Neutron and Spontaneous Fission in Uranium Ores

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The fission yields of the stable isotopes of xenon and krypton in natural fission have been determined for six samples of pitchblende and one sample of uraninite. The fission yields observed varied markedly from sample to sample. The nature of these variations and particularly the changes that occur in the "fine structure" of the mass yield curves at Xe^{132} and Xe^{134} indicate that both spontaneous fission of U^{238} and neutron fission of U^{235} occur in uranium minerals, the proportion of each depending on the uranium concentration, geological age, and the impurities in the mineral. This conclusion is consistent with estimates of the neutron flux in these ores based on the abundance of Pu^{239} in pitchblende.

INTRODUCTION

THE spontaneous fission of uranium was first reported in 1940[1,2] and a number of attempts were made to measure the fission half-life. More recently, Segrè[3] has reported on the spontaneous fission half-life of the individual isotopes of uranium and other heavy elements. The values given for U^{238} and U^{235} are, respectively, $8.04\pm0.3\times10^{15}$ and $1.87\pm0.6\times10^{17}$ years. In 1950 Macnamara and Thode identified fission products in gases extracted from uranium minerals. Their results showed the existence of five fission product isotopes of Xe and three of Kr, the distribution of which indicated an asymmetric mass fission yield curve similar to that obtained in the thermal neutron fission of U^{235}.[4] However, the curves were steeper, indicating a more selective process, and the ratio of Xe to Kr was larger. Both these facts suggested that some spontaneous fission of U^{238} was involved. Also the amount of fission product Kr and Xe obtained per gram of uranium in the mineral was of the order of magnitude expected, considering the spontaneous fission half-life and the age of the mineral.

Finally, some "fine structure" in the mass yield curve was evident from the high yield of Xe^{132}. Previous mass spectrometer studies of fission gas from $U^{235}+n$ fission had shown abnormally high yields at Xe^{133} and Xe^{134}.[5-7] This shifting of the fine structure to the lower masses again pointed to the spontaneous fission of U^{238} as the source of fission products in uranium minerals, since the Glendenin mechanism[8] put forth to explain these abnormal yields would qualitatively account for such a shift. Experimental evidence today[7,9] indicates that abnormal yields or fine structure in the mass yield curve are due to two closed shell effects; first, the structural preference in the initial fission process; second, the preferential liberation of fission neutrons from nuclides having 1 or 3 neutrons more than a closed shell. The latter explanation of fine structure, first suggested by Glendenin, would predict a shifting of fine structure to the lower masses by 1–2 mass units as we go from U^{235} to U^{238} fission.

Several years ago it was found in our laboratory[10] that the fission pattern of isotopes for Xe and Kr varied to some extent between gases extracted from Great Bear (Canada) and Belgian Congo pitchblendes. Both patterns showed the same characteristics, but the fission gases from the richer and younger Belgian Congo ore gave a pattern of isotopes closer to that obtained for $U^{235}+n$ fission; suggesting that both $U^{235}+n$ and spontaneous fission of U^{238} might be involved. Since that time, we have investigated a number of uranium ores to determine the nature and extent of natural fission. The results indicate that both neutron fission of U^{235} and spontaneous fission of U^{238} are involved, the extent of each depending on the concentration of uranium, the age of the mineral and the nature of the impurities. The results are given in this paper.

EXPERIMENTAL

The apparatus used in this laboratory for the extraction of Xe and Kr from neutron irradiated uranium metal has been described elsewhere.[11] The same apparatus, with minor modifications, was used for the extraction and purification of the rare gases from uranium minerals. A trap containing ascarite was inserted in the chemical drying train to remove the large quantities of CO_2 produced from carbonates in some of the minerals. A simple calcium furnace was installed after the drying train to carry out the initial rough purification of the released gases, which contained large quantities of nitrogen and oxygen. The final purification and volume measurement was identical to that described previously.[11]

* Holder of a Research Council of Ontario Scholarship 1951–1952.
[1] G. N. Flerov and K. A. Petrzhak, J. Exptl. Theor. Phys. U. S. S. R. **3**, 275 (1940).
[2] G. N. Flerov and K. A. Petrzhak, Phys. Rev. **58**, 89 (1940).
[3] E. Segrè, Los Alamos Scientific Laboratory Report, LADC-975, 1945 (unpublished).
[4] J. Macnamara and H. G. Thode, Phys. Rev. **80**, 471 (1950).
[5] H. G. Thode and R. L. Graham, Can. J. Research **A25**, 1 (1947).
[6] Macnamara, Collins, and Thode, Phys. Rev. **78**, 129 (1950).
[7] Wiles, Smith, Horsley, and Thode, Can. J. Phys. **31**, 418 (1953).
[8] L. E. Glendenin, Phys. Rev. **75**, 337 (1949).
[9] Dr. R. Wiles, M.Sc. thesis, McMaster University, Hamilton, Ontario, August, 1950 (unpublished).
[10] H. G. Thode, Trans. Roy. Soc. (Canada) **45**, 1 (1951).
[11] Arrol, Chackett, and Epstein, Can. J. Research **B27**, 757 (1949).

In the preliminary work, the mineral, in the form of a fine powder, was dissolved in concentrated sulfuric acid for $1\frac{1}{2}$ to 2 hours. This procedure produced satisfactory samples, but it was later found that the sulfuric acid contained large quantities of dissolved argon accompanied by traces of normal Xe and Kr. For this reason the later samples were prepared by heating the powdered mineral in an Inconel combustion tube to 1000–1200°C at which temperatures the pitchblende began to sinter. The rare gas samples obtained in this way contained a much smaller amount of normal Xe and Kr and the final samples removed at the highest temperatures contained almost pure fission product Xe and Kr. These samples made possible a more accurate determination of the fission yields and also permitted a study of the argon isotope abundances in the minerals. The final volume of the purified rare gas samples obtained from 200 gram samples of ore varied from 10 to 30 cubic millimeters. Mass spectrometer analysis showed the approximate composition to be 99.5 percent A, 0.25 percent Kr and 0.25 percent Xe.

All rare gas samples were analyzed on a conventional 180° direction focusing Nier-type mass spectrometer. The ion currents were amplified by an Applied Physics Corporation vibrating reed electrometer. The mass spectrometer had previously been calibrated with standard mixtures of xenon and krypton so that it was possible to determine the ratio of xenon to krypton from the mass spectrometer results. This permitted normalizing both the xenon and krypton fission yield data to an arbitrary value assumed for one of the xenon isotopes. The results of the earlier argon isotope studies have already been published.[12]

RESULTS

Figure 1 shows a typical mass spectrogram of the Xe isotopes in uraninite all recorded at one sensitivity. As noted previously,[4] stable Xe^{129} is present and 10-year Kr^{85} is absent in these naturally occurring fission product samples because of their great age. The particular sample for which the mass spectrogram in Fig. 1 was obtained was remarkably free from normal Xe gas as indicated by the absence of Xe^{130}. Other samples were found to contain a small percentage of normal Xe for which corrections had to be made to obtain the true fission isotope pattern. This correction was less than 20 percent in one case and less than 10 percent in all others. Also the argon present in the uraninite sample was almost free of A^{36}; the A^{38} to A^{36} ratio being 10 to 1 rather than 1 to 5 as in natural argon. This result confirms strikingly the earlier results of Fleming and Thode, which showed that A^{38} is formed in uranium minerals by nuclear processes.

The relative yields of the fission isotopes of Xe obtained for Xe gas extracted from 6 different samples of pitchblende and 1 sample of uraninite are given in Table I. In each case Xe^{136} was arbitrarily assigned a

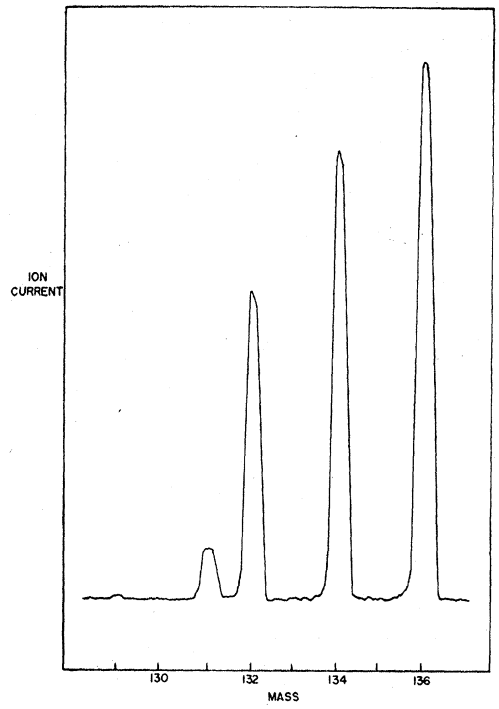

FIG. 1. Mass spectrogram of xenon from uraninite, Cardiff Township, Ontario.

value of 6.5 percent to coincide approximately with the smooth yield curve at this mass in the neutron fission of U^{235}.[13] Table I also gives the average uranium concentration and the geological age of each sample. The later value was determined by the lead isotope method.[14] It can be seen that the relative yields of the Xe isotopes vary markedly from sample to sample. Table II gives the relative fission yields of the Kr isotopes in gases extracted from two different uranium ores. Here again the values are normalized at 6.5 percent for Xe^{136}, the ratio of Xe to Kr having been determined. Although the errors involved in the Kr yield measurements are larger than for the xenon yields, because the absolute yields are lower, and because the contamination with normal Kr gas is greater (larger corrections necessary), the results nevertheless show significant differences between the two samples investigated.

These different patterns of isotopes found for the fission gas samples extracted from different uranium minerals cannot be due to isotope fractionation in sample preparation or to isotope fractionation due to different rates of diffusion of the isotopes from the minerals over the millions of years. (From He age studies it has been found that the loss of He from minerals is not great. The losses of Xe and Kr by

[12] W. H. Fleming and H. G. Thode, Phys. Rev. **90**, 857 (1953).

[13] The yield of 6.5 percent for Xe^{136} is based on a value of 3.0 percent for the yield of I^{131}. Recently this yield has been revised upward to 3.2 percent [Bartholomew, Brown, Hawkings, Merrit, Thode, and Yaffe, paper given at Annual Conference Chemical Institute of Canada, June 4–6, 1953 (unpublished)].

[14] A. O. Nier, Phys. Rev. **55**, 153 (1939).

TABLE I. Xenon fission yields.

Sample	% U_3O_8	Age (million years)	Fission yields (%) 129	131	132	134	136
Pitchblende, Katanga, Belgian Congo	65.21	640	0.217±0.036	1.27 ±0.04	3.91±0.06	6.03±0.03	6.50[a]
Pitchblende, Eagle Mine, Beaverlodge	45.5	1630	0.223±0.037	1.16 ±0.04	3.91±0.06	5.93±0.03	6.50
Pitchblende, Ace Mine, Beaverlodge	16.95	1600	0.226±0.035	1.07 ±0.04	3.89±0.07	5.79±0.06	6.50
Pitchblende, Lake Athabaska	13.99	1690	0.093±0.042	0.799±0.040	3.79±0.07	5.58±0.04	6.50
Pitchblende, Nesbitt Labine, Beaverlodge	27.55	···	0.107±0.060	0.830±0.059	3.80±0.06	5.56±0.05	6.50
Pitchblende, Great Bear Lake	36.46[b]	1370	0.103±0.062	0.798±0.054	3.73±0.08	5.54±0.6	6.50
Uraninite, Cardiff Township, Ontario	approx. 60% uranium	···	0.029±0.002	0.613±0.010	3.74±0.03	5.41±0.03	6.50
$U^{235}+n$	···	···	···	3.28	4.92	8.64	7.10

[a] Yield of 136 mass chain arbitrarily chosen to be 6.50 percent. Errors shown are "standard deviations."
[b] A mill concentrate, original concentration unknown.

diffusion should be very much smaller.) Several gas samples were prepared from each mineral studied and, where the gases were obtained by the heating of the powdered mineral, samples were taken off at different temperatures. In all cases the agreement between samples was within experimental error. Further, the difference found for each isotope are not proportional to the percentage mass differences and in the case of Xe^{132} the yields differ in quite a different way from that expected if diffusion processes were involved in the fractionation of the isotopes. Also, the mass yield curves for the different samples (see Fig. 3) are not displaced according to the age of the mineral involved. Finally, any fractionation of isotopes by a diffusion process which resulted in the depletion of the light isotopes of Xe to the extent found between samples would be accompanied by an almost complete loss of Kr which was not observed. It is apparent, therefore, that the differences in the yield patterns found between samples are due to the nature of the fission processes involved in uranium minerals.

Figure 2 shows a comparison of the mass fission yield curves (masses 129–136) for $U^{235}+n$ fission and for natural fission in Great Bear pitchblende. Figures 3 and 4 show how these mass yield curves vary from one uranium mineral sample to another in the Xe and Kr isotope ranges, respectively. Two points stand out. First the mass yield curves for natural fission are steeper, and second the "fine structure" characteristics are different. In the case of $U^{235}+n$ fission, Xe^{133} and Xe^{134} have abnormally high yields, whereas in natural fission the yield of Xe^{132} is abnormally high and the yield of Xe^{134} is markedly down. These considerations, together with the higher Xe to Kr ratio found for natural fission, led previously to the conclusion that spontaneous fission of U^{238} was involved in natural fission.

In recent investigations of fast neutron fission of U^{238},[15] it has been found that the slope of the fission yield curve in the Xe and Kr mass ranges for neutron fission of U^{238} is almost identical with that for neutron fission of U^{235}. Neutron fission of U^{238} cannot, therefore, account for the steepness of the fission yield curve observed in this mass range for natural fission. The fission cross section of U^{238} is so low that little neutron fission of U^{238} would be expected. This confirms the earlier conclusion that the main source of fission products in uranium ores is from the spontaneous fission of U^{238}.

However, a close study of the present results indicate that there is an appreciable amount of $U^{235}+n$ fission involved as well. The uranium mineral fission gas samples are listed in Table III in order of increasing steepness of the mass fission yield curves plotted in Fig. 3. Columns 2 and 3 give the "fine structure" effects for masses 132 and 134, respectively, in terms of the percentage that their yields are above a smooth curve drawn through the other yield points (masses 129, 131, 136). Column 4 gives the ratio of Xe to Kr in the fission gas samples. The results obtained for thermal neutron fission of U^{235} and for fast neutron fission of ordinary uranium are included for comparison. The latter results were obtained by irradiating ordinary uranium with fast neutrons, the energy distribution being such that an appreciable amount of $U^{238}+n$

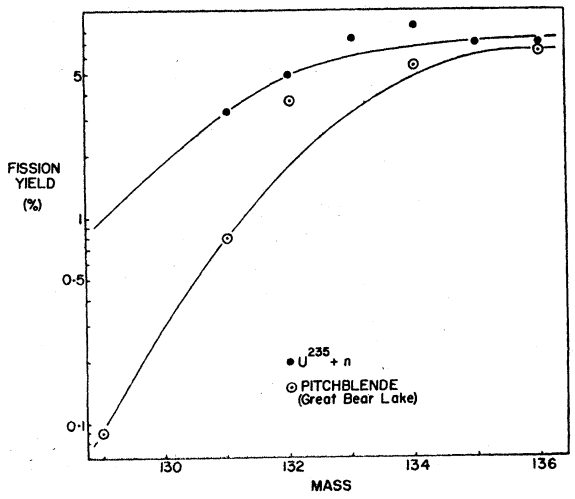

FIG. 2. Mass yield curves for natural fission and neutron induced fission of U^{235}.

[15] R. K. Wanless, Ph.D. thesis, McMaster University, October, 1953 (unpublished).

fission could be expected. It is clear from the results plotted in Fig. 5 and given in Table III that the effect of this contribution of $U^{238}+n$ fission is to increase the Xe to Kr ratio because of a shift in the whole mass yield curve toward the heavier masses and to decrease the yield of Xe^{134} and increase the yield of Xe^{132}. The fission yield results obtained for gases extracted from uranium minerals differ from those for $U^{235}+n$ fission in precisely the same way except that the curves are steeper, possibly due to the fact that spontaneous fission of U^{238} is involved rather than $U^{238}+n$ fission. It was pointed out previously[4] that since in spontaneous fission there is less energy available the process might be more selective and that a sharper grouping of the light and heavy fission fragments might be expected.

It can be seen from Table III and Fig. 3 that as the fine structure at masses 132 and 134 decreases and increases, respectively, the general shape of this mass yield curve approaches more closely to that of $U^{235}+n$ fission, indicating an increased contribution of $U^{235}+n$ fission in the samples. The remarkable relationship between the fine structure effects, steepness of the mass yield curves, and the ratio of Xe to Kr for the different

TABLE II. Krypton fission yields.

Sample	Fission yield (%) 83	84	86
$U^{235}+n$	0.67	1.27	2.45
Natural uranium, fast neutrons ($U^{235}+n$ and $U^{238}+n$)	0.47	0.98	1.63
Pitchblende, Belgian Congo	0.30±0.06	0.50±0.13	1.62±0.12
Pitchblende, Great Bear Lake	0.073±0.022	0.34±0.06	1.19±0.05

samples all confirm our conclusion that both spontaneous fission of U^{238} and neutron fission of U^{235} take place in uranium minerals, the proportion of each depending on the uranium content, the age of the

TABLE III. Fine structure variations.

Sample	% above smooth curve Mass 132	Mass 134	Xe/Kr
$U^{235}+n$ fission	0	24.5	5.05
Natural uranium irradiated with fast neutrons, average energy 0.5 Mev ($U^{235}+n$ and $U^{238}+n$)	6	17.9	6.7
Pitchblende, Belgian Congo	40	9.6	7.4
Pitchblende, Eagle Mine	40	7.8	···
Pitchblende, Ace Mine	47	6.1	···
Pitchblende, Lake Athabaska	75	3.1	···
Pitchblende, Nesbitt Labine	75	1.8	···
Pitchblende, Great Bear Lake	72	1.4	10.3
Uraninite, Cardiff Township	93	0.7	···

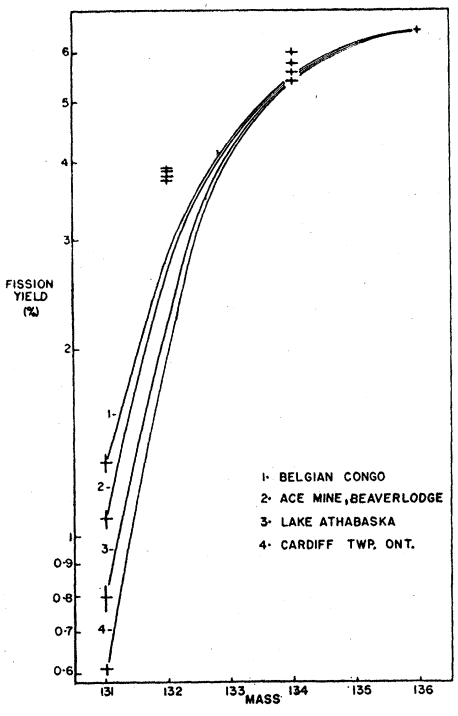

FIG. 3. Xenon fission yield variations in natural fission.

mineral, and the mineral impurities. Although there is little evidence of any fine structure in the Kr isotope mass range, the fission yield results for the Kr isotopes nevertheless support this conclusion.

The largest contribution of $U^{235}+n$ fission would be expected in very old ores, because of the higher U^{235}/U^{238} ratio when the ore was just deposited and in ores with high uranium concentrations. It is evident from Table I

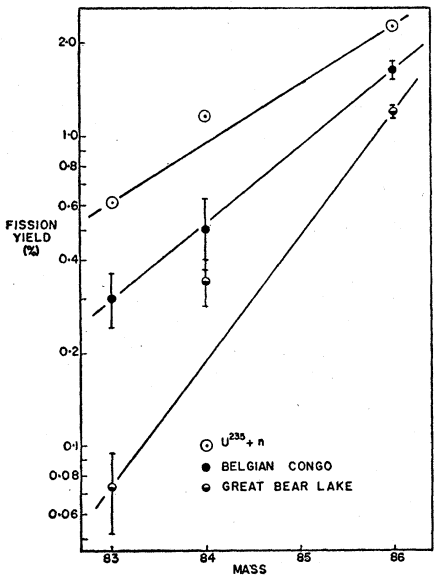

FIG. 4. Krypton fission yield variations in natural and neutron induced fission.

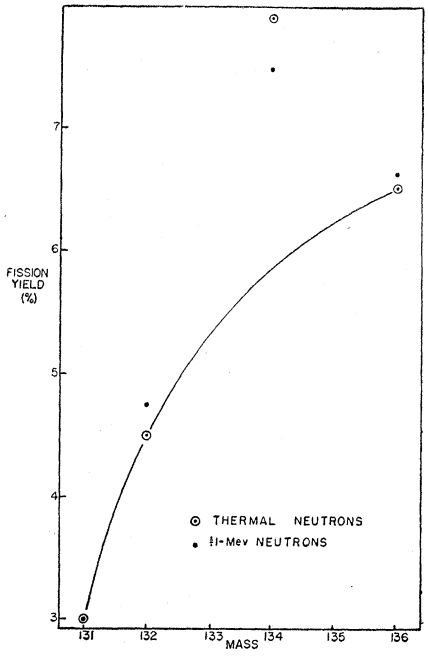

FIG. 5. Variation of neutron induced fission yields with neutron energy.

that in general the xenon fission yields most closely resembling those for $U^{235}+n$ fission are associated either with very high uranium content (Belgian Congo) or with a combination of high uranium content and old geological age (Eagle Mine). The uraninite sample appears to be an exception since it has a very high uranium content, but gives the lowest yields found. However, this sample contains the rare earth elements to the extent of several percent and the large neutron capture cross sections of some of these elements could account for the small amount of neutron fission observed. The fission gas from the Ace mine samples of pitchblende shows a higher proportion of $U^{235}+n$ fission in the ore in comparison to the others, considering its age and concentration. It is just possible that (α, n) reactions may be more important in this ore.

The fission isotope pattern for the uraninite mineral from Cardiff Township may represent that for spontaneous fission of U^{238}, although the results do not preclude some small amount of $U^{235}+n$ fission involved as well. An upper limit to the possible contribution of $U^{235}+n$ fission (and/or $U^{238}+n$ fission) can be set at 5 percent for this sample, since the yield of the 129 mass chain in $U^{235}+n$ (or $U^{238}+n$) fission is approximately 1 percent and the observed yield in this sample is certainly less than 0.05 percent allowing for a possible error in the value assumed for Xe^{136}.

DISCUSSION

The conclusion that both $U^{235}+n$ and spontaneous fission occur in nature in varying proportions seems a reasonable one in view of other considerations. First of all, the spontaneous fission rates of U^{235} and U^{238} as reported by Segrè show that only the spontaneous fission of U^{238} can be a factor. It is interesting to point out that the amounts of fission gas extracted from uranium ores per gram of uranium are of the order of magnitude expected considering the spontaneous fission half-life of U^{238} and the age of the samples. In this connection more quantitative measurements are now being made.

In regard to $U^{235}+n$ fission, Seaborg[16] has found appreciable quantities of Pu^{239} in uranium minerals which must have been formed by (n, γ) reactions of U^{238}. He calculates that the spontaneous fission neutrons would be sufficient to maintain the concentration of plutonium actually found. By the same reasoning, Seaborg[17] suggests that the neutron fission rate of U^{235} in these ores could be comparable to the spontaneous fission of U^{238}. Another source of neutrons for such reactions would be (α, n) reactions involving the light elements present in the minerals. The argon isotope studies reported previously[12] indicate that (α, n) and (α, p) reactions occur to an appreciable extent in uranium ores.

Studies of neutron and spontaneous fission in uranium and thorium minerals are being continued. A quantitative measure of the amount of fission gas present in ores per gram of uranium and a knowledge of the proportion of spontaneous fission that has occurred should make age calculations possible.

ACKNOWLEDGMENTS

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[16] G. T. Seaborg, Chem. Eng. News **23**, 2190 (1945).
[17] G. T. Seaborg (private communication).