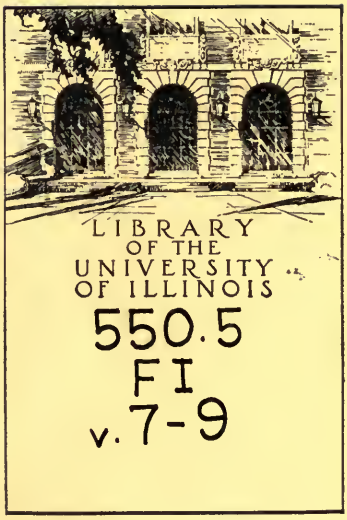
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RADIOACTIVE DETERMINATION OF PROTACTINIUM IN SILICEOUS TERRESTRIAL AND METEORITIC MATERIAL[1]

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In order to test more completely the validity of the general rule that the abundance-ratio of the isotopes of any element is a constant, independent of the source or of the mode of combination of the element, it is of interest and importance to determine such abundance-ratios in meteorites, which represent the only available specimens of extra-terrestrial matter. Atomic weight or isotopic abundance-ratios have been determined for carbon, oxygen, silicon, chlorine, iron, cobalt, and nickel by various workers;[5] and in the case of all the elements studied the isotopic abundance-ratios are not measurably different in meteoritic and in terrestrial matter.

In the case of radioactive elements, such as uranium, these abundance-ratios assume additional interest, in that by means of them a knowledge may be obtained of the difference in age between these atoms in the meteorite specimen and in terrestrial substances containing the same element. This subject was discussed in some detail by Evans (Pop. Astronomy, **46**, pp. 159–170, March, 1938), who derived the following expression for the differential age in years of uranium atoms in a meteorite and in the earth:[6]

[1] Contribution from Research Laboratory of Inorganic Chemistry, No. 75, and George Eastman Laboratory of Physics, Massachusetts Institute of Technology.

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[4] Professor of Chemistry, Massachusetts Institute of Technology.

[5] Baxter and Thorvaldson, Jour. Amer. Chem. Soc., **33**, p. 337, 1911; Baxter and Hoover, *ibid.*, **34**, p. 1657, 1912; Baxter and Parsons, *ibid.*, **43**, p. 507, 1921; Baxter and Hilton, *ibid.*, **45**, p. 694, 1923; Baxter and Dorcas, *ibid.*, **46**, p. 357, 1924; Jaeger and Dykstra, Kon. Akad. van Wetenschappen, Amsterdam, **27**, p. 393, 1924; Harkins and Stone, Jour. Amer. Chem. Soc., **48**, pp. 938, 3233, 1926; Manian, Urey and Bleakney, *ibid.*, **56**, p. 2601, 1934; Jenkins and King, Publ. Astr. Soc. Pac., **48**, p. 323, 1936.

[6] The numerical factor 2.8 has been changed from 1.46 given in the reference cited to 2.8 as the result of more recent work on the actinium series branching ratio by A. O. Nier (Phys. Rev., **55**, p. 150, 1939).

$$t_m - t_e = 2.8 \times 10^9 \log \left(\frac{R_e}{R_m} \right) \quad (1)$$

where t_m and t_e are the respective ages in the meteorite and in the earth, R_e = the ${}_{92}U^{235}$: ${}_{92}U^{238}$ activity-ratio observed in the earth today, and R_m is the same ratio measured in the meteorite.

The present paper reports the results obtained in a portion of a program for the determination of isotopic abundance-ratios in meteorites being carried on jointly in these laboratories; in particular, the determination of the isotopic ratio of ${}_{92}U^{235}$ (or AcU) to ${}_{92}U^{238}$ (or UI) in a specimen of the Pultusk[1] meteorite, which, because of its reported (Evans, loc. cit.) high heliocentric velocity (56 km. per sec.) has been considered as representing not only extra-terrestrial but possibly extra-solar material.[2] The sample used in this work was very kindly furnished to Professor Evans by Mr. Clifford C. Gregg, Director, and Mr. Henry W. Nichols, Chief Curator of the Department of Geology in Field Museum of Natural History, Chicago.

Nier (Phys. Rev., 55, pp. 150, 153, 1939) has recently checked the constancy of the isotopic abundance-ratio of U^{235}/U^{238} in terrestrial material by means of mass spectroscopic determinations on Pb^{207} and Pb^{206}.

In all but very young rocks radioactive equilibrium has been established in the three radioactive series; that is, the rate of disintegration is equal to the rate of formation of all members of each series derived from the three parent elements, ${}_{92}U^{238}$, ${}_{92}U^{235}$ and ${}_{90}Th^{232}$. Therefore, by determining the amount of any one member of a series present, the quantity of any other may be calculated. Thus the determination of the protactinium content of a specimen permits the calculation of the amount of the parent element AcU, and the determination of the radon content of the sample makes possible the calculation of the amount of the parent element UI present, and from these two values the abundance-ratio U^{235}/U^{238} may be obtained.

A method has been worked out by A. v. Grosse (Phys. Rev., **42**, p. 565, 1932) and others (Francis and Da-Tchang, Phil. Mag., **20**, p. 623, 1935) for the isolation of protactinium from other radioactive

[1] A shower of fragments of a stony meteorite fell in Pultusk, Poland, on January 30, 1868.

[2] Professor C. C. Wylie of the State University of Iowa has kindly communicated to us the results of his recent recalculation of the Pultusk trajectory observations, originally reported by Galle in 1868, following interviews with those who observed the meteorite fall. Professor Wylie's extensive experience in such interviews leads him to reduce the reported height of appearance of the meteorite. This has the effect of reducing the computed velocity so that the Pultusk meteorite would be of solar-system origin rather than extra-solar. Professor Wylie has just summarized his work in Science, 9, p. 264, September 22, 1939.

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elements. The present method is a modification of that of A. v. Grosse in that provision had to be made for the elimination of large amounts of silica and some 5 per cent of free metal, along with metal sulphides. The chemical analyses of two specimens of the Pultusk meteorite, as given in Farrington's compilation (Field Mus. Nat. Hist., Geol. Ser., **3**, pp. 195–229, 1911), are as follows:

Analyst and date	Spec. no.	SiO_2	Al_2O_3	FeO	CaO	Na_2O	K_2O	Fe	Ni	MgO
G. von Rath..... (1869)	82	41.54	1.17	14.04	0.28	1.34	....	11.51	0.65	26.73
R. Rammelsberg. (1870)	101	35.85	1.96	12.12	1.56	0.95	0.39	15.55	2.21	24.95

EXPERIMENTS

Preliminary work.—The preliminary work for testing the method was carried out on granite of known radium content. All solid reagents to be used were tested separately and a record made of their alpha activity. The efficiency of the method for the removal of radioelements other than protactinium and their isotopes was checked by adding known amounts of solutions of the salts of uranium, thorium, and polonium, respectively, and repeating all operations. These experiments proved that three separations (as described in Table 1 and the section on analytical procedure) removed 94 per cent of the added uranium, 100 per cent of the thorium, and 95 per cent of the polonium. Finally, a small sample of pure protactinium, deposited in zirconium pyrophosphate, and kindly furnished us for the purpose by Dr. A. v. Grosse, was converted into a highly dilute solution. The alpha activity of a portion of this solution was measured, and a known amount of it was carried through the chemical procedure. The activity of the recovered protactinium was determined, whereby it was demonstrated that 90 per cent $\pm$ 6 per cent of the protactinium could be recovered. In view of the many steps required in the analytical procedure employed, this recovery is considered to be satisfactory.

Sampling.—Due to the probability of surface leaching and contamination, only the inner portions of specimens of granite were used. These were ground, first in a steel mortar and finally in agate, both mortars being "rinsed" by grinding inactive sodium carbonate in them before use. After thorough mixing, a third of the finely ground material was reserved in a stoppered bottle for the radon determinations and the remainder used for the separation of protactinium. In the case of the Pultusk meteorite sample, all of the outer black layer, or "skin," was carefully removed and samples of the inner portions were prepared as in the case of the granite.

Analytical procedure.—A 50-gram sample of the siliceous material was treated with 100 cc. of aqua regia and heated on the steam bath for a half hour. After cooling, the diluted acid solution was filtered and the residue dried and ignited in platinum. The filtrate was evaporated and the residue dehydrated. The residue was taken up with concentrated *HCl*, followed by water, and the silica filtered and combined with the original residue. The dehydration process was then repeated. The combined residues were treated several times with 47 per cent hydrofluoric acid to which a few drops of concentrated sulphuric acid had been added, and evaporated to fumes after each treatment. Three times the calculated amount of *HF* was used to insure complete removal of silica, assuming the latter to be 50 per cent of the original sample. The residue then was heated to dull red heat and after cooling was treated with hot, concentrated *HCl* followed by hot water. There remained very little residue and this was filtered off and washed with hot water, dried, ignited, and reserved for future work, if necessary.

The filtrate was combined with that from the final dehydration and the solution was evaporated to 200 cc. To the cooled solution zirconyl chloride solution was added equivalent to 100 mg. of ZrO_2. An excess of 6 N H_3PO_4 was added and the solution stirred for several minutes. The precipitate of zirconium phosphate was allowed to stand at least two hours, then filtered. The precipitate was washed with 5 per cent *HCl*, dried, ignited, and weighed. The filtrate was reserved.

To the zirconium pyrophosphate, which contained the protactinium, 20 cc. of 2 per cent *HF* was added and the vessel heated until the solution was complete. After cooling, solutions of the nitrates of barium, lead, lanthanum, and bismuth, equivalent to 4 mg. of each element, were added. The insoluble sulphates and fluorides of these elements co-precipitate those of radioactive elements other than protactinium, as indicated in Table 1.

TABLE 1.—RADIOACTIVE SEPARATIONS FROM SOLUTION OF ZrP_2O_7+*Pa* IN 2 PER CENT *HF*

Reagent	Radioactive elements and isotopes removed
$Ba(NO_3)_2$	*Ra, MsTh*$_1$, *AcX, ThX*
$Pb(NO_3)_2$	*RaB, ThB, AcB, RaD, ThD, AcD, RaG*
$Bi(NO_3)_3$	*Po, RaC, ThC, AcC, RaE*
$La(NO_3)_3$	*Ac, MsTh*$_2$

After standing for one hour, the precipitates were filtered, using hard rubber funnels. The residues were discarded. This operation was carried out three times to assure satisfactory elimination of

radioactive contaminants because blanks on which only two separations had been made occasionally showed residual counts. The third filtrate was evaporated to dryness, the residue ignited at red heat for ten minutes, and after being cooled each residue so obtained was placed in a separate desiccator to avoid possible contamination.

A portion of the residue was transferred to an agate mortar and finely ground under alcohol. A suspension of the ground material was made in ethyl alcohol and poured upon a weighed silver disc, which had been sealed to a brass evaporating cylinder by means of rubber cement. The alcohol was evaporated in a heated cabinet in an atmosphere of well-aged and hence radioactively inert nitrogen. When the sample was dry, the cylinder and rubber cement were quantitatively removed from the disc and the disc plus the sample was weighed.

Measurement of activity.—The weighed disc, containing the protactinium with zirconium pyrophosphate deposit, was placed in the recording alpha counter. An ionization chamber of the parallel plate condenser type was used, the design and operation of which has been fully discussed by Finney and Evans (Phys. Rev., 48, p. 503, 1935). The ions formed by the alpha rays are collected, the current amplified, and the resulting galvanometer deflections recorded photographically upon sensitized bromide paper contained in a Telechron-driven drum camera which makes one revolution every two hours. Twenty consecutive hours of observation were generally employed in order to minimize the probable error. These could be recorded on a single sheet of 5 in. $\times$ 37.5 in. paper, by using a laterally moving light source.

The inner parts of the ionization chamber are made of spun copper and are easily removable for cleaning. Some contamination is, of course, inevitable, due to radioactive material in the walls of the ionization chamber, so that even without a radioactive sample in the chamber the record obtained will show some countable alpha rays. Careful cleaning and the use of inactive silver for the metal discs minimizes this "background."

A blank on all reagents was carried along in parallel with the samples and this served as a check on the completeness of removal of radioactive contaminants and on the overall manipulative procedures.

Calculated results and conclusions.—A sample of granite from Ontario, designated as "K.D. Fine," known to be low in radioactive material was selected for a representative terrestrial material. The

protactinium content was calculated from the observed alpha count per cm.^{2} of source by means of the following two equations, discussed in the paper of Finney and Evans (loc. cit.):

$$n_{a'}=\frac{N\mu\tau}{4}\left[\frac{2(R-\rho)-\tau}{(R-\rho)}\right] \tag{2}$$

in which

$n_{a'}$=alpha counts observed per cm.^{2} of source

N=alpha rays per cm.^{3} emitted in the source

R=3.61 air-cm.=mean range in air at 15°C. and 760 mm. for alpha particles from *Pa*

ρ=0.5 air-cm. (assumed maximum range of short range alpha rays not detected)

$\mu=15.6\times10^{-4}/d$=ratio of range of alpha rays in the solid to the range in air

$\mu\tau$=thickness of source in cm.

$\tau=\dfrac{\text{mass}}{\text{area}\times\text{density}\times\mu}$=source thickness in air-cm.

$$N=\frac{6.02\times10^{23}Q.\lambda.d}{W} \tag{3}$$

where

W=231=at. wt. of *Pa*

$\lambda=2.5\times10^{-9}\text{hr}^{-1}$=decay constant of *Pa*

Q=concentration of *Pa* in gm. per gm. of source

d=density of ZrP_2O_7

The probable error for each background run and determination of alpha rays due to protactinium was calculated in the usual way:

$$P.E.=0.67\left[\frac{\Sigma(x-\bar{x})^2}{n(n-1)}\right]^{1/2} \tag{4}$$

where

$\bar{x}$=the average of n individual observations of x.

The following tables summarize the results obtained with the granite and Pultusk meteorite.

PROTACTINIUM CONTENT OF GRANITE

Sample	Wt. original rock (gm.)	Wt. ZrP_2O_7 + *Pa* in mg. total	Wt. ZrP_2O_7 + *Pa* tested in mg.	Observed α count over background	Observed α count over blank	Observed α count for total sample	*Pa* in 10^{-12} gms. per gm. rock
Blank.....	.....	210	41.5	1.7±1.1	.....	.....	.....
No. 1.....	15.04	199	28.5	0.8±1.3	0±1.7	0±12	0.00±0.23
			42.1	10.0±1.2	8.3±1.6	39±8	0.76±0.16
No. 2.....	15.18	231	52.4	5.6±1.0	3.9±1.5	17±7	0.32±0.13
			47.7	7.4±0.9	5.7±1.4	28±7	0.52±0.13
					Mean.....	24.1±4.6	0.46±0.09

PROTACTINIUM CONTENT OF PULTUSK METEORITE

Wt. original sample in grams	Wt. ZrP_2O_7 $+Pa$ in mg. total	Wt. ZrP_2O_7 $+Pa$ in mg. tested	Observed α count over background	Observed α count for sample	Pa in 10^{-12} gms./gm. meteorite
Blank.....	111	42.7	0.0±0.8	0.	0.
51.....	110	27.3	0.8±0.6	3.2±2.4	0.018±0.013
		34.2	2.7±0.8	8.7±2.6	0.049±0.013
			Mean.....	6.0±1.7	0.035±0.011

In equation (1) above, the quotient of the activity-ratios R_e/R_m is equal to the quotient of the mass-ratios, since the radioactive decay constants and the atomic weights involved cancel out in the quotient.

The mean values of the radium content of these two specimens, as determined by Mr. Clark Goodman of the Physics Department of Massachusetts Institute of Technology, are $0.28\pm0.02\times10^{-12}$ g. *Ra* per gram for the granite and $0.023\pm0.005\times10^{-12}$ for the Pultusk meteorite. The corresponding observed weight-ratios, *Pa/Ra* for the granite, and similarly for the meteorite, become 1.64 ± 0.5 and 1.52 ± 0.5, respectively. From these results the conclusion may be drawn that, if the probable errors are considered, there is no appreciable difference in the age of terrestrial uranium atoms and those in this specimen of the Pultusk meteorite. From the chemical standpoint a more definite conclusion may be reached: The method employed for the separation and estimation of protactinium has proved satisfactory for as little as 10^{-13} gm. protactinium per gm. of siliceous material, and with larger samples this limit probably could be set much lower.

This investigation was materially assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, which is hereby gratefully acknowledged.

SUMMARY

The protactinium contents of a granite and of a specimen of a meteorite (Pultusk), both high in silica, have been determined by the co-precipitation of the protactinium with zirconium phosphate, followed by purification of the ignited pyrophosphate, employing a modification of the method of A. v. Grosse. The alpha activity of the protactinium thus isolated was measured on a recording alpha-counter and the concentration of protactinium in the two specimens of terrestrial and of meteoritic material calculated.

From these data and the corresponding radium concentrations of the same specimens determined independently, the weight-ratios

Pa:Ra have been derived for the two materials. From these results the conclusion has been reached that within the limits of error the age of the uranium atoms in this specimen of the Pultusk meteorite is the same as for terrestrial uranium.

The method is capable of estimating as little as 10^{-13} g. of *Pa* per gram of siliceous material, and the limit may probably be lower than this if larger samples are taken.

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