic weight series, such as uranium, for all members of any series are either odd or even, and differ in mass by $4n$. Hahn[5] and Western and Ruark[6] have shown that there is probably only one actinouranium isotope and of the two probable masses, 235 and 239, it appears to have that of the former.

Also by separating protactinium from uranium minerals and comparing its activity with other radioactive constituents of the same minerals it has been shown[7, 8] that the actinium series is independent of the U I series and the Ac U : U I ratio is constant for all uranium minerals regardless of source, thorium content, and uranium concentration, and that the present activity ratio of the Ac U to the U I series is approximately 4 : 100. With the latter ratio, the relative abundance of Ra G and Ac D from mass spectra data,[11] and the Pb : U ratios for several minerals calculations have been made from which it appears that the ratio of the decay contants, $\lambda_{(\mathrm{Ac\,U})} : \lambda_{(\mathrm{U\,I})}$, is between ten and eleven.[7, 9, 10]

PROBABLE GEOLOGIC AGES OF THE MINERALS

From the above values and ratios of Ac D to Ra G it is possible to determine the probable geologic ages of the uranium minerals by use of the following relation:

$$\frac{\mathrm{Ac\,D}}{\mathrm{Ra\,G}}=\frac{\text{Activity Ac U}}{\text{Activity U I}}\cdot\frac{\lambda_{(\mathrm{U\,I})}}{\lambda_{(\mathrm{Ac\,U})}}\cdot\frac{(e^{\lambda_{(\mathrm{Ac\,U})}t}-1)}{(e^{\lambda_{(\mathrm{U\,I})}t}-1)}. \quad (1)$$

Geologic ages have been estimated from the proportions of lead and uranium in minerals but with this method care must be taken to be certain that the minerals have not been altered by leaching by surface waters, or by other external processes since they were originally formed. In many cases it has been extremely difficult to determine to what extent the minerals have been altered. The ranges of the Pb : U ratios in Table I show the varying effects of alterations in samples of mineral from the same source. The separation of lead isotopes by selective solution has never been observed and therefore it is difficult to see how alterations could have changed to any extent the Ac D : Ra G ratio of a mineral of a definite age.

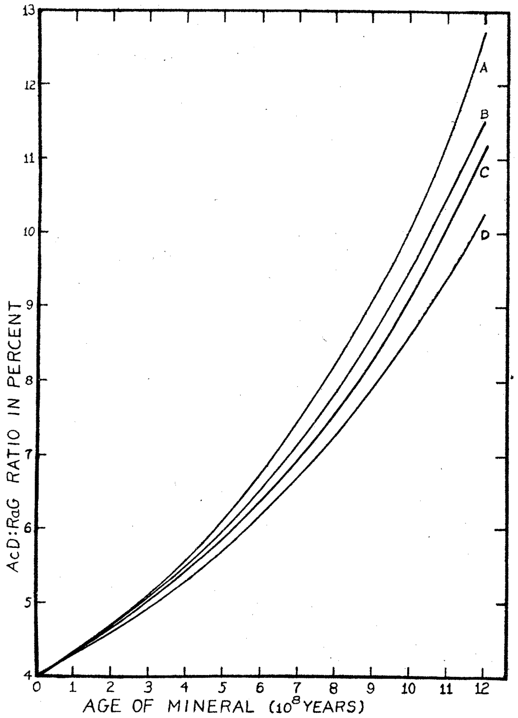

FIG. 2. Curves computed by Eq. (1); 4.0 percent present activity ratio of Ac U to U I. $\lambda_{(\mathrm{Ac\,U})}/\lambda_{(\mathrm{U\,I})}=11$: *A*, $\lambda_{(\mathrm{U\,I})}=1.6\times10^{-10}$ yr^{-1}; *B*, $\lambda_{(\mathrm{U\,I})}=1.5\times10^{-10}$ yr^{-1}. $\lambda_{(\mathrm{Ac\,U})}/\lambda_{(\mathrm{U\,I})}=10$: *C*, $\lambda_{(\mathrm{U\,I})}=1.6\times10^{-10}$ yr^{-1}; *D*, $\lambda_{(\mathrm{U\,I})}=1.5\times10^{-10}$ yr^{-1}.

Fig. 2 shows curves computed by Eq. (1) for variation of the Ac D : Ra G ratio in uranium lead with the age of the mineral. In plotting these curves two probable values, 10 and 11, for the ratio of the decay constants of Ac U and U I and also the limiting values of $\lambda_{(\mathrm{U\,I})}$($1.5\times10^{-10}$ yr^{-1} and 1.6×10^{-10} yr^{-1}) in current use[9, 14] were substituted in the above equation. The ages of the minerals from the Ac D : Ra G ratios are shown in Table I, row 9. Which of the four values for each mineral is the most nearly correct cannot be determined until better experimental agreement is found for the decay constants of Ac U and U I. The ages, however, with the exception of the Great Bear Lake pitchblendes, are not far from age estimates by other methods.

The slightness of difference in the ages of the Great Bear Lake pitchblende from two samples with different proportions of ordinary lead contamination indicates that the age for this material from the Ac D : Ra G ratios is to be preferred to the much higher estimate by Marble[15] from the Pb : U ratio. He did not think the sample desirable for a highly accurate age determination but it was the best which had thus far come from the region. Also the large variation in the Pb : U ratio shows that many deposits of this mineral have been subject to alteration. Through incomplete geological studies there is a conflict of opinion of the age, ranging

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[15] J. P. Marble, J. Am. Chem. Soc. **58**, 434 (1936).

from Keweenawan to Kewatin.[16] From the above lead analyses it appears to have been formed at about the time of formation of the Wilberforce uraninite which is thought to be Middle Pre-Cambrian.

The method proved successful in showing that Colorado carnotite is a more recent formation. For very young minerals accurate ages cannot be expected since the Ac D : Ra G ratio is very sensitive to a small error in the content of Pb^{207}. If the percentage of Pb^{207} for the above lead were decreased 0.2 percent (within the limit of experimental error), the ratio of Ac D : Ra G would be changed from 0.0475 to 0.0420 and the ages from curves of Fig. 2, from approximately 200×10^6 yr to 60×10^6 yr.

QUANTITY OF LEAD REQUIRED

The Paschen-Schüler hollow cathode discharge tube[17] used in this work requires between two and four grams of pure metallic lead for a steady discharge. Only a small fraction of the lead is lost, however, after several days' operation. The major portion of the lead left in the stainless steel hollow cathode after an investigation can be removed with a steel blade and the remainder by placing the cathode in hot nitric acid for several minutes. After polishing the outside and inside with very fine emery cloth and washing, the cathode is ready to be used with another sample.

Some modification of this type tube will have to be made if leads are to be analyzed from rocks, meteorites, and other sources which contain very small quantities of lead. The more intense lines could just be detected with 15 mg of lead electrolytically deposited inside of a water-cooled cathode, which was tried some time ago by one of us (J. L .R.), of the type used by Kopfermann[18] with 100 mg of Th D. To operate this type of tube the surface of the deposited lead must be smooth, clean, and bright. The most satisfactory surfaces were obtained with a dilute lead perchlorate solution with a small amount of meat peptone added. The solution was put in the hollow cathode and a small lead wire electrode was placed in the center. To insure a firm coating the cathode should be rotated and only a few milliamperes of current used. Whether or not cathodes with very small amounts of deposited lead can be used for isotopic analyses with the success of the larger tube can be determined only by further investigations.

ACKNOWLEDGMENTS

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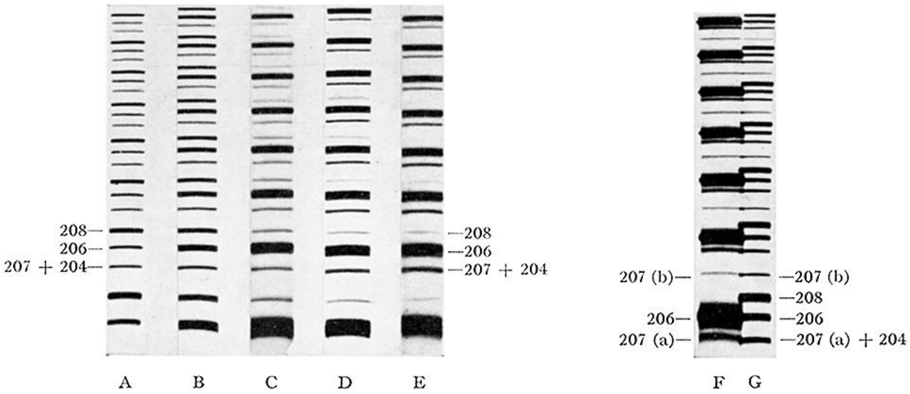

FIG. 1 (left). λ5372, etalon spacer 5.194 mm. A. Ordinary lead; B. Colorado carnotite; C. Wilberforce uraninite; D. Great Bear Lake pitchblende (Pb extracted by Riblett); E. Katanga pitchblende. (Right) λ5372 etalon spacer 3.561 mm. F. Katanga pitchblende; G. Ordinary lead.