Entropies at 298.16°K.

The entropies were calculated in the usual manner. The portions above 51°K. were obtained by Simpson-rule integrations of C_p *vs.* log T plots. The following empirical sums of Debye and Einstein functions, which fit the measured data over the entire temperature range to within the amounts shown in parentheses, were used in making the extrapolations to 0°K.

$$Ca_2SiO_4:\ D\left(\frac{216}{T}\right) + 3E\left(\frac{340}{T}\right) + 2E\left(\frac{749}{T}\right) + E\left(\frac{1238}{T}\right) \quad (0.5\%)$$

$$Ca_3SiO_5:\ D\left(\frac{188}{T}\right) + 4E\left(\frac{329}{T}\right) + 3E\left(\frac{714}{T}\right) + E\left(\frac{996}{T}\right) \quad (1.0\%)$$

$$Zn_2SiO_4:\ D\left(\frac{146}{T}\right) + 3E\left(\frac{343}{T}\right) + 3E\left(\frac{1012}{T}\right) \quad (1.2\%)$$

The entropy results appear in Table II.

TABLE II

MOLAL ENTROPIES

	Ca_2SiO_4	Ca_3SiO_5	Zn_2SiO_4
0–51°K. (extrap.)	1.55	2.08	2.90
51–298 16°K. (meas.)	28.96	38.20	28.46
$S^\circ_{298.16}$	30.5 ± 0.2	40.3 ± 0.3	31.4 ± 0.3

Related Thermal Data

Employing the heat of formation values obtained by King[3] and entropy values from the compilation of Kelley,[8] the free energies of formation at 298.16° K. from the oxides (quartz and calcium oxide) and from the elements may be calculated. The results are given in Table III. For comparison, values for calcium metasilicate (wollastonite), the heat of formation of which was determined by Torgeson and Sahama,[9] also are included.

TABLE III

FREE ENERGIES OF FORMATION

Substance	$\Delta H_{298.16}$	$\Delta S_{298.16}$	$\Delta F^\circ_{298.16}$
From oxides			
$CaSiO_3$	−21,250	−0.4	−21,130
Ca_2SiO_4	−30,190	1.5	−30,640
Ca_3SiO_5	−26,980	1.8	−27,520
Zn_2SiO_4	−6,990	0.5	−7,140
From elements			
$CaSiO_3$	−378,600	−68.4	−358,200
Ca_2SiO_4	−539,500	−91.9	−512,000
Ca_3SiO_5	−688,100	−116.6	−653,300
Zn_2SiO_4	−378,700	−91.0	−351,600

It is evident that tricalcium silicate is thermodynamically unstable at room temperature with respect to the β-variety of the orthosilicate and calcium oxide ($\Delta F^\circ_{298.16} = 3{,}120$); but the orthosilicate is stable with respect to wollastonite and calcium oxide ($\Delta F^\circ_{298.16} = -9{,}510$). The much greater stability of calcium orthosilicate with respect to the oxides, as compared with zinc orthosilicate, is striking and in line with the known chemistry of these substances.

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(8) K. K. Kelley, *U. S. Bur. Mines Bulletin*, 477 (1950).

(9) D. R. Torgeson and Th. G. Sahama, THIS JOURNAL, **70**, 2156 (1948).

BERKELEY 4, CALIF. RECEIVED JANUARY 22, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Occurrence of Plutonium in Nature

BY CHARLES A. LEVINE* AND GLENN T. SEABORG

Plutonium has been chemically separated from seven different ores and the ratios of plutonium to uranium determined. This ratio was found to be fairly constant ($\sim 10^{-11}$) in pitchblende and monazite ores, in which the uranium content varied from 50 to 0.24%, and substantially less in carnotite and fergusonite. All the plutonium obtained was Pu^{239}, probably formed by the U^{238} in the ore through capture neutrons and decay by $U^{238} + n \longrightarrow U^{239} \xrightarrow{\beta^-} Np^{239} \xrightarrow{\beta^-} Pu^{239}$. The sources of neutrons include the spontaneous fission of uranium, (α,n) reactions caused by the action of α particles from the heavy radioactive elements on the nuclei of light elements in the ore, and cosmic rays. In the cases of the pitchblende ores, the spontaneous fission of uranium and (α,n) reactions contribute the major portion of the neutrons. In thorium ores which contain a low abundance of uranium, neutrons from (α,n) reactions are probably dominant. The lower concentration of plutonium in carnotite and fergusonite is a result of the presence of neutron absorbing impurities in these ores. No isotopes of plutonium other than Pu^{239} were found. An upper limit for Pu^{238} in Canadian and Belgian Congo pitchblendes was set at one part Pu^{238} in 4×10^{15} parts ore. An upper limit for the hypothetical Pu^{244} in Brazilian monazite was set (assuming a half-life of 10^8 years for Pu^{244}) at one part Pu^{244} in 3.6×10^{11} parts ore. It is postulated that U^{233} and the "missing" neptunium (4n + 1) radioactive series are present in nature in minute quantities, formed by the absorption of neutrons by Th^{232}, thus: $Th^{232} + n \longrightarrow Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233}$. Smaller amounts of Np^{237}, from the reactions $U^{238}(n,2n)U^{237} \xrightarrow{\beta^-} Np^{237}$, are also present. The amounts of transplutonium elements present in nature seem to be too small to detect by present means unless some unknown, very long-lived isotopes exist.

I. Introduction

The discovery of naturally occurring plutonium was reported in 1942 by Seaborg and Perlman[1] who chemically separated the plutonium from a sample of Canadian pitchblende concentrate and estimated the plutonium content of the ore to be roughly one part in 10^{14} by weight. From considerations of possible methods of formation of plutonium, it was assumed that the plutonium was Pu^{239}.

Because of the more complete knowledge of the chemical properties of plutonium and the availability of the multi-channel differential pulse

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* Now at the Dow Chemical Company, Pittsburg, Calif.

(1) G. T. Seaborg and M. L. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 1.3 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949); THIS JOURNAL, **70**, 1571 (1948).

analyzer[2] by means of which a radioactive isotope can be identified by the characteristic energy of its decay, it was decided to separate plutonium chemically from various ores, investigate its isotopic composition, and determine its probable origin.

Since the possibility existed that the plutonium found by Seaborg and Perlman[1] was not Pu^{239}, a search was also made in some cases for Pu^{238} and Pu^{244}. If the plutonium were Pu^{238}, it could have come only from the U^{238} which decayed by the simultaneous emission of two β particles. It has previously been shown that the "half-life" for this transformation is greater than 10^{18} years.[3]

The most logical method for the formation of Pu^{239} would be the capture of a neutron by a U^{238} nucleus, forming U^{239} which decays to Pu^{239} by the emission of beta particles through the decay chain: $U^{238} + n \longrightarrow U^{239} \xrightarrow{\beta^-} Np^{239} \xrightarrow{\beta^-} Pu^{239}$. The neutrons available for capture would be those emitted during the spontaneous fission of uranium, those resulting from the action of alpha particles on the nearby light elements, and those from cosmic rays.

From considerations involving the assumption of a smooth energy surface in the heavy region, and from the systematics of α decay,[4] it may be postulated that the Pu^{244} nucleus is stable with regard to decay by β particle emission, and the half-life for decay by α particle emission might possibly be as long as 10^8 years. This would result in Pu^{244} having a sufficiently long lifetime so that if any Pu^{244} were present at the time of formation of the earth, it might still be detectable. (It should also be mentioned that there might be an irregularity in the energy surface, due, for example, to a closed shell of 148 neutrons, such that Pu^{244} might be shorter lived than 10^8 years by many orders of magnitude.) Since the chemical properties of plutonium are similar to the chemical properties of uranium, thorium and the rare earth elements, a search for Pu^{244} was undertaken using ores of uranium, thorium and rare earth elements.

The plutonium was separated chemically from samples of pitchblende ores taken from Colorado, the Belgian Congo and the Great Bear Lake region of Canada, from samples of monazite ores from North Carolina and Brazil, from a sample of fergusonite ore originating in Colorado, and from a sample of carnotite ore from Colorado. The ratios of plutonium to uranium in all of these ores were determined, and from considerations discussed in part IV, an attempt has been made to draw some conclusions as to the origin of the plutonium.

II. Experimental Work

A. Pitchblende Ores.—The plutonium was separated from the pitchblende by the following chemical procedure. A 100-g. sample of the ore was digested for three hours with 200 ml. of concentrated nitric acid. In some samples, a tracer amount of Pu^{238} which had been pre-oxidized to the hexapositive state was added in order to determine the amount of plutonium lost during the chemical separation. The liquid was separated by filtering and the residue treated in a similar fashion with another portion of nitric acid. The filtrates were put aside and the residue fused with sodium carbonate. The fusion mixture was washed with water and then digested with nitric acid. The solution was separated by filtering, the precipitate washed, and the filtrate and washings added to the previous filtrates. The residue was treated with hydrofluoric acid plus a few drops of sulfuric acid, evaporated to dryness, and then extracted with hot concentrated nitric acid. The remaining residue was fused again with sodium carbonate, washed, extracted with nitric acid and the extracts added to the previous filtrates.

The filtrates were then evaporated by boiling to reduce the volume, and diluted with water until the nitric acid concentration was about 2 *N*. Sulfur dioxide gas was bubbled through the solution to reduce any Pu(VI) to Pu(IV). Three-tenths of a mg. of La^{+++} was added per ml. of solution, the solution made 3 *N* in hydrofluoric acid, and the lanthanum fluoride precipitate centrifuged and washed. The lanthanum fluoride precipitate (containing any plutonium) was heated with three separate portions of 40% potassium hydroxide solution in order to metathesize it to lanthanum hydroxide. The lanthanum hydroxide was dissolved in a minimum amount of concentrated nitric acid, and diluted until the nitric acid concentration was about 1 *N*. The solution was made 0.1 *N* in sodium bromate and heated in a water-bath for one hour to oxidize any plutonium to the hexapositive state. The solution was cooled and made 2 *N* in hydrofluoric acid in order to precipitate the lanthanum (hexapositive plutonium stays in solution).

Three of these "lanthanum fluoride cycles" were carried out, reducing the volume of the solution each time. The plutonium was then oxidized a fourth time (the volume being about 0.5 ml.), the solution saturated with ammonium nitrate, and the plutonium extracted into diethyl ether. The ether solution was washed with 10 *N* ammonium nitrate and then evaporated on a one-inch platinum disk, giving an invisible, essentially weightless sample of plutonium.

B. Monazite Ores.—The plutonium was separated chemically from the monazite ores as follows. One kilogram of the monazite was ground and digested for five hours in 1300 ml. of concentrated sulfuric acid. This was found to be a better means of breaking down this quantity of ore than either the strong alkali digestion or fusion processes. A tracer amount of Pu^{238} was added in order to determine what fraction of the naturally occurring plutonium survived the chemical procedures. The digestion mass was cooled, diluted about 1:1 with water, and added to 8.5 liters of concentrated hydrochloric acid. This was stirred for one day to ensure that any plutonium was freed from the insoluble chlorides which precipitate. The liquid was filtered from the residue. The residue was washed with concentrated hydrochloric acid, and the wash liquid added to the original filtrate. The solution was subjected to conditions under which plutonium is separated together with uranium and iron, these appearing in dilute hydrochloric acid solution.[5]

To this solution was added a trace of nitric acid, sulfur dioxide to reduce hexapositive plutonium to the tetrapositive oxidation state, 0.1 mg. of La^{+++} per ml. of solution, and the solution made 2 *N* in hydrofluoric acid. The plutonium was carried by the precipitated lanthanum fluoride, which was then metathesized with 40% potassium hydroxide as described previously, the resulting hydroxide dissolved in nitric acid, made 0.1 *N* in sodium bromate, heated for one hour in a water-bath to oxidize the plutonium, and then saturated with ammonium nitrate. The plutonium and the remaining uranium were extracted into diethyl ether, then re-extracted from the ether by shaking the ether with water containing sulfur dioxide. The water extract containing the plutonium and uranium was evaporated to reduce its volume, 0.2 mg. of La^{+++} per ml. of solution was added, and the solution made 2 *N* in hydrofluoric acid in order to precipitate the lanthanum fluoride and the plutonium. The lanthanum fluoride was metathesized to the hydroxide, dissolved in nitric acid, and the plutonium oxidized with bromate as before. The lanthanum was precipitated as the fluoride, the filtrate and washings reduced with sulfur dioxide, and stirred while 0.2 mg. of La^{+++} per ml. of solution were added very slowly. This was digested 1.5 hours to improve the carrying of the tetrapositive

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[2] A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, *ibid.*, Paper No. 16.8.

[3] C. A. Levine, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 296 (1950).

[4] I. Perlman, A. Ghiorso and G. T. Seaborg, *ibid.*, **77**, 26 (1950).

[5] D. A. Orth and K. Street, Jr., private communication (June, 1950).

plutonium by the lanthanum fluoride. The precipitate was centrifuged, washed, metathesized to the hydroxide, dissolved in nitric acid, and the plutonium oxidized to the hexapositive state by bromate. This solution (about 0.5 ml.) was saturated with ammonium nitrate and the plutonium extracted into diethyl ether. The ether was evaporated on a platinum plate as before to give an essentially weightless sample of plutonium.

C. **Fergusonite Ore.**—The plutonium was separated from the fergusonite ore as follows. A 280-g. sample of the ore, ground to pass a 100 mesh screen, was treated with three successive portions of hydrofluoric acid in a platinum dish. A known quantity of Pu^{238} tracer was added in order to determine the fraction of naturally occurring plutonium which survived the chemical procedures. Each portion of hydrofluoric acid was evaporated almost to dryness before the next portion was added. After the final treatment, the solution was diluted and the residue filtered off. The residue contained the insoluble fluorides and any Pu(IV) which might have been in the ore, while the filtrate contained any Pu(VI) which might have been present. Sulfur dioxide was bubbled through the filtrate to reduce any plutonium to the tetrapositive state and 0.2 mg. of La^{+++} per ml. of solution was added slowly. The solution was stirred and digested in order to increase the amount of the Pu(IV) carried by the lanthanum fluoride which precipitated.

The lanthanum fluoride precipitate was added to the original residue, the combined residues metathesized to the hydroxide by treating with three separate portions of 40% potassium hydroxide solution, and the hydroxides washed and treated with hydrochloric acid. This hydrochloric acid solution was filtered, the residue washed, and filtrate and washings set aside. The residue was treated in the same manner as the original ore sample: given a hydrofluoric acid treatment, washed, metathesized to the hydroxide, the hydroxide dissolved in hydrochloric acid, filtered and washed. The solution was subjected to conditions under which plutonium is separated together with uranium and iron, these appearing in dilute hydrochloric acid solution.

The acid concentration was adjusted to 1.5 *N*, a bit of nitric acid added, sulfur dioxide bubbled through the solution to ensure that all the plutonium was in the tetrapositive state, and 0.2 mg. of La^{+++} per ml. of solution was added. The solution was then made 3 *N* in hydrofluoric acid and the lanthanum fluoride which precipitated was centrifuged and washed. This lanthanum fluoride precipitate carried the plutonium. Three complete "lanthanum fluoride cycles," as described in the section above on pitchblende ores, were carried out, the plutonium oxidized with bromate, and extracted into diethyl ether. The ether was washed with 10 *N* ammonium nitrate and evaporated on a platinum disk, giving an essentially weightless sample of plutonium.

D. **Carnotite Ore.**—Five hundred grams of carnotite ore was subjected to the following treatment to separate the plutonium. The ore plus a known amount of Pu^{238} was digested with 800 ml. of hot concentrated nitric acid for five hours, washed and digested with another portion of nitric acid. The liquids were set aside and the residue digested for five hours with hot aqua regia. The remaining residue was well washed and the extract and washings added to the previous extracts. To test the residue for uranium content, a portion was treated with hydrofluoric acid in a platinum dish, and the supernatant made alkaline with potassium hydroxide. The precipitate formed was pure white, indicating that no more than minute quantities of uranium remained in the residue. The effectiveness of uranium extraction should be an indication of the effectiveness of extracting any plutonium which is present in the ore.

The combined extracts were evaporated by boiling to reduce the volume, and then diluted to a final nitric acid concentration of 1.5 *N*. The solution was made 0.1 *N* in sodium bromate and heated for one hour to ensure that all plutonium present was in the hexapositive state. The solution was made 3 *N* in hydrofluoric acid and the insoluble fluorides which precipitated were washed and discarded. Sulfur dioxide gas was bubbled through the filtrate and washings to reduce Pu(VI) to Pu(IV). The solution was then stirred while 0.2 mg. of La^{+++} per ml. of solution was slowly added. The lanthanum fluoride precipitate (carrying the plutonium) was metathesized to lanthanum hydroxide and dissolved in nitric acid. This solution was made 0.1 *N* in bromate ion and heated to oxidize the plutonium to Pu(VI). Three of these "lanthanum fluoride cycles" were carried out, the plutonium then oxidized with bromate and extracted into diethyl ether as described previously. The ether was evaporated on a one-inch platinum plate giving an essentially weightless deposit containing the plutonium.

E. **Counting and Yield Determination.**—The platinum plates on which the carrier-free plutonium was deposited were placed in the ionization chamber of the differential pulse analyzer apparatus.[2] In this apparatus, the ionization chamber is connected, through an amplifier and 48 channel pulse discriminating circuit, to a set of 48 fast mechanical counting registers. Thus α particles of different energies are counted on different registers and it is possible to determine separately the characteristics and measure the intensity of activity of each of a number of radioactive isotopes in a mixture, provided that they decay with different energies. For example, Pu^{238} and Pu^{239} can be distinguished separately by counting the number of 5.51 Mev. α particles originating from $Pu,^{238}$ and 5.15 Mev. α particles originating from Pu^{239} which are recorded in a unit time.

The amount of naturally occurring plutonium not lost in the chemical processing, in the case of the Colorado pitchblende, was 26% of that originally present. This was determined from the ratio of the activity of the Pu^{238} tracer in the final residue to the activity of the Pu^{238} added. The chemical yields in the cases of the Belgian Congo and Canadian pitchblendes were estimated at 10% by considering the losses at each step of the chemical procedure. No tracers were added in these cases in order that a search might be made for Pu^{238}. The chemical yield from Brazilian monazite was 25%, and from Carolina monazite, 17%. These also were determined by the use of Pu^{238} which was added as tracer. The chemical yields of plutonium in the cases of the fergusonite and carnotite ores, as determined by Pu^{238} tracer method, were 5 and 12%, respectively.

III. Results

The number of α-particles emitted per minute from the plutonium fractions which were chemically separated from the seven ores are summarized in Table I. From these data, the plutonium contents of the ores are calculated, using the value 24,000 years for the half-life of Pu^{239}. These are in reality lower limits for the plutonium contents of the ores (except fergusonite and carnotite) since the possibility exists, in all cases, that some of the plutonium remained in the ore residues after the chemical treatment.

IV. Discussion

The results of this investigation are in agreement with the data obtained by Seaborg and Perlman[1] if the chemical yield of plutonium obtained by them is reestimated. Considering the now-known chemical properties of plutonium, a 10% yield of plutonium from the Canadian pitchblende by the chemical separation process used by them appears reasonable. A recalculation of their data indicates one part plutonium per 1.8×10^{12} parts ore, or a Pu^{239} to ore ratio of 5.5×10^{-13}. The original calculations[1] assumed a high chemical yield and the results were rounded off in a conservative manner actually representing a lower limit. These investigators called attention to the importance of the spontaneous fission of uranium as a source of neutrons for the formation of the Pu^{239}.

Garner, Bonner and Seaborg[6] searched for naturally occurring plutonium in the three ores, carnotite, hatchetollite and fergusonite. They found Pu^{239} present in carnotite to the extent of

(6) C. S. Garner, N. A. Bonner and G. T. Seaborg, THIS JOURNAL, **70**, 3453 (1948); National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 1.10 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

TABLE I

SUMMARY OF RESULTS

	U, %	Total α particles per min. (Pu fraction)	5.15 Mev. α-particles per min. (Pu^{239})	5.51 Mev. α-particles per min. (Pu^{238})	4.5–4.7 Mev. α-particles per min.	Chemical yields, %	Pu^{239}/ore (by wt.)	$Pu^{239}/U \times 10^{12}$
Canadian pitchblende	13.5	1.5	0.66	0.0	0.0	10[a]	9.1×10^{-13}	7.1
Belgian Congo pitchblende	38	9	3.2	0.0	.0	10[a]	4.8×10^{-12}	12
Colorado pitchblende[f]	50	20	3.4	15.4[b]	.0	26	3.8×10^{-12}	7.7
Brazilian monazite	0.24	14	0.36	10[c]	.0	25	2.1×10^{-14}	8.3
N. Carolina monazite	1.64	15	.3	10[b]	.0	17	5.9×10^{-14}	3.6
Colorado fergusonite	0.25	1	$<$ .01	0.3[d]	.0	5	$<1 \times 10^{-14}$	<4
Colorado carnotite	10	5	$<$ .15	3.6[e]	$<$ .1	12	$<4 \times 10^{-14}$	<0.4

[a] Yield assumed from considerations of chemistry involved. [b] Pu^{238} equivalent to 60 α particles per minute added to the original ore sample. [c] Pu^{238} equivalent to 40 α particles per minute added to the original ore sample. [d] Pu^{238} equivalent to 6 α particles per minute added to the original ore sample. [e] Pu^{238} equivalent to 30 α particles per minute added to original ore sample. [f] Sample consisted of 46 g. of ore.

about one part in 10^{14}. They were able to set an upper limit for the amount of plutonium in fergusonite of one part in 10^9.

The Pu^{239} content of these ores appears on the surface to possibly be related to the uranium content. Thus, the same ratio of plutonium to uranium, within a factor of about three, is maintained in ores whose uranium content varies from 50% to 0.24% (except for the carnotite and fergusonite). From the results in the cases of the pitchblendes and monazites, one might suspect that a genetic relationship, involving long-lived progenitors, exists. However, it is also possible to explain these results in another way. It appears quite reasonable that the Pu^{239} has been formed through neutron absorption by U^{238} nuclei as described in Part I. The neutrons available for absorption would be those emitted during the spontaneous fission of uranium, those emitted by nuclei of light elements reacting with α particles, and those from cosmic radiations. The relative importance of each of these sources can be estimated very roughly.

Assuming an average of two neutrons per fission, and a spontaneous fission decay constant of 1.1×10^{-16} per year[7] for U^{238}, about 1.1 neutrons per gram of uranium are emitted per minute due to spontaneous fission. A 100-g. sample of ore containing 13.5% uranium will emit about 15 neutrons per minute by this means.

As suggested previously[8] there is another source of neutrons to be considered. One gram of uranium and the decay products in equilibrium with it emit about 6×10^6 α particles per minute whose maximum energies range from 4.2 to 7.68 Mev. These α particles, impinging on the nuclei of the light elements present, cause reactions whereby neutrons are emitted (α,n reactions). Roberts[9] has reported on the number of neutrons emitted when thick samples of the light elements are bombarded with 5.3 Mev. α particles. Stuhlinger[10] has given the excitation functions for the neutron emitting reactions involving α particles on boron and beryllium with α particle energies up to 8.8 Mev. With these data and those of others,[11–15] the number of neutrons emitted per α particle (of a given energy) impinging on a target of a light element can be estimated. Using the chemical analysis of a sample of Canadian pitchblende reported by Marble,[16] it can be calculated that in a 100-g. sample of ore containing 13.5% uranium, fifteen to twenty neutrons per minute will be formed due to the action of α particles on the nuclei of the light elements in the ore (α,n reactions). However, if, for example, as much as 1% of beryllium, boron, or lithium is present in the ore in addition to the elements reported in the analysis, the additional neutron yields due to (α,n) reactions in such a 100-g. sample would be about 100, 40 and 10 neutrons per minute, respectively.

Montgomery and Montgomery[17] have estimated the neutron intensity at sea level in the cosmic radiation to be about 0.1 neutron per cm.^{2} per minute. Although the actual cosmic ray neutron intensity in the ores may be somewhat higher than this (due to the action of other types of cosmic rays on the ore), the neutron contribution from cosmic rays to the total neutron flux in the ores seems small.

For a typical 100-g. sample of pitchblende ore containing 13.5% uranium, then, somewhat more than some thirty neutrons per minute are available from the sources mentioned above. Simple calculations show that the U^{238} in this sample must capture some ten to fifteen neutrons per minute, or something less than about 30–50% of those available, in order to account for an equilibrium concentration of one part Pu^{239} per 1.4×10^{11} parts uranium. A consideration of the neutron absorption cross sections of the elements in the ore, together with their abundances from the above mentioned analysis, indicates that absorption of this fraction of the neutrons by the uranium is reasonable.

(7) G. Scharff-Goldhaber and G. S. Klaiber, *Phys. Rev.*, **70**, 229 (1946).

(8) G. T. Seaborg, *Chem. Eng. News*, **25**, 358 (1947).

(9) J. H. Roberts, U. S. Atomic Energy Commission Declassified Document MDDC-731 (January, 1947).

(10) E. Stuhlinger, *Z. Physik*, **114**, 185 (1939).

(11) E. Segrè and C. Wiegland, U. S. Atomic Energy Commission Declassified Document MDDC-185 (1949).

(12) R. L. Walker, U. S. Atomic Energy Commission Declassified Document AECD-2383 (1948).

(13) I. H. Halpern, *Phys. Rev.*, **74**, 1234 (1948).

(14) L. N. Ridenour and W. J. Henderson, *ibid.*, **52**, 889 (1937).

(15) H. L. Anderson, U. S. Atomic Energy Commission Unclassified Document NP-851 (1948).

(16) J. P. Marble, *Am. Mineral.*, **24**, 272 (1939).

(17) C. S. Montgomery and D. D. Montgomery, *Phys. Rev.*, **56**, 10 (1939).

It should be emphasized that these estimations of the neutron flux are necessarily quite approximate. Thus, values for the spontaneous fission decay constant of U^{238}, varying from about half to twice the value quoted and used above, have been reported.[18–20] Similarly, the estimation of the neutron flux from the (α,n) reactions is subject to error due to the uncertainty of the composition of the ores and the lack of precise knowledge for the yields of the (α,n) reactions; the estimation of the numbers of neutrons from this source could be in error by a factor of two or possibly even more. Therefore, the relative importance of these two major sources for the neutrons may differ somewhat from that suggested in this discussion.

A situation similar to the Canadian pitchblende exists in the cases of the other pitchblende ores having a greater uranium content. More neutrons are available due to spontaneous fission of the uranium and the (α,n) reactions, but the high uranium content of the ore absorbs them, so the plutonium to uranium ratio remains essentially constant. It should be mentioned that when an appreciable fraction of the neutrons is absorbed by uranium, the additional neutrons which result from the fission of U^{235} contribute significantly to the production of Pu^{239}.

Somewhat different considerations seem to apply in the cases of the monazite ores. In view of the smaller concentration of uranium in monazite, the ratio of Pu^{239} to uranium in monazite might be expected to be more definitely smaller than the ratio in pitchblende if a major source of neutrons were still the spontaneous fission of U^{238}, since the relatively large amounts of elements other than uranium in the ore would capture neutrons, leaving a smaller proportion of neutrons available for capture by the U^{238}. Neutrons due to the spontaneous fission of thorium would not compensate for this effect since the spontaneous fission rate of thorium is smaller than that of uranium by a factor of about fifty.[21] However, the contribution of neutrons from (α,n) reactions is relatively more important. The α particles emitted in the decay of thorium and its daughters will give rise to (α,n) reactions with nuclei of the light elements in the same manner as the α particles from the uranium decay chains. One gram of thorium and its decay products will produce 1.5×10^6 α particles per minute capable of producing neutrons in this manner. Thus, for example, a 100-g. sample of a typical monazite which contains 6.5% thorium, 1.6% uranium and light elements in about the same abundance as in the pitchblende used in the previous example, will emit about two neutrons per minute due to spontaneous fission and about five or ten neutrons per minute due to (α,n) reactions. In order to maintain the Pu^{239} to uranium ratio seen in North Carolina monazite, about 0.4 neutron per minute must be captured by the uranium. If just the uranium and thorium competed for the neutron capture, the uranium in the ore would capture somewhat less than half of those available. Monazite ore, however, contains an appreciable amount of the rare earth elements, which capture neutrons with appreciable cross sections, so that the low fraction of the available neutrons captured by the uranium is reasonable. As the ratio of uranium to thorium in the thorium ores decreases, the number of neutrons obtained from (α,n) reactions becomes even more an important factor. Thus the number of neutrons produced in the ore per gram of uranium is greater in the cases of the monazite ores than in the cases of the pitchblende ores, this effect somewhat compensating for the number of neutrons captured by nuclei other than U^{238} in the monazite ores.

Since these explanations for the source of the plutonium in ores suggest that the presence of large amounts of neutron absorbing impurities, together with small amounts of uranium (or thorium), should reduce the ratio of Pu^{239} to uranium, the fergusonite and carnotite ores were investigated in order to test these suggestions further. Carnotite is a potassium uranyl vanadate, while fergusonite is a niobate and tantalate of the rare earth elements with a small amount of uranium. In carnotite, the large amounts of potassium and vanadium would be expected to capture most of the available neutrons. Tantalum, having a high neutron absorption cross section, would be expected to capture most of the neutrons available in fergusonite. In the case of the carnotite ore, the ratio of Pu^{239} to uranium present was set at 0.4×10^{-12} and this should probably be considered to be an upper limit. This is a factor of ten to thirty below the ratio found in the pitchblendes and monazites. Garner, Bonner and Seaborg,[6] working with a five-kilogram sample of ore, reported one part Pu^{239} per 10^{14} parts carnotite ore. On the assumption of the same uranium content, this puts the value of the ratio of Pu^{239} to uranium in carnotite below the value of the ratios in pitchblende and monazite by a factor of forty to one hundred Thus it can be seen that the presence in the ore of elements with high neutron absorption cross sections tends to decrease the amount of Pu^{239} present relative to the uranium content. Of the neutrons available in the ore, a smaller fraction can be utilized for the production of Pu^{239}. In the case of the fergusonite ore, less than 0.01 α particle per minute due to Pu^{239} was seen, this being the lower limit of detection in this experiment. Unfortunately, this lower limit corresponds to the same order of magnitude as the Pu^{239} contents of the pitchblende and monazite ores investigated. With larger samples of fergusonite, a better limit could be set.

Studies by Peppard, and co-workers,[22] limited to Belgian Congo pitchblende, are in agreement with these results so far as they go. They found one part Pu^{239} per 1.4×10^{11} parts Belgian Congo pitchblende concentrate (45.3% uranium). After chemically separating microgram amounts of plutonium from very large amounts (ton quantities) of Belgian Congo pitchblende, they could

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detect no plutonium isotopes other than Pu^{239} by mass spectrographic analysis, by differential pulse analysis, or by neutron irradiation studies.

In the present investigation, no evidence for naturally occurring Pu^{238} was found in the plutonium fraction separated from any of the ores. In the cases of the Canadian and Belgian Congo pitchblendes, an upper limit for the Pu^{238} content could be set at one part Pu^{238} in more than 4×10^{15} parts ore by weight. A better figure than this could not be obtained due to the relatively high background activity in the pulse analysis apparatus. Since the Pu^{238} could only have come from double β decay of U^{238}, a lower limit of about 3×10^{17} years can be set for the half-life of U^{238} decaying by the simultaneous emission of two β particles. It has already been shown that this half-life is greater than 6×10^{18} years.[3] Peppard, *et al.*,[22] using a differential pulse analyzer, gave a limit on the ratio of Pu^{238} to Pu^{239} in Belgian Congo pitchblende of less than 3×10^{-6} by weight. This, together with the concentration of Pu^{239} which they found, sets a lower limit for the half-life of U^{238} decaying by the simultaneous emission of two β particles at 4×10^{18} years.

As mentioned in Part I, on the basis of the radioactive properties estimated through the use of the systematics of α decay,[4] it is conceivable that a long-lived β stable plutonium isotope of mass 244 might exist in nature. The half-life of this isotope is estimated, on the hypothesis of a smooth energy surface, to be at least 10^7 years, and possibly as long as 10^8 years. It should decay by emitting an α particle of 4.5–4.7 Mev. energy. If, for example, a 10^8 year Pu^{244} had amounted to 4% of the ore at the time of the origin of the earth, approximately four parts in 10^{11} parts ore would still remain. From the lack of α activity in the 4.5–4.7 Mev. region, we can set an upper limit for the presence of Pu^{244} in the Canadian pitchblende ore of about 50 parts Pu^{244} per 10^{11} parts pitchblende. Peppard, and co-workers,[22] through mass spectrographic analysis of microgram quantities of plutonium obtained from wastes resulting from the processing of ton quantities of Belgian Congo pitchblende for uranium, showed the total content of plutonium isotopes other than Pu^{239} to be less than 1% by weight of the total plutonium. The Pu^{244} content in the Belgian Congo pitchblende is thus limited to less than one part in 1.4×10^{13} parts ore. This indicates that either no appreciable quantities of Pu^{244} were deposited with the Belgian Congo pitchblende, or that the half-life of the hypothetical Pu^{244} is less than about 10^8 years.

Since the chemical properties of the lower oxidation states of plutonium are quite similar to the chemical properties of thorium and the rare earth elements, it is conceivable that a hypothetical long-lived plutonium, formed at the time of the origin of the earth, would be found in thorium-rare earth minerals, such as monazite. The plutonium sample separated from the Brazilian monazite had an α activity in the 4.5–4.7 Mev. region which was less than 14% of the intensity of α activity due to Pu^{239}. For a half-life of 10^8 years for the hypothetical Pu^{244}, the Pu^{244} content of the monazite ore is limited to less than one part Pu^{244} per 3.6×10^{11} parts ore by weight. With the equipment now available, a five- to ten-kilogram sample of ore would allow such a Pu^{244} isotope of about 4% initial abundance to be identified.

It is of interest to note some other isotopes probably existing in nature which would be formed in a manner analogous to the mechanism postulated for the formation of Pu^{239}. As was pointed out by Garner, Bonner and Seaborg,[6] the capture of a neutron by thorium will result in the formation of U^{233} and the "missing" neptunium (4n + 1) radioactive series, thus: $Th^{232} + n \longrightarrow Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233}$. It has been indicated above that the number of neutrons available for capture in a typical thorium ore such as monazite is a factor of some five below the number available in pitchblende. Since the neutron capture cross section of Th^{232} is about the same as that of U^{238}, and the half-life of U^{233} is a factor of about five greater than the half-life of Pu^{239}, the ratio of U^{233} to Th^{232} in monazite should be about the same order of magnitude as the ratio of Pu^{239} to U^{238} in pitchblende: about one part U^{233} per 10^{11} parts of thorium. The presence of any of the members of this series would be difficult to detect due to the presence of the other radioactive isotopes resulting from the other natural radioactive series.

The Pu^{239} itself will capture neutrons and, by a series of steps, will form other transuranium elements, thus: $Pu^{239} + n \longrightarrow Pu^{240}$; $Pu^{240} + n \longrightarrow Pu^{241} \xrightarrow{\beta^-} Am^{241}$; $Am^{241} + n \longrightarrow Am^{242} \xrightarrow{\beta^-} Cm^{242}$. Probably, however, only very minute quantities of these other transuranium elements exist in nature. Unless some other long-lived transuranium progenitor, with a half-life comparable to geological time, exists, the ratio of naturally occurring Am^{241} to Pu^{239} is smaller than the ratio of Pu^{239} to U^{238} by a very large factor, and the amounts of natural americium and curium are undetectable by present means. Since the neutron capture cross sections of Pu^{239}, Pu^{240} and Am^{241} are known, it is possible to calculate approximately how much of the other transuranium elements are present. Neptunium will be present as a result of the reactions $U^{238}(n,2n)U^{237} \xrightarrow{\beta^-} Np^{237}$, but the requirement of high energy neutrons (greater than about 6 Mev.) reduces the concentration of the Np^{237} to a value somewhat below that of the Pu^{239}, but still sufficiently large to be detectable.

V. **Acknowledgments.**—We wish to express our deep appreciation to A. Ghiorso for the pulse analyses of the various samples in order to determine their content of Pu^{239} α activity, and to S. G. Thompson for many helpful suggestions with respect to the chemical procedures. This work was performed under the auspices of the U. S. Atomic Energy Commission.

BERKELEY, CALIF. RECEIVED FEBRUARY 12, 1951