[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

Search for Elements 94 and 93 in Nature. Presence of 94^{239} in Carnotite[1]

BY C. S. GARNER,[2] N. A. BONNER[3] AND G. T. SEABORG

This report describes further attempts to find a long-lived isotope of the element 94 (as well as 93) in nature. The probable presence of 94^{239} in pitchblende concentrate (Great Bear Lakes region, Canada) has been reported.[4] However, the concentration of this isotope amounted to about only one part in 10^{14}, and it was established that there was not present as much as one part in 10^{9} of any other isotope of 94 or 93.

In the present work, samples of carnotite (a potassium–uranium vanadate), fergusonite (a rare earth–uranium columbate–tantalate) and hatchettolite (a uranium columbate–tantalate) were subjected to chemical treatment designed[5] to separate elements 94 and 93 from members of the uranium, thorium and actinium radioactive series which would interfere in the detection of α- and β-particle-radioactivity from the former. The final fraction from each ore in the form of a thin sample was tested for α- and β-radioactivity. These experiments indicate the probable presence of 94^{239} in carnotite. In case there might be present isotopes of 94 or 93 which were not α- or β-particle-active, tests for fissions with slow neutrons and with fast neutrons were made. Since it is likely that any isotope of 94 or 93 would either undergo fission with slow neutrons with a cross section of the order of that of U^{235} or with fast neutrons with a cross section of the order of that of U^{238}, the presence of an amount of 94 or 93 of the order of one microgram could be established by such neutron fission tests. In the present work no detectable amounts of 94 or 93 were found by these neutron tests.

Experimental

About 5 kg. of carnotite (Colorado region), two-thirds kilogram of hatchettolite (Arizona–New Mexico region) and one-half kilogram of fergusonite (Arizona–New Mexico region) were separately treated by a procedure similar to that used for the pitchblende concentrate.[4] Each ore was treated with hot aqua regia over a long period of time until there appeared to be no further action. The residue from each ore was fumed with concentrated sulfuric acid, then with nitric acid, the extract being removed from time to time. This process was repeated until the last extract gave no fluoride-insoluble material when made 3 N in hydrofluoric acid. After reduction with sulfur dioxide, each extract, as well as the original aqua regia leach, was diluted with water, then made 3 N in hydrofluoric acid to remove insoluble fluorides. The various fluoride precipitates from a given ore were combined and dissolved in fuming sulfuric acid, followed by dilution with water and treatment with dilute nitric acid. The residues were treated as before[4] (and residues from subsequent steps in the procedure were similarly treated). The solutions were warmed and potassium peroxydisulfate and silver nitrate added to oxidize any 94 or 93 present, then the acidity adjusted to from 1 to 6 N in nitric acid and hydrofluoric acid added to again precipitate the rare earth and thorium fluorides, the 94 and 93 remaining in solution in this step. After removal of the fluoride precipitates by centrifugation, each solution was fumed with sulfuric acid to remove the hydrofluoric acid and decompose the peroxydisulfate, then with sulfur dioxide to reduce the 94 and 93 to their lower (fluoride-insoluble) oxidation states. Lanthanum and cerous nitrates were added as carriers and the fluorides precipitated by the addition of hydrofluoric acid.

Each fluoride precipitate was then dissolved by fuming with sulfuric acid and taken through five more similar cycles, in a manner like that described in the pitchblende report.[4] After removal of a fluoride precipitate ("test precipitate") from each oxidized solution in the last cycle, the hydrofluoric acid was removed by fuming and after reduction and dilution, 0.2 mg. of rare earth (La^{+++} + Ce^{+++}) carrier was added and precipitated as fluoride onto a platinum disc ("final precipitate"). The "test precipitates" were made in order to demonstrate that there was a negligible amount of isotopes of thorium (UX_1, Io) present in the solutions at this stage. The "final precipitates" would contain any 94 or 93 present in the original ores which had survived the lengthy chemical treatment. (Calibration experiments using 50-year[6] 94 as a tracer showed that the yield of 94 in the above procedure subsequent to the first oxidation and reduction cycle would probably be at least 60%.) The rare earth carrier material was shown to be free of α-particle contamination.

Results

No beta-activity above the background of the Geiger-Müller counter could be detected in the "final precipitates" and "test precipitates" from the three ores. Using a battery-operated ionization chamber and linear amplifier (calibrated counting efficiency about 45%), and counting for thirty minutes per sample, the following alpha-activity was found:

Ore	Final precipitate, counts/hr.	Test precipitate, counts/hr.
Carnotite ($\sim$5 kg.)	167	44
Fergusonite (0.5 kg.)	8	20
Hatchettolite ($\sim$0.7 kg.)	24	44

The above figures are corrected for the α-particle background count of the ionization chamber and for the activity of the platinum discs used, in all cases the total correction amounting to 6 counts/hr. or less.

The tests for fissions with neutrons were made by placing the final samples successively on one

---

[1] This article was issued as a secret report in connection with the Plutonium Project in August, 1942. The experimental work was done at the University of California during 1942. The report is unchanged from its original form except for slight editing to make it conform to Journal standards.

[2] Now at the Department of Chemistry, University of California at Los Angeles, Los Angeles, California.

[3] Now at the Department of Chemistry, Washington University, St. Louis, Missouri.

[4] G. T. Seaborg and M. L. Perlman, THIS JOURNAL, **70**, 1571 (1948).

[5] G. T. Seaborg and A. C. Wahl, *ibid.*, **70**, 1128 (1948).

[6] G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. C. Wahl, *Phys. Rev.*, **69**, 366 (1946) (submitted January 28, 1941); G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *ibid.*, **69**, 367 (1946) (submitted March 7, 1941).

electrode of an ionization chamber connected to a linear amplifier and recording system adjusted to record the impulses due to fissions. With neutrons (slow and fast) from a one-gram radium–beryllium source in the presence of a suitable amount of paraffin, the final samples gave the following results:

Carnotite	1 fission in 20 hours
Fergusonite	0 fission in 3 hours
Hatchettolite	0 fission in 8 hours

When the samples were replaced by a "standard" 200-microgram uranium sample, the fission-counting rate amounted to 70 per hour without a cadmium shield and 18 per hour with a cadmium shield. The fission-counting rate due to the 1.4 microgram of U^{235} present in the "standard" uranium sample was therefore 52 per hour. Assuming that the slow neutron fission cross section of any 94 or 93 would be of the same order of magnitude as that of U^{235}, it can be concluded that there was present in any of the final samples no more than a small fraction of a microgram of any isotope of 94 and 93 capable of undergoing fission with *slow* neutrons. Any isotopes which might be present and which did not undergo fission with slow neutrons would probably undergo fission with fast neutrons with a cross section of the same order as that of U^{238}. We can, therefore, place an upper limit of the order of a microgram on the amount of any isotope of 94 or 93 which was present and capable of undergoing fission with *fast* neutrons, and so we can say that there was not present an amount of 94 or 93 as much as one part in 10^{10} in the carnotite and one part in 10^9 in the fergusonite or hatchettolite.

The definite α-counting rate of the carnotite sample may well be due to 94^{239} [7] formed in the following decay chain as the result of absorption of uranium spontaneous fission neutrons by U^{238}

$$U^{239} \xrightarrow[23\text{ m.}]{\beta^-} 93^{239} \xrightarrow[2.3\text{ d.}]{\beta^-} 94^{239}$$

The rate of 167 alphas per hour would correspond to about 3×10^{-6} microcurie of 94^{239} or about 6×10^{-5} microgram of 30,000-year 94^{239} (about one part in 10^{14} of carnotite). This amounts to only a fraction of a per cent. of the amount to be expected if a large proportion of the uranium spontaneous fission neutrons were absorbed by the U^{238}, but this is not surprising in view of the other neutron-absorbing materials which might be present in the carnotite and in view of the fact that the carnotite deposit may have been a small one so that no large fraction of the neutrons was absorbed. The presence of 94^{239} in carnotite (and pitchblende) and probably in any large concentrated deposits of uranium implies, of course, the existence of the equilibrium amount of 23-minute U^{239} and 2.3-day 93^{239}.

It is of interest to point out that in uranium ores which contain an appreciable amount of thorium, there should be present some long-lived U^{233} formed[8] according to the following decay chain as the result of the absorption of uranium spontaneous fission neutrons by thorium^{232}

$$Th^{233} \xrightarrow[23.5\text{ m.}]{\beta^-} Pa^{233} \xrightarrow[27.4\text{ d.}]{\beta^-} U^{233}$$

Uranium deposits containing of the order of a few per cent. of thorium might well contain of the order of one part in 10^{15} of U^{233}. Thus, in a sense, U^{233} might be listed as one of the uranium isotopes present in nature. U^{233} would be a member of the hitherto "missing" $4n + 1$ radioactive series.

We are grateful for the help of J. W. Gofman and R. B. Duffield, who performed the neutron test experiments for us.

This paper is based on work performed under Contract Number W-7405-eng-48 with the Manhattan District in connection with the Radiation Laboratory of the University of California.

Summary

Samples of carnotite, fergusonite and hatchettolite were subjected to chemical treatment designed to isolate elements 94 and 93. No evidence for the presence of appreciable amounts of 94 or 93 was found, and the tests with slow neutrons and with fast neutrons established the upper limits of the concentrations of these elements as one part in 10^{10} of carnotite, one part in 10^9 of fergusonite and one part in 10^9 of hatchettolite. A small alpha-particle counting rate in the final fraction from the carnotite indicates the presence of 94^{239} in the carnotite at a concentration of about one part in 10^{14}. The probable presence of 94^{239} in pitchblende had previously been established, and the 94^{239} in both carnotite and pitchblende is probably formed as a result of the absorption by U^{238} of some of the neutrons emitted in the uranium spontaneous fission process.

BERKELEY, CALIFORNIA RECEIVED FEBRUARY 18, 1948

---

[7] J. W. Kennedy, G. T. Seaborg, E. Segrè and A. C. Wahl, *Phys. Rev.*, **70**, 555 (1946) (Submitted May 29, 1941).

[8] G. T. Seaborg, J. W. Gofman and R. W. Stoughton, *Phys. Rev.*, **71**, 378 (1947) (submitted as a secret report April 14, 1942).