On the Origin of the Actinium Series of Radioactive Elements

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Data on the actinium series gathered from carefully selected material have been correlated. It can be definitely concluded from these data that the actinium series is independent and the decay much more rapid than in the uranium-radium series. The significance of this fact for geology (age determinations, heat evolution) is pointed out.

THE experimental material on the actinium series and its theoretical interpretation has been so far extremely conflicting.[1] This is chiefly due to the fact that the determinations of the chemical composition, geologic age, activity ratio of the actinium to the uranium-radium series, the chemical atomic weights of uranium leads and lately the isotopic constitution of these leads have never been determined with the same material for all investigations.

Thanks to the help and cooperation of Mme. Pierre Curie, Mme. Irene Joliot-Curie and Drs. G. Baxter, K. Fajans, O. Hönigschmid, A. C. Lane and H. Schlundt we were able to gather and to investigate a valuable collection of uranium-minerals and preparations from uranium-lead atomic weight determinations.

F. W. Aston had the great kindess to investigate in his mass-spectrograph some lead preparations from these sources, and it is to him that the credit for clearing the problem is due.[2]

We laid special stress on the determination of the so-called "branching ratio" or as we may better call it now "activity ratio." The older determination of O. Hahn and L. Meitner[3] (3 percent), and newer ones of J. Wildish[4] (1.5–5 percent) and E. Gleditsch and co-workers[5] (2.7–3.3 percent) are all based on the separation of protactinium with tantalum and seem to us un-

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[1] For older literature see St. Meyer and E. v. Schweidler, *Radioktivität*, 1927, p. 490. J. Wildish, Jour. Amer. Chem. Soc. **52,** 163 (1930). E. Gleditsch and E. Foyn, Comptes Rendus **194,** 1571 (1932). E. Gleditsch and S. Klementsen, Comptes Rendus **194,** 1731 (1932). G. Kirsch, *Geologie und Radioktivität*, p. 184, 1928. F. W. Aston, Nature **123,** 313 (1929). Lord Rutherford, Nature **123,** 313 (1929). A. Holmes, Nature **126,** 348 (1930). A. F. Kovarik, Science **72,** 122 (1930). G. B. Baxter and A. D. Bliss, Jour. Amer. Chem. Soc. **52,** 4850 (1930). For summaries on the actinium problem see: M. C. Neuburger, Sammlung chem. and chem.-techn. Vorträge **26,** No. 10/11 (1921). G. Elsen, Zeits. f. anorg. Chem. **180,** 304 (1929). G. Elsen, Chemisch Weekblad **25,** 517 (1928); **28,** 1, 7, 714 (1931). G. Elsen, Rec. des Trav. chim. Plays-Bas **51,** 284 (1932).

[2] F. W. Aston, Nature **129,** 649 (1932).

[3] O. Hahn and L. Meitner, Phys. Zeits. **20,** 529 (1919); Zeits. f. Physik **8,** 202 (1922).

[4] Reference 1.

[5] Reference 1.

reliable since it could be shown through the isolation of element 91[6] that its chemical properties widely differ from those of tantalum,[7] just as those of its neighbors uranium and thorium differ from their lower homologues, tungsten and hafnium.

Our determination of the Pa:UI ratio was carried out, in collaboration with Dr. I. D. Kurbatov, at the Chemical Institute of the Technische Hochschule in Berlin-Charlottenburg.[8]

TABLE I.

		1	2	3	4	5
1	Mineral Geographical origin	Carnotite[a] Colorado, U.S.A.	Kolm[b] Gullhogen, Westergotland, Sweden	Pitchblende[c] Katanga, Belg. Congo, Africa	Pitchblende[d] Morogoro, East Africa	Pitchblende[e] Wilberforce, Canada
3	Chemical analysis U %	19.09	0.43[9]; 0.41	72.26	70.45	53.52[11]; 52.71
	Th %	0	0.0	0.01[10]	ab. 0.2	10.37[11]
	Pb %	trace	0.026[9]	6.68	8.30	9.26[11]
4	Isotopic consti- Pb 206%			93.3[12]		85.9[12]
	tution of Pb 207%			6.7[f]		8.3[g]
	208%			0.0		5.8
	others			0.0		0.0
	Percentage of RaG			93.3[13]		85.9
	AcD			6.7		8.3
	ThD			0.0		5.8[14]
6	Chem. atomic weight of Pb		206.013[15] ±0.008	206.048[16]		206.195[17]
7	Phys. atomic weight of Pb		206.058 ±0.01	206.067[18]		206.20[18]
8	Pb:U ratio	very small	0.061	0.0924	0.1178	0.1730
9	RaG:UI ratio	very small	0.058	0.086	0.1093	0.1486
10	Geological age in years	<70.10[6]	404.10[6]	591.10[6]	748.10[6]	987.10[6]
11	Pa-α activity in mg. U_3O_8 for every 1 g U in the mineral	28.0	27.9	27.8	27.6	28.2
12	Number of disintegrating Pa-atoms for 100 decaying UI-atoms		4.0±0.1, mean value, calculated from row 11			
13	Number of AcD atoms for 100 atoms RaG in U-Pb		4.8±1.8[19]	7.2±0.3		9.7+0.3 −1.0

[a] Obtained from H. Schlundt; from the same lot used by J. Wildish (reference 4) for which he obtained Pa:UI = 5.16:100.

[b] Obtained from A. C. Lane, from the same general lot used for G. P. Baxter's kolm lead atomic weight determination.

[c] Obtained from Mme. Pierre Curie and Mme. Irene Joliot-Curie.

[d] Obtained from F. Kranz, Bonn, Germany.

[e] Obtained from A. C. Lane and G. P. Baxter, from the same lot used for the Wilberforce lead atomic weight determination.

[f] The lead tetramethyl used by F. W. Aston was prepared from the original $PbCl_2$ used by O. Hönigschmid. According to private information from Dr. Aston the lead from Mme. Curie's sample had an identical isotopic constitution.

[g] The material used by F. W. Aston was prepared from G. P. Baxter's original atomic weight preparation.

[6] A. v. Grosse, Naturwiss. **15**, 766 (1927); Nature **120**, 621 (1927); Ber. d. Deut. Chem· Ges. **61**, 233 (1928).

[7] A. v. Grosse, Jour. Amer. Chem. Soc. **52**, 1742 (1930).

[8] Part of these results were reported at the meeting of the Chicago Section of the Amer. Chem. Society on September 25, 1931; see also G. Elsen, Chem. Weekblad **28**, 714 (1931).

[9] R. C. Wells and R. E. Stevens, Jour. Washington Acad. of Science **21**, 412 (1931).

[10] The Th was separated with UX_1, added as indicator, concentrated and the Th-content determined with W. Noddack's x-ray spectrograph at the Physikalisch-Technische Reichsanstalt, Berlin-Charlottenburg.

[11] R. C. Wells, Jour. Amer. Chem. Soc. **52**, 4852 (1930).

[12] F. W. Aston, Nature **129**, 649 (1932).

[13] Since the mineral contains practically no Th, and therefore no ThD, the absence of Pb^{208} indicates the absence of ordinary lead, the latter containing 49.55 percent Pb^{208} (see Aston, reference 12).

[14] From the Th-content and age we calculate, using Th = 6, $1.10^{-11}a^{-1}$, the percent of ThD = 6, 0 indicating the absence of ordinary lead.

Our method consisted in precipitating the Pa from a strongly acid (HNO_3, HCl) solution of the U-mineral together with added Zr (in the proportion of 20–50 mg ZrO_2, in the form of oxychloride or nitrate, to 1 g U) by an excess of H_3PO_4, and freeing the filtered Pa-ZrP_2O_7 precipitate from adsorbed radioactive impurities (especially Io, Ra, and Po) through the addition and subsequent separation (repeated if necessary) of minute quantities (2–10 mg) of Th, Ba, Bi (and Te), Pb and La salts. The method was tested with radioactively pure Pa preparations in different concentrations and found to separate 98–99 percent of the available Pa in a radioactively pure state. The activity of the Pa preparation was compared with that of pure U_3O_8, both in extremely thin layers, in an ordinary Rutherford α-electroscope and expressed in mg U_3O_8.

The results of all determinations and investigations with our material are correlated in Table I.

These data all support A. Piccard's[20] and especially Lord Rutherford's[21] ideas about the actinium series. The following conclusions can be drawn:

1. The actinium series is independent of the U-Ra series. It is derived from a U-isotope, the actino-uranium (Ac-U), which occurs in all U-minerals in a constant ratio to UI, independent of the geological age, geographic origin, thorium content and uranium concentration. 4.0 atoms Ac-U, or of any other member of the Ac-family, decay for every 100 UI-atoms disintegrating, i.e., the activity ratio of the Ac to the U-Ra series is 4:100. Our determinations completely support the older results of Stefan Meyer, V. F. Hess and G. Kirsch.[22,23,24]

2. AcD, the end product of the actinium series, has an atomic weight of 207 (or more exactly 207.010 ± 0.01), therefore Ac $= 227$ and Pa $= 231$.

3. The AcD content of uranium lead (and therefore also its atomic weight) increases with the geological age of the mineral. From the AcD content in U-Pb of minerals of definite age and the activity ratio the half period of Ac-U can be calculated (see formula 2 below); the best value is $T_{(AcU)} = 4.0 \times 10^8$ years, $\lambda_{(AcU)} = 5.5 \times 10^{-17}$ sec.$^{-1}$.

Fig. 1 shows the increase of AcD content in uranium lead with the age of the mineral. The theoretical curve is calculated for $T_{(AcU)} = 4.0 \times 10^8$ years.

The values of AcD content, derived from chemical atomic weight determinations of uranium leads of different ages, including kolm[25] and also oldest pitchblendes, for instance, from Black Hills, South Dakota[26] (at. wt. $= 206.07_1$

[15] G. P. Baxter and A. D. Bliss, Jour. Amer. Chem. Soc. **52**, 4848 (1930).

[16] O. Hönigschmid and L. Birkenbach, Ber. Deut. Chem. Ges. **56**, 1837 (1923).

[17] G. P. Baxter and A. D. Bliss, Jour. Amer. Chem. Soc. **52**, 4851 (1930).

[18] F. W. Aston, reference 12.

[19] Value tentatively calculated from the chem. atomic weight of kolm lead.

[20] A. Piccard, Arch. sciences phys. and natur. **44**, 161 (1917); A. Piccard and E. Stahel, same journal (5) **3**, 541 (1921).

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

[22] St. Meyer and V. F. Hess, Wiener Ber. (Akad. d. Wiss.) **128**, 909 (1919).

[23] St. Meyer, Wiener Ber. (Akad. d. Wiss.) **129**, 483 (1920).

[24] G. Kirsch, Wiener Ber. (Akad. d. Wiss.) **129**, 309 (1920).

corrected age = about 1300.10^6 years) are, within experimental errors, in agreement with this theoretical curve.

4. The AcU content of the element uranium, independent of source, equals at present 0.4 percent by weight. It was much larger in former geological epochs, i.e., over 4 percent about 1600×10^6 years ago; it will diminish in the future, for instance in about 1600.10^6 years the content will be only 0.03 percent. Similarly the activity and heat evolution due to the actinium series and their importance for geology were much larger in past times, equalling about half the value of the uranium series in the earliest part of the earth's history. (The determination of the AcU/UI or Pa/UI ratio affords a method of measuring the "age of uranium" in meteorites as compared with our uranium on earth.)
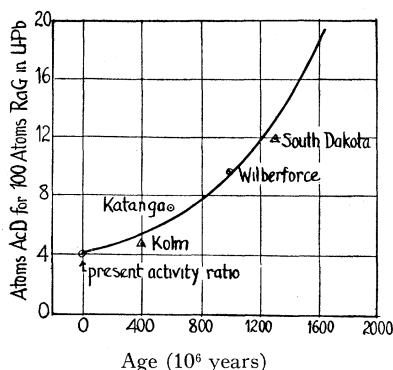

Age (10^6 years)

Fig. 1. Theoretical curve for $T(\text{AcU}) = 4.0 \times 10^8$ years. Triangles with dots are calculated from chemical atomic weight determinations.

5. Owing to the more rapid decay of AcU it is necessary to make corrections in geological age calculations.[27]

The exact age (t) is

$$t = 1/\lambda_{(\text{UI})} \cdot \log_e \left(1 + \frac{238\,\text{U} - \text{Pb}}{206\text{UI}(1 + r)} \right)$$

(1)

where r is the ratio of AcD to RaG in U-Pb (see Fig. 1) and

$$r = R \cdot \frac{\lambda_{(\text{UI})} \left(e^{\lambda_{(\text{AcU})} t} - 1 \right)}{\lambda_{(\text{AcU})} \left(e^{\lambda_{(\text{UI})} t} - 1 \right)}$$

(2)

when R is the activity ratio of Ac to U-Ra series, i.e., 0.040.

[25] Compare G. P. Baxter and A. D. Bliss, Jour. Amer. Chem. Soc. **52**, 4850–51 (1930).

[26] T. W. Richards and L. P. Hall, Jour. Amer. Chem. Soc. **48**, 706 (1926).

[27] A. Holme's objections (Nature **126**, 348 (1930)) to Lord Rutherford's conclusions (Nature **123**, 313 (1929)) are only correct so far as Aston's first value for the AcD content in U–Pb was too high, owing to the so-called "hydride effect," i.e., coincidence of the Pb^{207} line with the Pb^{206} H^1 line. With the help of a nearly pure ThD (94.1 percent Pb^{208}) which we owe to the kindness of Professor K. Fajans (for its source and at wt., see K. Fajans, Sitzungsber. Heidelberg. Akad. d. Wiss. 1918 A, Abh. 3, 0. Hönigschmid, Zeit. f. Elektrochemie **25**, 91 (1919)), Aston was able to measure this effect and correct for it in his subsequent determinations.

Since t occurs also in the correction factor it is easier to calculate the RaG:UI and U-Pb:U ratios for set values of t and derive the age from the Table II ($T_{(AcU)} = 4.0 \times 10^8$ years).
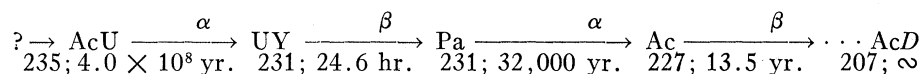
TABLE II.

Age, t (years)	RaG: UI ratio or g RaG for 1g UI	U-Pb: U ratio or g U-Pb for 1g U
0×10^6	0.0000	0.0000
100	0.0139	0.0145
200	0.0280	0.0293
300	0.0423	0.0445
400	0.0569	0.0600
500	0.0718	0.0760
600	0.0868	0.0924
700	0.1022	0.1094
800	0.1177	0.1269
900	0.1335	0.1450
1000	0.1495	0.1638
1100	0.1658	0.1835
1200	0.1824	0.2040
1300	0.1992	0.2258
1400	0.2164	0.2492
1500	0.2337	0.2733

6. 1 g U contains in equilibrium $2.7_3 \times 10^{-7}$ g Pa, since $T_{(Pa)} = 32,000$ years.[28] 1 g Ra is associated with 0.8_1 g Pa at the present geological time; in the past it was more common than radium (1600×10^6 years ago about 10 g Pa occured for every g of Ra) and in the future it will become rapidly rarer (in 1600×10^6 years the Pa:Ra-ratio will be only 0.06).

7. The pleochroic haloes discovered by S. Iimori and Y. Yoshimura[29] cannot be due to the Ac-series, since these have always occurred together with the U-Ra-series on earth.

8. The transformation scheme for the actinium series is as follows (atomic weight, period):[30]

$$? \to \underset{235;\, 4.0 \times 10^8 \text{ yr.}}{\text{AcU}} \xrightarrow{\alpha} \underset{231;\, 24.6 \text{ hr.}}{\text{UY}} \xrightarrow{\beta} \underset{231;\, 32,000 \text{ yr.}}{\text{Pa}} \xrightarrow{\alpha} \underset{227;\, 13.5 \text{ yr.}}{\text{Ac}} \xrightarrow{\beta} \cdots \underset{207;\, \infty}{\text{AcD}}$$

The only fact not in harmony with the other data on the actinium series presented here is the presently accepted value for the atomic weight of uranium (238.14, O = 16). The atomic weights of all members of the three series can be calculated with precision, if the atomic weight of their corresponding end product is known, by adding to it, step by step, the well-known masses of particles and energies emitted during each distintegration.

From Aston's recent measurements[31] we have for the physical atomic weight of $Pb^{206} = 206.01 \pm 0.01$ or 205.96 ± 0.02 on the chemical scale, using

[28] A. v. Grosse, Naturwiss. **27**, 505 (1932).

[29] S. Iimori and Y. Yoshimura, Scient. pap. Inst. Tokyo **5**, 11 (1926).

[30] "?" indicates that there still is a possibility for the existence of a second actino-uranium, see also A. v. Grosse, reference 28.

[31] F. W. Aston, Nature **129**, 649 (1932).

R. Mecke's[32] conversion factor (1.00022). From this starting point the calculated values for the following members of the U-Ra-series are:[33]

Radio element	Phys. at. wt., $0^{16} = 16$		Chem. at. wt., $0 = 16$	
RaF (Po)	210.02		209.97	
Ra-Em	222.05	± 0.02	222.00	$\pm$ab. 0.02
Ra	226.06		226.01	
UI	238.08		238.03	

This atomic weight of UI and Aston's observation[34] that it constitutes at least 97 percent of the element uranium indicate that the value 238.14 for the latter is too high.

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[32] R. Mecke and W. H. J. Childs, Zeits. f. Physik. **68**, 362 (1931).

[33] Our complete data were published in F. G. Houterman's report—Ergebnisse der exakten Naturwissenschaften, p. 199, 1930.

[34] F. W. Aston, Nature **128**, 725 (1931).