



LXXVII. The ratio between uranium and radium in minerals. II

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Evidence is also given of a limit to the penetrating power of Röntgen radiation. Unless the laws of scattering somewhere break down, the lowest possible value for $\frac{\lambda}{\rho}$ is about .2. This has been approached in the case of absorption by carbon.

LXXVII. *The Ratio between Uranium and Radium in Minerals.* II. By RUTH PIRRET, B.Sc., and FREDERICK SODDY, M.A., F.R.S.*

IN a previous paper on this subject (Phil. Mag. 1910 [6] xx. p. 345), a short account was given of the determination of the ratio of radium to uranium in Ceylon thorianite and a specimen of Portuguese autunite. The preliminary results went to confirm those of Mlle. Gleditsch (*Compt. Rend.* 1909, cxlviii. p. 1451; cxlix. p. 267) in that the ratio in autunite was found to be considerably lower than in pitchblende; but the results with thorianite were not equally conclusive. Only one specimen of thorianite was compared with the old pitchblende standards prepared some years ago. Further investigations with several different specimens of thorianite, pitchblende, and autunite were therefore carried out on the same lines.

Uranium Analysis.—The methods of estimating the uranium in thorianite and autunite have already been described. In the case of the pitchblendes the mineral was first dissolved in nitric acid, the solution diluted, filtered, evaporated to dryness, the residue dissolved in hydrochloric acid, treated with sulphuretted hydrogen and filtered. The filtrate, after heating and oxidizing, was poured into a mixture of ammonium hydrate, sulphide, and carbonate, corked, and left over night. The filtrate from this precipitate was heated, acidified by nitric acid, and the uranium precipitated by microcosmic salt and sodium thiosulphate in presence of acetic acid. The precipitate was ignited in a porcelain crucible and weighed in the form of a green compound of constant composition. It was then converted, by means of a few drops of strong nitric acid, into uranium pyrophosphate and weighed again after ignition at a dull red heat (Brearley's 'Analytical Chemistry of Uranium,' p. 7). In some cases Patera's Method (Fresenius, 'Quantitative Analysis,' vol. ii. p. 310) was employed, or a modification of it in which, instead of the uranium being weighed as sodium uranate, it was, after separation by

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means of sodium carbonate, estimated as pyrophosphate as before.

Table I. contains the results of the estimation of uranium in the various minerals. The thorianites were all specimens of Ceylon thorianite. "Th I, Th I *a*, Th I *b*" were from the same sample of the variety richest in uranium and containing a small residue (3 per cent.) insoluble in acid. "Th X₂" was a poor specimen of the mineral, and contained nearly 24 per cent. of insoluble material. "Th CCC" and "Th E" were specimens of mixtures of the two varieties (which differ chiefly in their respective high or low percentage of uranium). The pitchblende "PI" was a specimen from Joachimsthal which contained comparatively little uranium and proved troublesome in the analysis and unsatisfactory in the results. The other ("J.P.A" and "J.P.B") was a picked

TABLE I.

		Percentage of Uranium.					
		(1)	(2)	(3)	(4)	(5)	Mean.
Ceylon Thorianites.	{ Th I, Th I <i>a</i> , Th I <i>b</i> ...	20·80 <i>a</i>	20·11 <i>c</i>	19·86 <i>c</i>	19·32 <i>c</i>	19·80 <i>c</i>	} 20·06
	Th X ₂ 1 & 2	20·56 <i>b</i>	20·28 <i>d</i>	19·99 <i>d</i>	19·74 <i>d</i>	20·15 <i>d</i>	
	{ Th CCC	9·49 <i>a</i>	10·71 <i>d</i>	10·40 <i>d</i>	} 10·00
	Th E	9·39 <i>b</i>	
	{ Th E	13·02 <i>a</i>	14·04 <i>a</i>	13·44 <i>a</i>	} 13·61
Th E	13·20 <i>b</i>	14·14 <i>b</i>	13·82 <i>b</i>		
Joachimsthal Pitchblendes.	{ PI	17·21 <i>a</i>	17·42 <i>a</i>	} 17·62
	PI	17·93 <i>b</i>	17·95 <i>b</i>	
	{ J.P.A, J.P.B	33·35 <i>c</i>	28·06 <i>c</i>	30·81 <i>d</i>	34·99 <i>a</i>	31·20 <i>e</i>	} 31·86
	J.P.A, J.P.B	33·57 <i>d</i>	28·22 <i>d</i>	34·71 <i>b</i>	
	{ G.E.A.P.	62·37 <i>a</i>	60·73 <i>a</i>	61·77 <i>c</i>	61·34 <i>a</i>	61·01 <i>b</i>	} 61·23
German East African pitchblende. {	61·39 <i>b</i>	59·98 <i>b</i>		
Portuguese* Autunites.	{ A I, A II	72·30 <i>c</i>	} 71·3
	A I, A II	70·31 <i>d</i>	
	{ S I	20·04 <i>a</i>	19·90 <i>a</i>	19·54 <i>d</i>	21·56 <i>d</i>	19·95 <i>a</i>	} 20·10
	S I	19·65 <i>b</i>	
Pilbarite	{	47·82 <i>a</i>	47·85 <i>a</i>	} 48·44
	49·30 <i>b</i>	48·79 <i>b</i>	
	{	20·45 <i>a</i>	21·16 <i>a</i>	} 21·28
.....	20·85 <i>b</i>	21·72 <i>b</i>		

* The other autunites referred to in Tables II. and III. were used in connexion with other work (*Le Radium*, 1910, vii. p. 295), and details of the uranium analysis need not be given.

a denotes that the uranium was weighed as the green compound before conversion into pyrophosphate.

b " " " " as uranium pyrophosphate.

c " " " " as U₃O₈.

d " " " " as UO₂.

e " " " " as sodium uranate.

specimen of Joachimsthal pitchblende containing a much larger proportion of uranium. "G.E.A.P." was a German East-African pitchblende. The autunites were all specimens of Portuguese autunite. A specimen of the new mineral pilbarite was obtained from Mr. Simpson of the West Australian Government Survey. It is described in the 'Australian Mining Standard,' 7/9/10 (Chem. News, 1910, cii. p. 283).

Method of Estimation of Radium.—The radium was estimated in the solution of the mineral by the emanation method. The apparatus used was at first (series A) that described by one of us (Phil. Mag, 1909 [6] xviii. p. 846). Later a new apparatus was employed with a microscope of about four times less magnifying power. With this instrument the leaf was charged positively instead of negatively, and was not kept charged during the period of three hours preceding the measurements (series B and C). A period of about three months elapsed between series B and C. In all twenty-seven radium preparations were used including the six old pitchblende standards already described (*loc. cit.*), representing twelve different minerals. These were prepared by dissolving quantities of minerals which could be accurately weighed, and taking a known fraction by weight of the solution.

Table II. shows the results. Column (1) gives the designation of the preparation, those bracketed being of the same specimen of the same mineral. Column (2) gives the number of milligrams of uranium in the preparation. Columns 3, 4, 5 give the number of divisions of leak of the electro-scope-leaf per minute in the three respective sets of observations, and 6, 7, 8 the same per milligram of uranium present.

The old standards I. to VI. had existed for nearly four years, and comparing the results in Table II. with the determinations previously published (*loc. cit.*) made at the time of preparation, the variations among the standards are rather larger than they were initially, but do not show any certain influence of age. "R I" and "R II" were made up on June 16, 1910, from a solution of radium bromide obtained from Professor Rutherford, and described by him as containing 1570×10^{-12} gram of radium. The Rutherford-Boltwood ratio is assumed in stating the quantity of uranium in these (3.4×10^{-7} gram of radium per gram of uranium).

TABLE II.

Specimen.	Uranium (milligrms).	Leak (divisions per 1 min.).			Leak per 1 min. per 1 milli- gram Uranium.			
		A.	B.	C.	A.	B.	C.	
Pitchblendes.	{ St. I.	·308	20·28	3·99	65·83	[12·98]
	{ St. II.	1·49	19·72	20·88	13·23	14·23
	{ St. III.	·696	9·56	9·83	13·74	14·14
	{ St. IV.	6·66	86·80	13·02
	{ St. V.	·149	9·70	1·80	65·10	[12·10]
	{ St. VI.	·74	9·75	10·01	13·23	13·53
	{ P.I.	·395	23·55	4·91	5·02	59·62	12·43	12·71
	{ J.P.A.	·171	2·25	13·16
	{ J.P.B.	·3539	4·66	5·00	13·17	14·13
{ G.E.A.P. ...	·6534	49·64	10·39	10·56	75·97	15·90	16·16	
R I	·2077	14·80	2·61	2·71	71·25	[12·54]	[13·07]	
R II	1·0066	72·20	14·25	14·85	71·78	14·17	14·77	
Ceylon Thorianites.	{ Th I	·6103	41·16	8·81	8·93	67·44	14·43	14·62
	{ Th Ia	3·027	43·65	43·64	14·42	14·41
	{ Th Ib	1·926	27·88	14·47
	{ Th X ₁ (1) ..	8·4103	111·5	13·25
	{ Th X ₂ (2) ..	1·03	13·91	13·51
	{ Th OCC ...	·3475	4·56	4·68	13·14	13·46
	{ Th E	3·168	41·64	13·14
Portuguese Autunites.	{ A I	·834	24·28	5·12	29·1	6·14	...
	{ A II	·92	26·22	4·42	28·5	4·80	...
	{ A A I	·568	26·18	5·33	46·1	9·39	...
	{ A A II	1·69	16·29	9·63	...
	{ A B I	·562	16·24	3·29	28·9	5·85	...
	{ S I	2·531	8·43	3·33
	{ A D	1·265	12·92	10·22
Pilbarite ...	1·359	12·10	8·90	

Discussion of Results.—In interpreting the results of Table II. it must be remembered that the determinations have not all equal weight. The specimens on which the A series of measurements was performed contained as a rule too small quantities of radium to give the best results with the less sensitive electroscopes and method employed in the B and C series. The measurements of Table II. enclosed in square brackets may be at once eliminated from further consideration on this account. In addition many of the solutions had been prepared a considerable time, and may have undergone changes by keeping. Three months elapsed between the measurements in the B and C series, and it is evident from the Table that the sensitiveness of the instrument had somewhat increased in the interval, as has been observed before with the old instrument.

The first thing is to reduce the three series of measurements given in the last three columns of Table II. to a common standard. This has been done by taking first the mean value in each of the three series for each of the minerals, except the autunites, and then taking the mean of these means. The result is, in divisions per milligram of uranium :—

A 68·00, B 13·79, C 14·24.

Hence to reduce all the determinations to the same standard as the C series, the A series must be multiplied by the factor 0·212, and the B series by 1·033. This has been done in Table III.

TABLE III.

	Divisions per milligram of Uranium (reduced values).			
	A (cor.).	B (cor.).	C.	Means.
St. I.	13·95	} 13·85
St. II.	13·66	14·23	
St. III.	14·18	14·14	
St. IV.	13·44	
St. V.	13·82	
St. VI.	13·66	13·53	} 12·72
P. I.	12·64	12·82	12·71	
J.P.A.	13·58	} 13·77
J.P.B.	13·59	14·13	
G.E.A.P.	16·10	16·41	16·16	16·22
R I	15·10	} 14·90
R II	15·20	14·62	14·77	
Th I	14·32	14·89	14·62	} 14·60
Th Ia.	14·88	14·41	
Th Ib.	14·47	
Th X ₂ (1)	13·68	} 13·55
Th X ₂ (2)	13·51	
Th CCC.	13·56	13·46	
Th E	13·14	
A I.	6·20	6·32	} 7·15
A II.	6·05	4·96	
AA I.	9·80	9·68	
AA II.	9·94	
AB I.	6·12	6·03	
AS I.	3·33	
AD.	10·22	
Pilbarite	8·90	

Dealing first with the pitchblendes, the mean results for the old standards are :—

A 13·83, B 13·74, C 13·97,

which gives a mean result for this mineral of 13·85. The mean of the three determinations for the mineral “J. P. A” and “J. P. B” is 13·77. So that from these two results the mean value 13·8 may be taken with considerable confidence as representing Joachimsthal pitchblende. The specimen P I, giving a mean result of 12·72, must be rejected, for, as will be seen from Table I., its uranium analysis is far from satisfactory. Indeed this mineral proved most troublesome to analyse, the uranium content being low and the proportion of foreign constituents high. The mean of the four determinations with Rutherford’s radium standard is 14·9; so that, if this is taken as the primary standard, the ratio of radium to uranium in Joachimsthal pitchblende is $3·15(\times 10^{-7})$. The original value given by Rutherford and Boltwood was 3·8, which was lowered subsequently to 3·4 owing to an error in the uranium analysis (Boltwood, *Am. Journ. Sci.* 1911, xxv. p. 296). The radium solution provided by Professor Rutherford was part of the original employed by these investigators; so that, assuming the solution has not changed since its preparation, our results indicate that the corrected value is still somewhat high. The value we have arrived at, $3·15(\times 10^{-7})$, is in good agreement with the following results of Mlle. Gleditsch, obtained with Mme. Curie’s standards of radium (Mme. Curie, *Radioactivité*, ii. p. 441):—St. Joachimsthal pitchblende 3·21, Norwegian Clèveite 3·23, Bröggerite 3·22, Portuguese chalcocite 3·24.

Dealing now with the thorianites, the Table shows that although the first specimen investigated, “Th I,” as recorded in the last paper, gives an undoubtedly higher value than Joachimsthal pitchblende, it is alone of those examined in this respect. Five different uranium analyses and six estimations of the radium in three solutions of this mineral give the mean result 14·6, which is about 6 per cent. higher than that for Joachimsthal pitchblende. Even if the highest uranium result and the lowest radium result are compared, the value arrived at would still be as high as the mean for Joachimsthal pitchblende. But the other thorianites examined give an entirely different result. The mean five determinations on the three minerals is 13·47. Omitting “Th E,” for which only one determination has so far been done, the mean is 13·55. Hence the later results have not confirmed

these of Mlle. Gleditsch that the ratio for thorianite is 20 per cent. higher than for pitchblende. It is interesting to notice that investigations published subsequently to Mlle. Gleditsch's work (Marckwald, *Ber. Chem. Ges.* 1910, xliii. p. 3420; Soddy, *Trans. Chem. Soc.* 1911, xcix. p. 72) show that in separating the radium she must also have separated the mesothorium quantitatively from the thorianite, though this does not account for her results.

We are inclined to ascribe the undoubtedly high value obtained for "Th I" to contamination with radium before it came into our hands. All the other specimens were samples of large quantities purchased direct from the importers, but "Th I" was obtained from a retail dealer who handles radium preparations and sells spinthariscopes. We attach no importance to the high result for the single specimen of German East-African pitchblende, as the same doubt arises. It came to us through Mr. Russell from Prof. Marckwald's laboratory, where chemical work on radium has long been carried on.

With regard to the autunites, all of which came from various mines in Portugal, the values range from that of "A D," which has 74 per cent. of the equilibrium amount, to that of "A S," which has only 24 per cent. and is the lowest yet recorded, that described by Mr. Russell (*Nature*, Aug. 25, 1910) from Autun, France, having 27 per cent. It is interesting to note that both these specimens "A D" and "A S" were from the same property (compare *Ann. Reports, Chem. Soc.* 1910, vii. p. 264). The pilbarite is also low (64 per cent.), but the mineral, described as probably a hydrous pseudomorph of an anhydrous parent mineral, is evidently much altered.

The main point at issue, that possibly the life-period of ionium is sufficiently extended to cause the equilibrium ratio of radium to uranium to be less in a geologically recent mineral like Joachimsthal pitchblende than in an ancient mineral like thorianite, although no doubt still an open one, certainly receives no support from these measurements.

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