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OCCURRENCE OF THE TRANSURANIUM ELEMENTS IN NATURE

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INTRODUCTION

Whether uranium, with an atomic number of 92, is last in the series of elements or whether elements heavier than uranium can exist, is a question that has interested chemists ever since the discovery of the Periodic Law. The correct answer to this question could only be given by contemporary chemists and physicists when heavy elements lying beyond uranium in the Periodic Table were produced artificially in 1940. Mendeleev himself admitted the possibility of extending the Periodic System to include elements heavier than uranium. Later, a great deal of work was devoted to the investigation of the possible existence of transuranium elements and to the structure of their electron shells.

Attempts to detect transuranium elements in nature have been made for some time. Reports have repeatedly appeared in the literature concerning their natural occurrence but, after more careful study, these data have mostly proved to be incorrect. The chief reasons for the lack of success were: (1) unreliable methods of investigation; (2) wrong placing of the transuranium elements in the Periodic Table, whereby they would constitute a group of analogues to osmium, iridium, and platinum, i.e. element 93 should be the analogue of manganese and rhenium, element 94, of ruthenium and osmium, and so on. On this hypothesis, Loring and Druce[1-4] undertook a search for element 93 in samples of manganese and rhenium using X-ray analysis. They discovered weak lines in the wave-length region predicted for this element. They considered this as proof (though not conclusive) of the presence of element 93 in manganese ores. It was established later that the observed lines belonged to other elements.

In 1934 Koblic reported[5] that he had discovered element 93, for which he proposed the name "bohemium", in

Bohemian (Jachymov) pitchblende. Koblic assumed that the element he had discovered was an isotope of element 93 with a mass number of 240. He was of the opinion that pitchblende contained 1% of bohemium. However, X-ray and chemical analysis[6] showed that the material obtained by him was really a mixture of silver tungstate and vanadate, after which Koblic withdrew any claim to the discovery[7].

In 1938, Hulubei and Gauchois[8,9] reported the discovery of element 93 in various minerals such as betafite, monazite, columbite, and tantalite. They suggested the name "sequanium" for this element, but their findings also were not subsequently confirmed.

In 1941 Wahl[10], while making a mass-spectrometric study of columbite and tantalite, noticed a line corresponding to mass 237, which he supposed to belong to an isotope of the first transuranium element. However, this assertion also proved to be mistaken.

It has now been established that all the neptunium isotopes are β-emitters of short half-life; this is the obstacle to their discovery. Only neptunium-237 emits α-particles, with a half-life of 2.20×10^6 years, but even this period of time is small compared with the age of the earth. Even if this element once existed in rocks, then owing to its insufficiently long half-life it would have disintegrated long ago. The neptunium-237 found in natural uranium specimens is formed continuously from the uranium.

After 1936 several reports also appeared in the literature, concerning the occurrence of element 94 in minerals. During studies of the radioactivity of various minerals, pleochroic halos of abnormal radii ($\sim 5\ \mu$)[11-18] and α-particles with a path-length of 1.8 and 2.9 cm in air[19-21] were discovered; the path-lengths agreed with those calculated for the particles producing the pleochroic halos. This activity could not be ascribed to any radioactive element known at that time. Chemical investigation revealed two characteristic features of the source of the radiation: (1) precipitation with sulphides in strongly acid solutions; (2) volatility from hot oxidising solutions (HNO_3, H_2SO_4).

These two activities corresponding to path-lengths of 1.8 and 2.9 cm are always found in constant ratio, throughout all chemical operations. The chemical similarity apparently indicated the existence of two isotopes of the same element, or the presence of nuclear isomerism. The constant quantitative relationship between the activities is evidence of a genetic link between the two isotopes, one giving rise to the other by one α-disintegration and two β-disintegrations, as is the case with $^{238}U - {}^{234}U$ and $^{232}Th - {}^{228}Th$:

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta^-} {}^{234}Pa \xrightarrow{\beta^-} {}^{234}U, \quad (1)$$

$$^{232}Th \xrightarrow{\alpha} {}^{228}Ra \xrightarrow{\beta^-} {}^{228}Ac \xrightarrow{\beta^-} {}^{228}Th. \quad (2)$$

On account of the chemical similarity of the unknown source to osmium and because of the fact that osmium itself is inactive, Schintlmeister assumed that the activity was due to eka-osmium, i.e. element 94. From the laws of α-disintegration of heavy nuclei, Schintlmeister[22] inferred that the α-particles with path-lengths of 1.8 and 2.9 cm could be ascribed to nuclei of element 94 with masses 244 and 240. This question was given much attention in Germany, since it was considered possible that the parent element could be split under the influence of neutrons, and the natural raw materials could thus be used to produce energy.

After study of the properties of plutonium had shown that they differed from those of osmium, it became evident that Schintlmeister's assumptions were mistaken. Furthermore, with the heavy elements, the energy of α-disintegration of β-stable nuclei has a tendency to increase rather than to decrease as Schintlmeister supposed.

According to Levinos and Kurtis[23], certain technical uranium preparations have a greater specific activity than the corresponding pure compounds. They ascribed the difference to the presence of an α-active impurity, with chemical properties similar to those of uranium, which could be element 94. However, this suggestion was not confirmed and was apparently mistaken.

Reports by Gysae and Korschling[24,25] that they had found α-emitters, with α-particle path-lengths of ~ 2 and 3 cm, whose properties were similar to those of plutonium or neptunium, were similarly not authenticated. It is rather doubtful whether any isotope of plutonium or neptunium would emit α-particles of such low energy.

The first sound evidence for the existence of transuranium elements in nature was provided by the work of Seaborg and Perlman, dating from 1942, i.e. from a time when the properties of the transuranium elements had already been thoroughly studied.

OCCURRENCE OF PLUTONIUM IN NATURE

The occurrence of plutonium in nature was first proved by Seaborg and Perlman[26] in 1942. The isolation of plutonium from 400 g of pitchblende which contains ~ 40 different elements was based on the property of Pu^{III} and Pu^{IV} to coprecipitate with the rare-earth fluorides. In the highest oxidation state, Pu^{VI}, plutonium behaves like uranium; it does not coprecipitate with the fluorides of the lanthanides, but, in contrast to uranium, it is reduced considerably more easily. By means of repeated oxidation-reduction cycles the plutonium was separated from the uranium and from the other elements. Using radiochemical methods, it was shown that the concentration of plutonium in natural specimens is 10^{-14} g per g of uranium.

Since the half-lives of plutonium isotopes are very small in comparison with the age of the earth, the amount of plutonium found cannot be the undecayed residue of the originally existing element. Its presence can be explained by radioactive processes which continuously produce a minute quantity of plutonium, while the observed quantity represents the equilibrium between formation and disintegration of the element. The most probable mode of formation of this element may be expressed as follows:

$$^{238}U(n, \gamma)^{239}U \xrightarrow[23\ min]{\beta^-} {}^{239}Np \xrightarrow[2{\cdot}3\ days]{\beta^-} {}^{239}Pu. \quad (3)$$

In particular, the reaction involving neutron capture by the ^{238}U nuclei is identical with that which occurs in a uranium reactor during the production of plutonium. It follows from reaction (3) that the isotope ^{239}Pu constitutes the main part of the plutonium formed in minerals. Garner, Boner, and Seaborg[27] obtained much the same result in isolating plutonium from carnotite (see Table).

Using a Wilson cloud-chamber, Chatterjee[28] also observed minute quantities of ^{239}Pu in uraninite.

These first data on the existence of plutonium in nature were of a preliminary character and could not claim high accuracy. The isolation of such small concentrations of plutonium presented great difficulty, because its separation from macro-impurities and especially from radioelements whose activity is more than 10^6 times greater

Summary of results on the extraction of plutonium from ores.

Ore	Sample, g	Uranium content, %	Quantity extracted, counts/min	Chemical yield, %	Ratio × 10^{11} ^{239}Pu : ore	Ratio × 10^{11} ^{239}Pu : U	References
Uranium ore (Canada)	400	—	1.5	80	0.1*		26
Carnotite	5000		2.8	60	0.1		42
Uranium ore (Canada)	100	13.5	0.66	10	9.1	0.71	29
Congo	10	38	3.2	10	48	1.2	
Colorado	40	50	3.40	26	38	0.77	
Brazilian Monazite	1000	0.24	0.36	25	0.21	0.83	
N. Carolina	1000	1.64	0.3	17	0.59	0.36	
Colorado fergusonite	280	0.25	0.01	5	0.1	0.4	
Colorado carnotite	500	10	0.15	12	0.4	0.04	
Congo uranium ore	2000	45.3	43.0	4.3	70±7	1.5±0.2	30
Uranium ore	2000	43.5	400	33.3	87	2.0±0.3	31

* Yield is much too low. After recalculation by Peppard, the ratio ^{239}Pu: ore becomes 5.5×10^{-13}.

than that of plutonium, was a very complex operation. Seaborg and Levine[29] later worked with samples of uranium pitchblende, monazite, carnotite, and fergusonite. Isolation of the plutonium was achieved by means of lanthanum fluoride cycles. The results obtained by Seaborg and Levine are also included in the Table.

It is interesting to note that the ratio of plutonium to uranium was found to be almost constant ($\sim 10^{-11}$) in pitchblende and monazite, where the uranium content varies from 50 to 0.24%, and much lower in carnotite and fergusonite. This is evidence both that the plutonium content is dependent on the uranium content and also of the probability of the formation of natural plutonium from ^{238}U according to Eqn. (3), as discussed above.

Peppard et al.[30] have also studied the extraction of plutonium from uranium ores. They found 7.0 ± 0.7 parts of plutonium per 10^{12} parts of ore concentrate. After certain corrections, made by Peppard, their values agree fairly well with the data from the original work of Seaborg and Perlman[26], in which it was assumed that the extraction was very efficient. If new data on the behaviour of plutonium are taken into account, recalculation of their results gives one part of plutonium per 1.8×10^{12} parts of ore or a ratio of ^{239}Pu to ore of 5.5×10^{-13}.

Starik et al.[31] worked out a new scheme to increase the yield of plutonium during its purification, since the fluoride method is very complex and gives low yields. In Peppard's work[30], the activity of the isolated natural plutonium was only of the order of tens of counts per minute. The method of isolation devised by Starik involves coprecipitation of plutonium with uranium diacetate and subsequent extraction with diethyl ether. By this method it was possible to remove all the residual α-active elements. From 2 kg of ore, Starik's method gave a quantity of plutonium which had an activity of 400 counts per minute; this corresponds to a ^{239}Pu : U ratio of $(2.0 \pm 0.3) \times 10^{-11}$. This result is shown in the Table, together with the earlier data.

The work of Peppard et al.[30], in which microgramme quantities of plutonium were isolated, enabled a detailed study of the isotopic composition of natural plutonium to be made. Since, according to the work of Seaborg and Perlman[26], about 100 tons of ore are needed to produce 1 mg of plutonium, the extraction was carried out from the aqueous waste produced during the working up of uranium pitchblende to uranium. The aqueous waste contains practically all the soluble parts of the ore concentrate, except for the uranium, the concentration of which has been reduced to negligible proportions.

Extraction of plutonium from this raw material, which is a saturated solution of metal nitrates together in nitric acid, was accomplished by extraction with tributyl phosphate, followed by purification using TTA-cycles*. Plutonium-239 was identified by measurement of the energy of the α-particles, determination of the ability of the material to undergo fission under the influence of thermal neutrons, mass-spectrographic analysis, and radiochemical methods. None of these methods detected any isotopes other than ^{239}Pu. The upper limit for the ratio of ^{238}Pu to ore (Congo and Canadian ore) had been established earlier by Levine and Seaborg as $1 : 4 \times 10^{15}$ (by weight). Measurement of the α-particle energy with a multi-channel differential pulse analyser enabled Peppard to establish the upper limit for the ratio ^{238}Pu : ^{239}Pu as less than 3×10^{-6} (by weight). Since ^{238}Pu can only arise as a result of a two-fold β-disintegration of ^{238}U,

$$^{238}U \xrightarrow{\beta^-} {}^{238}Np \xrightarrow{\beta^-} {}^{238}Pu, \qquad (4)$$

the calculated half-life of ^{238}U for the emission of two β-particles is 10^{18} years, which is in full agreement with other data[32]. The presence of plutonium isotopes with larger atomic masses was investigated by determining the ability of a sample of natural plutonium to undergo fission when irradiated with neutrons in a uranium pile, and by mass-spectrography. However, these experiments did not give a positive result, so that one is justified in assuming that the content of heavy plutonium isotopes is below the limit of sensitivity of the methods of determination. The upper limit for the sum of the isotopes ^{240}Pu, ^{241}Pu, and ^{244}Pu cannot exceed 1% (mass-spectrographic data) and that for ^{242}Pu (on the basis if neutron irradiation), cannot exceed 0.01%.

The general behaviour of α-active nuclei give grounds for assuming the presence of the isotope ^{244}Pu in nature, since, with increase in mass number, the half-life of β-stable α-active nuclei increases. The isotope ^{244}Pu is β-stable and emits α-particles with an energy of 4.5–4.7 MeV with a half-life of $(7 \pm 2) \times 10^7$ years[33]. This is comparatively small, so that the probability of detecting ^{244}Pu in nature is negligible. If ^{244}Pu does exist in nature, it must be accompanied by equilibrium quantities of ^{240}U, ^{240}Np, ^{240}Pu, ^{236}U, ^{232}Th, and all its decay products. The upper limit for ^{244}Pu in Congo uranium pitchblende is not more than one part in 1.4×10^{13} parts of ore. Since the chemical properties of plutonium in its lower oxidation states are similar to those of thorium and the rare-earth elements, it is possible that the long-lived isotope ^{244}Pu might be found in the ores of these elements. It is for the same reason that ^{244}Pu was not found in uranium ores. In a sample of plutonium extracted from Brazilian monazite the proportion of ^{244}Pu is not more than 14% of the ^{239}Pu content. Peppard, taking the half-life of ^{244}Pu to be 10^8 years, calculated the possible content of this isotope in Brazilian monazite and found the upper limit to be $1 : 3.6 \times \times 10^{11}$ (by weight), which indicates the incidental presence of large quantities of this isotope at the time of formation of the earth. Diamond and Barnes[34] found the half-life of ^{244}Pu to be $(7.6 \pm 2) \times 10^7$ years. If the formation of the

* TTA-cycles consist, essentially, of the formation of chelate complexes of Pu^{IV} with thenolytrifluoroacetone, which can be isolated by extraction with benzene.

elements took place 5.5×10^9 years ago and the quantity of ^{244}Pu formed at that time was half that of ^{232}Th, the ratio of ^{232}Th to ^{244}Pu in thorium ores today would be 10^{32}. If the half-life is taken as the upper limit, 9.6×10^7 years, a quantity of ore corresponding to 34 kg of thorium could contain 10^{-13} g of ^{244}Pu.

NEUTRON SOURCES

The question of neutron sources is very important in a study of the origin of natural plutonium. The chief source of neutrons in uranium ores is undoubtedly the spontaneous fission of uranium. If it is assumed that ^{239}Pu arose as a result of neutron capture by ^{238}U nuclei, the observed ^{239}Pu content is too great to be due to the neutron flux produced by spontaneous fission of natural uranium (24.2 ± 0.5 fissions per gramme per hour)[35]. Taking the equilibrium ratio of $^{239}Pu : ^{238}U$ to be $(1.5 \pm 0.2) \times 10^{-11}$, Peppard calculated the quantity of ^{239}Pu (128 ± 17 atoms) formed per hour from 1 g of ^{238}U. The number of neutrons produced by uranium fission is insufficient for the formation of this quantity. However, the neutron flux produced by the interaction of high energy α-particles from elements of the uranium series with light elements such as, for example, boron, oxygen, magnesium, silicon, etc., present in the ore can supplement this deficiency. In addition, to the total number of neutrons must be added those produced by the action of cosmic rays and those from the ^{235}U nuclei. The ^{235}U nucleus can capture a neutron and itself undergo fission with formation of several neutrons (an average of 2.5).

The average intensity of these sources can only be established with great difficulty, owing to the many variables (depth of the ore deposit, uranium content, content of boron, oxygen, magnesium, silicon, etc.). If one reckons that an average of two neutrons are produced per fission[36] and that the fission constant of uranium is 1.1×10^{16}, we can conclude that 1 g of ^{238}U emits approximately 1.1 neutrons per minute by spontaneous fission. Thus 100 g of ore containing 13.5% of uranium produce about 15 neutrons per minute; 1 g of uranium, together with its decay products, emit approximately 6×10^6 α-particles per minute, the maximum energy of which is in the range 4.2–7.68 MeV. 100 g of Canadian pitchblende, containing 13.5% of uranium, can produce 15–20 neutrons per minute as a result of (α, n)-reactions. The yield is appreciably greater if light elements are present in high concentration. The neutron intensity from cosmic radiation is 0.1 neutron per cm^2 per min at sea level[37]. Although this quantity can be greater, the proportion of neutrons from cosmic radiation in the total neutron flux is relatively small.

It should be emphasised that these estimates of neutron flux are very approximate, if only because the fission constant of uranium, according to different authors[38,39], may differ from that quoted above. In addition, the estimate of the neutron flux from (α, n)-reactions is subject to errors due to insufficient knowledge of the chemical composition of the ores and to lack of accurate information about the yield of (α, n)-reactions. Consequently, the actual intensity of the main sources may differ appreciably from that described.

In ores with high uranium content, more neutrons are emitted by uranium fission and by (α, n)-reactions, but the ratio of ^{239}Pu to ^{238}U generally remains constant. In monazite ores the situation is different. In view of their low uranium concentration, the ratio of plutonium to uranium can be less than in uraninite. If the main source of neutrons is taken to be the spontaneous fission of ^{238}U, the other elements present in the ore capture a large quantity of neutrons and only a small proportion is captured by the ^{238}U. Neutrons from the spontaneous fission of ^{232}Th do not make up this deficiency, because the spontaneous fission of ^{232}Th is many times less frequent than that of uranium ($T_{1/2} = 10^{20}$ years)[40] so that the contribution of neutrons from (α, n)-reactions is of great importance. 1 g of thorium in equilibrium with its decay products emits 1.5×10^6 α-particles per minute able to take part in (α, n)-reactions. For a constant ratio of ^{239}Pu to uranium, 1 g of North Carolina monazite must absorb about 0.4 neutron per minute. Since the ratio of U to Th in thorium ores is less, the role of neutrons from (α, n)-reactions is greater. These neutrons form the greater part of the neutron flux. Thus the number of neutrons produced in 1 g of uranium in monazite ores is greater than in uranium ores and the neutrons absorbed by other nuclei are fairly well compensated for.

It follows from this that a high content of elements absorbing neutrons and a low uranium (or thorium) content reduce the ratio of ^{239}Pu to uranium. This rule is well confirmed in the case of carnotite and fergusonite. The chemical composition of carnotite is $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$ and that of fergusonite is $Y(Nb, Ta)O_4$ with some erbium, cerium, dysprosium, iron, calcium, and uranium. These elements absorb neutrons with a high effective cross-section which may explain the low ratio of ^{239}Pu to uranium in carnotite and fergusonite, since only a small part of the total number of neutrons are used to produce ^{239}Pu.

OCCURRENCE OF NEPTUNIUM IN NATURE

It follows from the nuclear properties of neptunium that none of its isotopes can exist in nature, unless it was formed comparatively recently or is formed continuously by radioactive processes in thorium and uranium ores. The fact that ^{239}Pu is present in nature means that traces of 2.3 day ^{239}Np should be found in uranium minerals because of its continuous formation from ^{238}U by neutron capture. In addition, Seaborg has shown that ^{237}Np can be present in uranium minerals; this is the parent isotope of the $(4n+1)$ radioactive series, resulting from the formation of β-active ^{237}U by the action of fast neutrons on uranium in the nuclear reaction

$$^{238}U(n, 2n)^{237}U \xrightarrow{\beta^-} {}^{237}Np. \qquad (5)$$

Since only a very small proportion of neutrons have the necessary energy of about 6 MeV, the possibility of ^{237}Np formation is low. As a result, the concentration of ^{237}Np is many times less than that of natural plutonium-239. Peppard et al.[41] succeeded in extracting ^{237}Np from the residues of the processing of Congo pitchblende.

It is well known that when ^{237}Np disintegrates, ^{229}Th is formed ($T_{1/2} = 7.34 \times 10^3$ years), while ^{238}U disintegrates to ^{230}Th ($T_{1/2} = 8.0 \times 10^4$ years):

$$^{237}Np \xrightarrow{\alpha} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U \xrightarrow{\alpha} {}^{229}Th, \qquad (6)$$

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta^-} {}^{234}Pa \xrightarrow{\beta^-} {}^{234}U \xrightarrow{\alpha} {}^{230}Th. \qquad (7)$$

The half-lives of these isotopes are fairly large compared with the age of the mineral seam but are nevertheless small in relation to the age of the earth. It follows from this that the ratio of the activities of ^{229}Th to ^{230}Th and ^{237}Np to ^{238}U should be similar, if the ^{229}Th isotope were formed from ^{237}Np only by reaction (6). However, ^{229}Th can also be formed in another way.

Garner et al.[27] suggested that in uranium ores having a small thorium content another member of the $(4n+1)$ radioactive series can be produced — the isotope ^{223}U, formed by the reaction

$$^{232}Th(n, \gamma)^{233}Th \xrightarrow[23\cdot5\ min]{\beta^-} {}^{233}Pa \xrightarrow[27\cdot4\ days]{\beta^-} {}^{233}U. \qquad (8)$$

This disintegrates further, giving ^{229}Th. The extent to which this reaction affects the ^{229}Th content is not known at present.

The weight ratios of thorium to uranium in Congo ore, established by Peppard et al.[41], are given below:

$$^{229}Th : {}^{230}Th = (3.4 \pm 0.3) \times 10^{-10};$$

$$^{229}Th : {}^{232}Th = (4.0 \pm 0.6) \times 10^{-11};$$

$$^{233}U : {}^{238}U = (1.3 \pm 0.2) \times 10^{-13}.$$

Assuming that all the ^{233}U found in the ore was formed by reaction (6), it was established that in Congo pitchblende ^{237}Np is present in concentrations corresponding to a ratio of ^{237}Np to ^{238}U of $(1.8 \pm 0.4) \times 10^{-12}$. However, the possibility that reaction (8) has an appreciable influence is not excluded. In such a case, the actual concentration of ^{237}Np could differ from that quoted.

OCCURRENCE OF THE TRANSPLUTONIUM ELEMENTS IN NATURE

Other elements can be produced in the earth's crust in a similar manner to ^{239}Pu, ^{233}U, and ^{237}Np. The isotope ^{239}Pu can absorb further neutrons and be gradually converted to other transuranium elements:

$$^{239}Pu(n, \gamma)^{240}Pu(n, \gamma)^{241}Pu \xrightarrow{\beta^-} {}^{241}Am(n, \gamma)^{242}Am \xrightarrow{\beta^-} {}^{242}Cm.$$

Since the ^{239}Pu content of uranium and thorium minerals is very low and the neutron flux in these ores is too weak, i.e. it cannot be compared to that obtaining in a uranium reactor where these reactions take place easily, only theoretical data can at present be adduced concerning the presence of elements of atomic number greater than 94 as a result of (n, γ)-reactions.

It is possible that part of the ^{239}Pu is a decay product of a long-lived parent transplutonium element. Accurate data regarding this possibility are not available at present, but the energy of α-disintegration tends to increase as one passes to the heavier transuranium elements and the half-life is correspondingly reduced. Consequently, it does not seem possible that an isotope of plutonium or some other heavy element could exist in nature in a more or less stable state and hence there is little chance that ^{239}Pu could be formed as a decay product of a heavier, long-lived parent substance. Of the plutonium isotopes, ^{244}Pu is a possible exception. However, even its half-life is less by several powers of ten than the age of the earth. Of the other transplutonium elements, ^{247}Cm attracts attention. The isotope ^{247}Cm is β-stable and emits α-particles with a half-life greater than $(4-9) \times 10^7$ years[42]. From the laws governing spontaneous fission, it follows that the half-life for fission is greater than that of ^{255}Fm (6×10^8 years)[43]. The decay of ^{247}Cm proceeds as follows:

$$^{247}Cm \xrightarrow{\alpha} {}^{243}Pu \xrightarrow{\beta^-} {}^{243}Am \xrightarrow{\alpha} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu \xrightarrow{\alpha} {}^{235}U.$$

If one assumes that the formation of the material of the earth took place $(5-9) \times 10^9$ years ago, the quantity of ^{247}Cm formed in that time, together with the heavier isotopes of the $(4n+3)$ radioactive series which disintegrate to give ^{247}Cm, can be estimated from the measured variations in the proportions of daughter isotopes with even mass numbers, namely $^{235}U : {}^{238}U$, reflected in the inconstancy of the $^{235}U : {}^{238}U$ ratio.

Since curium resembles the rare earths in its chemical properties, ^{247}Cm should be sought in the rare-earth minerals. If it is assumed that ^{247}Cm does not disintegrate completely in a period of time greater than forty times the half-life, then in order that ^{247}Cm should be found, it must have a half-life of at least 1.3×10^8 years. This assumes the age of the earth to be 5×10^9 years; if it is 9×10^9 years, the half-life of ^{247}Cm must be 2.2×10^8 years. Assuming that the time elapsing between the formation of ^{247}Cm and the distribution of curium and uranium among the separate mineral phases was less than 7 half-lives, a measurable change in the ratio $^{235}U : {}^{238}U$ (not less than 2%) can be observed in rare-earth minerals, in which the ratio rare earths : $U \geq 1000$. In older minerals or minerals with a low uranium content, this enrichment by ^{235}U will be more pronounced.

It is interesting to note that isotopes such as ^{244}Pu and ^{247}Cm, together with their decay products, could have been important sources of radioactive heat in the first 500 million years after their formation[44,45]. It has been calculated that when one atom of ^{244}Pu disintegrates to ^{232}Th, 6.28×10^{-13} cal are liberated, and when ^{247}Cm disintegrates to ^{235}U, 6.23×10^{-13} cal are liberated (65% of the energy in a β-disintegration is lost in the form of neutrinos).

Except for the long-lived isotopes ^{244}Pu and ^{247}Cm, the isotopes of the transuranium elements found in nature are formed from uranium and thorium either by radioactive decay or by neutron irradiation. Naturally, the question arises whether at some time elements heavier than uranium existed in nature and have not survived to the present day only because of their short half-life. This question, which is closely related to the problem of the formation of the elements, has not yet been settled. The discovery of technetium in the spectra of certain stars and the sun supported the theory that the heavy elements are being formed continuously in the stars by nuclear processes, since the longest-lived isotope of this element, ^{99}Tc, has a half-life of only 2.4×10^5 years. It is supposed that the formation of heavy elements occurs in the explosion of supernovae. A great step forward in this field was made by the study of class I supernovae[46,47]. These stars are characterised by a high maximum in their luminosity: 50–100 days after the maximum, the relation between the logarithm of the luminosity and time become linear during the next 600 days; in other words, the "half-life" is 55 ± 1 days[48]. This naturally suggests the idea that the energy of these stars comes from the disintegration of some isotope having a half-life of about 55 days. Such isotopes could be ^{7}Be or ^{89}Sr, but since their energy of decay is small (57 and 600 keV respectively), the quantity of the isotopes required to provide the enormous amount of energy radiated by the star would be such that the amount of disintegration products would considerably exceed their proportion present in the Universe[49,50]. In 1952, during the explosion of a hydrogen bomb[51], the isotope ^{254}Cf was observed; this is formed from uranium under the influence of a powerful neutron flux. ^{254}Cf is a β-stable isotope whose half-life of spontaneous fission is 56.2 ± 0.7 days[52], 60 ± 10 days[33], or 85 ± 15 days[43], in good agreement with the observed astrophysical value of 55 ± 1 days. α-Activity has not been observed, but this is natural, since theoretical considerations show the half-life of this isotope to be about 10^2 years for α-emission[43]. In one fission, 200 MeV are liberated

so that 10^{47} ergs (the energy radiated by a star) correspond to the disintegration of 10^{29} g of ^{254}Cf; this is in agreement with the observed distribution of the fission products in the Universe.

It is important to elucidate how ^{254}Cf is produced. One can assume that the process takes place in the same way as in the artificial production of the isotope, i.e. by the absorption of neutrons produced by nuclear reactions at stellar temperatures. The isotope ^{56}Fe, which is present in sufficient quantity in stellar material and which has a high capture cross-section for neutrons, captures neutrons up to the saturation point, which lies below the threshold of neutron instability; this occurs at $N = 0.7A$, $Z = 0.3A$. The nucleus produced undergoes β-disintegration and again absorbs a neutron. Because of the supersaturation with neutrons, the times [half-times? (Ed. of Translation)] of the β-disintegrations do not exceed 0.1 sec, so that the formation of ^{254}Cf takes about 7 sec. The explosion of a star has a velocity of about 10^3 km sec^{-1}. Since the radius of the star is $10^{10}-10^{11}$ cm, there is an interval of 10–100 sec, which is quite sufficient for the synthesis of ^{254}Cf to occur. Other classes of stars do not possess the necessary conditions for ^{254}Cf to be formed in sufficient quantity to have a decisive influence on their behaviour.

Other heavy elements are also produced in the explosion of supernovae. But because of their nuclear properties they cannot play a similar part in the behaviour of the star after the explosion. A possible exception is the ^{250}Cm isotope which resembles ^{254}Cf in many respects[52]. One can expect that it also decays predominantly by spontaneous fission and not by α-disintegration.

The predicted half-life for the α-disintegration of ^{250}Cm is about 10^{15} years and that for spontaneous fission $(1-10)\times$ $\times 10^4$ years. The fission of ^{250}Cm could be an important source of energy in old "remains" of type I supernovae, such as the Crab nebula which is apparently the remains of the supernova of 1054. The Crab nebula radiates $5.7\times$ $\times 10^{42}$ ergs $year^{-1}$ or about 10^5 times less than at the initial instant. If the quantities of ^{254}Cf and ^{250}Cm formed in the explosion were equal, then the radiation produced at the present moment from the spontaneous fission of ^{250}Cm would be 10^{-5} of the initial energy of the ^{254}Cf and could be the source of all the energy radiated by the Crab nebula.

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