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ON THE EXISTENCE OF NATURAL SPONTANEOUSLY-FISSIONING SUPERHEAVY ELEMENTS*

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ABSTRACT

Unusual spontaneously-fissioning activities were observed with the aid of the mylar foil technique in technical grade HfO_2. Volatile deposits were isolated from HfO_2 after thermochromatographic separation of $HfCl_4$ in a stream of chlorinating gas. Fission tracks were measured over a period of four years through eleven exposures of 13 μm thick mylar foils on separated fractions. The fractions taken at 525, 650 and 680°C show some unknown spontaneously-fissioning radioactivity.

Similarly, a spontaneously-fissioning activity was separated on anionite in 9M to 8M HCl fractions from an enriched hafnium oxychloride solution.

The 680°C fraction showed fission fragment tracks in the first and all subsequent exposures. The tracks in the 525°C and 650°C fractions did not begin to appear until approximately 500 days after separation; they are growing at this time in these fractions.

A majority of the tracks in the 525, 650 and 680°C fractions are unusually "fat" in comparison with neighboring ^{238}U-tracks exposed simultaneously on mylar (two to three times thicker) and some have long range. The observed "fat" tracks are best explained as evidence of fission fragments from a natural, superheavy element.

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1. INTRODUCTION

During the last ten years many theoretical predictions were made about islands of stability of superheavy elements, first for Z=126 closed shell [1] and later for Z=114 [2-7], Z=120 [8] and Z=164 [9-12] closed shells.

Some of these predictions suggest the existence of natural, superheavy elements close to the doubly-magic nucleus^{298} (114) with half-lives long enough so they could be found in nature [13].

The extensive effort searching for high neutron multiplicities in natural materials [14] has not confirmed the existence of natural superheavy elements. Other attempts to find spontaneously-fissioning superheavy elements in nature have not been conclusive yet [15, 16].

However, there are some indications that such elements could exist in nature. "Piles of tracks" (3 to 6 tracks originating from one point) were found on mylar foils after a 20-month exposure to large sources (1000 cm^2) of Bi_2O_4 and Au [17]. The local density of these tracks was up to one hundred times greater than that which could originate from a grain of pure uranium. More conclusive indications on the possible existence of natural superheavy elements were presented [18]. A growing or decaying fission was observed in the fractions from direct thermochromatographic chlorination of 1.4 g HfO_2 as well as in the fractions from separation of 50 g of the same HfO_2. The latter was first chlorinated to $HfCl_4$. Thereafter most of the Hf was precipitated as hafnium oxychloride and separated by filtration.

This paper contains the extended results from [18] for the separation of 50 g HfO_2 only, after an additional 2.5 years of measurement. The results for the 1.4 g direct separation of HfO_2, also published in [18], are not presented in this paper. The reason is that they are not comparable with the results from

the 50 g HfO_2 dry-wet chemistry. The fractions from the 1.4 g separation were twice strongly irradiated with electrons. This may have caused the decaying fission activity with $T_{\frac{1}{2}} \sim 300$ days in the fraction of U^{IV} (Fig. 3 of [18]) and also the growth of the fission activity in the 575°C fraction (Fig. 4 of [18]). At this time it is also not excluded that the effect in Fig. 4 of [18] was due to Cf-contamination added during the second electron irradiation cycle (after the first 478 days of measurement). Such added contamination could also produce the effect of coupled fission tracks in Fig. 8 of [18].

The 50 g dry-wet chemistry was done without any irradiation and with strict care to avoid any contamination during the measurements.

The results of [18] were not confirmed with other HfO_2 samples [19]. However, the latter results can not be compared with the results of [18] because the starting samples of HfO_2 and the chemistry used in their preparation and purification were different. Only identical starting samples and identical chemistry are comparable. Additionally, the principal detection technique (neutron multiplicity counting) was different than in this investigation (direct observation).

2. EXPERIMENTAL METHODS

2.1 The Mylar Foil Technique

For observing spontaneous fission in HfO_2 and its chemical fractions, the mylar foil technique was used as follows: a 400×600 mm mylar foil, folded into two 400×300 mm pages, was used throughout the investigation. The foil was lying in air in close contact with several measured fractions. Exposure for the duration of the measurement was to mylar page No. 1.

The thickness of the mylar foil was chosen to be 13 μm because two pages of mylar (26 μm) are thicker than the range of ^{252}Cf fission fragments with an energy of 110 MeV. Thus, no one fragment of ^{252}Cf penetrates both pages No. 1 and No. 2 of the mylar foil. The mylar page No. 2 generally served as a detector for background fission tracks or tracks with an energy greater than that from ^{252}Cf fission fragments.

Each separated fraction was exposed either 9 or 11 times to the mylar foil (usually 100 to 300 days in each exposure). This allows measurement of the time distribution of fission fragments from each fraction.

After each single exposure the mylar foil was homogeneously developed in a solution of 6M NaOH (90 to 105 min at 60°C using a constant-temperature bath). Then the foils were washed 8 to 10 times in non-distilled water and dried with filtration paper. Next a sheet of ozalid paper was placed under the dry mylar foil and both sheets mounted on a plexiglass plate. The edges were sealed and held down with black electrical insulation tape. The assembly was then placed in an 80°C oven containing NH_3 vapor for a period of approximately 30 minutes (second development). The first development in 6M NaOH produces tracks on mylar page No. 1 in places where fission fragments passed the foil. Each track is a small hole of approximately circular cross section (~ 2 to 4 μm diameter).

Each hole allows a small stream of NH_3 vapor to penetrate the mylar foil and stain the ozalid paper (during the second development). A fission fragment penetrating the mylar foil is revealed as a small blue dot on the ozalid paper and marked with a circle on the mylar foil.

Naturally, all other holes in the mylar foil including mechanical cracks and related defects also form a blue dot or circle on the ozalid paper. However, all "crack holes" can be reliably distinguished from fission tracks by additional microscopic scanning of the corresponding hole in the mylar foil. The regular fission tracks, when developed briefly in NaOH, form either thin black cylinders or two black cones with a narrow neck in the middle of the foil (due to incomplete dissolution of mylar in the central part of the foil).

Strongly developed fission tracks are visible under the microscope with 200 X magnification as regular cylindrical holes with sharp "spiral-bored" walls.

The areas marked on the mylar foil above the blue dots were microscopically scanned on both pages and dots from irregular holes or cracks were eliminated. Only dots corresponding to regular fission tracks were counted as tracks (hole produced by track).

For each mylar foil the detection efficiency E_T was tested by a standard ^{252}Cf calibration source (page No. 2 of the mylar foil was exposed to the known fission fragments in four places just before development in 6M NaOH). The efficiency is defined as $E_T = \frac{\text{No. of tracks detected}}{\text{No. of tracks generated}}$; it was determined separately for each foil and was found to be in the range of 0.15 to 0.35. The reason for a detection efficiency < 1.0 is because the mylar foil thickness is ~60% of the fission fragment range; only fragments with incidence angles in excess of $\sim 40^{\circ}$ can penetrate completely and be detected. Thus the number of fissions present

or generated, N_F, can be calculated knowing E_T and the number of tracks detected, N_T, as $N_F = N_T/E_T$.

2.2 Radioactivity Measurements and Statistical Considerations

All separated fractions were measured with a standard alpha-pulse-height analyzer (using an alpha-chamber with a grid and a 4000 channel analyzer) for the presence of natural uranium or thorium.

To calculate the number of fissions caused by ^{238}U in some fractions containing natural uranium, the following ratio was thoroughly measured:

U_F/U_α = spontaneous fission rate of ^{238}U/decay rate of ($^{238}U + ^{234}U$) using the same alpha-pulse-height analyzer. There were 163 cases of ^{238}U spontaneous fissions (SF) detected and 250.42×10^6 alpha-pulses ($^{238}U + ^{234}U$), which result in the ratio:

U_F/U_α = 1 SF : 1.535×10^6 alpha-pulses from ($^{238}U + ^{234}U$) .

This ratio was obtained with a 52% geometry for alpha-measurements and corresponds to 6.65×10^{15} years for the spontaneous fission half-life of ^{238}U. (The best value in the literature [20] is 6.5×10^{15} years.)

Using the ratio $U_F/U_\alpha = 1/1.535 \times 10^6$ the number of fissions caused by the presence of uranium in each of the chemical fractions was calculated.

The thorium (^{232}Th) fission rate at Orsay (~ 100 m above sea level) was found to be about 1/600 of the ^{238}U fission rate. A maximum of 0.3 mg ^{232}Th was found in some fractions resulting in ~0.2 fissions in 1000 days; this was negligible in all the cases investigated.

The error bars used in the following graphs contain the same percentage error as the square root of the really observed events; they are proportional to $\sqrt{N_T}$.

2.3 Chemical Methods

To avoid accidental contamination by ^{252}Cf during all chemical processes, the work was done in a laboratory where ^{252}Cf had never been chemically processed. All chemical tubes, beakers, dishes and evaporation lamps were new. Similarly, all manipulations with mylar foils were done in a completely inactive laboratory. During exposure all mylar foils were covered on page No. 2 by 10 mg/cm^2 of new plastic foil, used similarly for the basic support of sources of separated fractions. To prepare such sources, the chemically separated fractions were evaporated onto foils of Pt, mica, Al or teflon*.

Technical grade HfO_2 was used as starting material since the presence of spontaneously-fissioning elements was observed in it by the mylar-foil technique (during 1969 and 1970). In 1970 alpha-measurements and neutron irradiation of this HfO_2 also indicated that it contained approximately 0.2% natural uranium. This HfO_2 was probably prepared from an ore (ZrO_2—sands of Australian origin) by chlorination and distillation of $HfCl_4$ followed by purification methods which did not separate very well all the uranium originally present in the ore. A sample of 50 g HfO_2 was used for the combined dry-wet chemistry. It was first transformed to $HfCl_4$ by $COCl_2$ fast chlorination of HfO_2 at 540°C. This chlorination resulted in ~76 g of crude $HfCl_4$ which was dissolved in H_2O until saturation. Hafnium oxychloride was precipitated by adding one volume of 12M HCl and five volumes of acetone. The fine crystalling Hf-oxychloride thus precipitated was filtered, the filtrate evaporated, and the remainder dried and heated to 800°C. By this method 950 mg of concentrate (fraction C) was prepared, containing most of the U, Th and other impurities present in the original HfO_2.

*Polytetrafluoro ethylene

The 900 mg from fraction C was separated in an 800 mm long thermochromatographic tube, using $COCl_2$ supplied at a linear velocity of 10 mm/sec [21]. The temperature gradient along the tube is shown in Fig. 1.

The quartz tube was cut into 11 parts after completion of the thermochromatographic separation. Each part was washed with 1 ml 6M HCl and the solution evaporated onto Pt-foil. All 11 Pt-sources were measured for spontaneous fission (by repeated exposure on mylar).

The main difference between the direct chlorination (ordinarily used) and the dry-wet process is as follows: in direct chlorination all elements present in HfO_2 can be separated and are distributed along a thermochromatographic tube; in dry-wet chemistry the less volatile elements remain in the residue after the first crude HfO_2-chlorination and the elements coprecipitating by acetone with Hf-oxychloride are removed before thermochromatographic separation. Elements like U, Th and alkaline elements (Ra, Fr) do not coprecipitate with Hf-oxychloride and they were possibly enriched in the dry-wet chemistry process. This was observed directly, i.e., the amount of U grew from 0.2% in the original HfO_2 to ~2% in fraction C.

The dry-wet chemistry was later extended as follows: The bulk of fine Hf-oxychloride crystals from the acetone precipitation was dissolved in water and left for 150 days. During this time the solution crystalized freely. Then 83.5 g of crystaline Hf-oxychloride hydrate (large white crystals with no uranium content) were separated from 63 ml of yellow Hf-oxychloride filtrate, the latter containing 40 mg Hf-oxychloride and 0.25 mg of uranium per ml. This filtrate was 3 to 4 times richer in U (in ratio to Hf) than the original HfO_2; it was also enriched with Th and elements of group II and I (fraction F). Five ml of this fraction F (corresponding to the enrichment from 4 g of original HfO_2) were mixed with

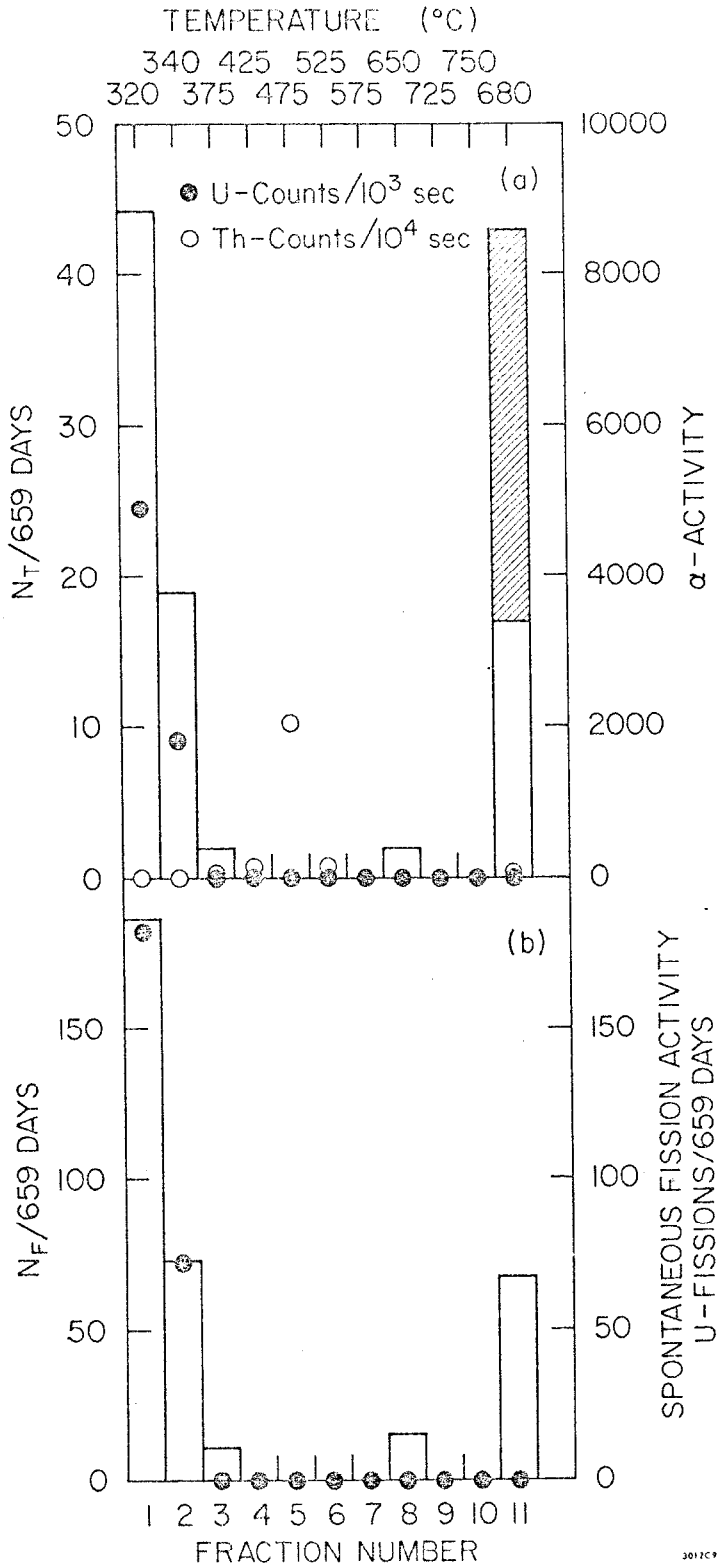

Fig. 1. Thermochromatogram for 659 days exposure. (a) Alpha and spontaneous fission activity measurements for the dry-wet process of 50 g HfO_2: chlorination of fraction C, (b) calculated number of fission events N_F (histogram), and calculated fission events from natural uranium.

10.5 ml 13M HCl and passed through an anionite column. The latter was 35 mm long, 6 mm in diameter and contained Dowex 1X8 (solution was 9M in HCl, input volume was 15 free column volumes). The column was first washed by 8M HCl (18 free volumes separated in 3 fractions), then by 3M HCl (18 free volumes separated in 2 fractions) and finally by 0.6M HCl (21 volumes separated in 2 fractions). The separated fractions were evaporated on weighed squares of mica (25 cm^2 or 50 cm^2), then measured for U distribution with an alpha-chamber and for mass distribution (Hf-oxychloride) by weighing. The mica sources prepared in this fashion were measured for spontaneous fission with the mylar foil technique.

3. RESULTS OF SPONTANEOUS FISSION MEASUREMENTS

The spontaneous fission results from the dry-wet chemistry of 50 g of HfO_2 are presented in Fig. 1. Figure 1(a) shows the observed number of track holes (N_T), and also the uranium and thorium distribution from the thermochromatographic separation of 900 mg of concentrate by the dry-wet process (fraction C) for the first 659 days of measurements (Th-fractions contain mostly ^{230}Th). The data for U and Th were obtained by alpha-measurements. Figure 1(b) shows the calculated number of fissions, N_F, which includes the detection efficiency E_T. The results presented in Fig. 1 are quoted from [18] (Fig. 5). In that experiment an unusual fission activity was observed in fraction No. 11 soon after separation (at 680°C, just after the chlorination point). To obtain greater statistics for this important fraction, the entire surface of the mylar foil which was in contact with source No. 11 was microscopically scanned (approximately 3 cm^2 on each foil). In addition to 17 track-holes this scanning also revealed 26 tracks not passing all the way through the foil. The number of these additional tracks (26) is represented by the shaded area in Fig. 1. The recalculated number of fissions,

N_F, is again shown in Fig. 1(b) together with the spontaneous fission background caused by the presence of uranium in some of the fractions No. 1 through No. 11. It is evident that the fission events in fraction Nos. 1, 2 and 3 correspond exactly to the amount of uranium present (the peak of U is at ~320°C). Unusual fission events were observed in fraction No. 8 (at 650°C) and especially in No. 11 (at 680°C). The latter fraction is approximately in the thermal position where bivalent chlorides ($RaCl_2$, $PbCl_2$) or actinium chloride should be deposited [22].

In addition to the unusual fission activity found in the 680°C fraction, there were repeatedly strange "fat" tracks observed on source No. 11 during the first 659 days of exposure. There were approximately equal numbers of fat tracks and regular tracks. These fat tracks were originally thought to be either defects accidentally located in the foil of source No. 11 or assumed to be regular fission tracks which were overdeveloped due to a higher local concentration of NaOH (the latter being caused by local overheating and evaporation of water from NaOH). These tracks were therefore almost all discarded in Fig. 5 of [18]. However, such fat tracks later started to appear regularly in exposures to source No. 11 and also to source Nos. 6 through 10. In exposure Nos. 1, 4 and 7, one heavy fission fragment also passed through both the top and the bottom foil. Moreover, since the 7th exposure there was often an excess of fat tracks over regular tracks observed.

In the last long exposure (502 days) there appeared 6 fat plus 2 regular tracks on source No. 11, also 5 fat tracks plus one regular track on source No. 8, 7 fat tracks on source No. 6, and 2 fat tracks plus one regular track on source Nos. 7, 9, and 10 together. Two of the fat tracks from the 502 day exposure penetrated two mylar foils, or a total of 26 μm of mylar.

The source Nos. 6 through 11 were placed on the mylar foils together with sources of uranium for calibration purposes. One uranium foil was located to the left of the source and several others to the right. Thus, the uranium fission tracks were developed very regularly on either side of the fat tracks during the last development of the mylar foils in 6M NaOH. There were also 4 regular fission tracks "mixed in" with 20 fat tracks and no local overdevelopment appears to have taken place. Many of the observed regular and fat tracks from the 502 day exposure are presented in Figs. 2 and 3.

Figure 2 shows microscope photographs of 5 fat track events for which the fission fragments had enough momentum to pass through both top and bottom foils (2(a-b), 2(d-e), 2(g-h), 2(j-k) and 2(m-n)). All pictures are at 400x magnification. The right hand column depicts californium and uranium fission tracks for comparison and calibration. Figure 2(c) is a Cf-event, the remainder are U-events. These fission events originated in sources placed next to the sources (on the same foil) which produced the two-foil fat tracks (2(a-b), 2(d-e), etc.).

Figure 3 shows a representative sample of fat tracks which penetrated only one foil. The fat tracks are either cylindrical or they are composed of two tracks (double tracks) as can be seen in Figs. 3(m, n, o). The two-track events 3(m) and 3(n) could be interpreted as cases of triple fissions with two of the tracks located in the mylar foil and one track in opposite direction and not detected. The separation of the two tracks in Fig. 3(o) is substantial. They might be due to two different fission events, originating perhaps in a particularly large, rich crystal. For comparison, Fig. 3(k) depicts a californium event, and Figs. 3(f), 3(g) and 3(l) are ^{238}U events. Since fission tracks from Cf are very similar to ^{238}U tracks and since these tracks are very different from fat tracks, it appears that the fat tracks are not due to Cf-contamination.

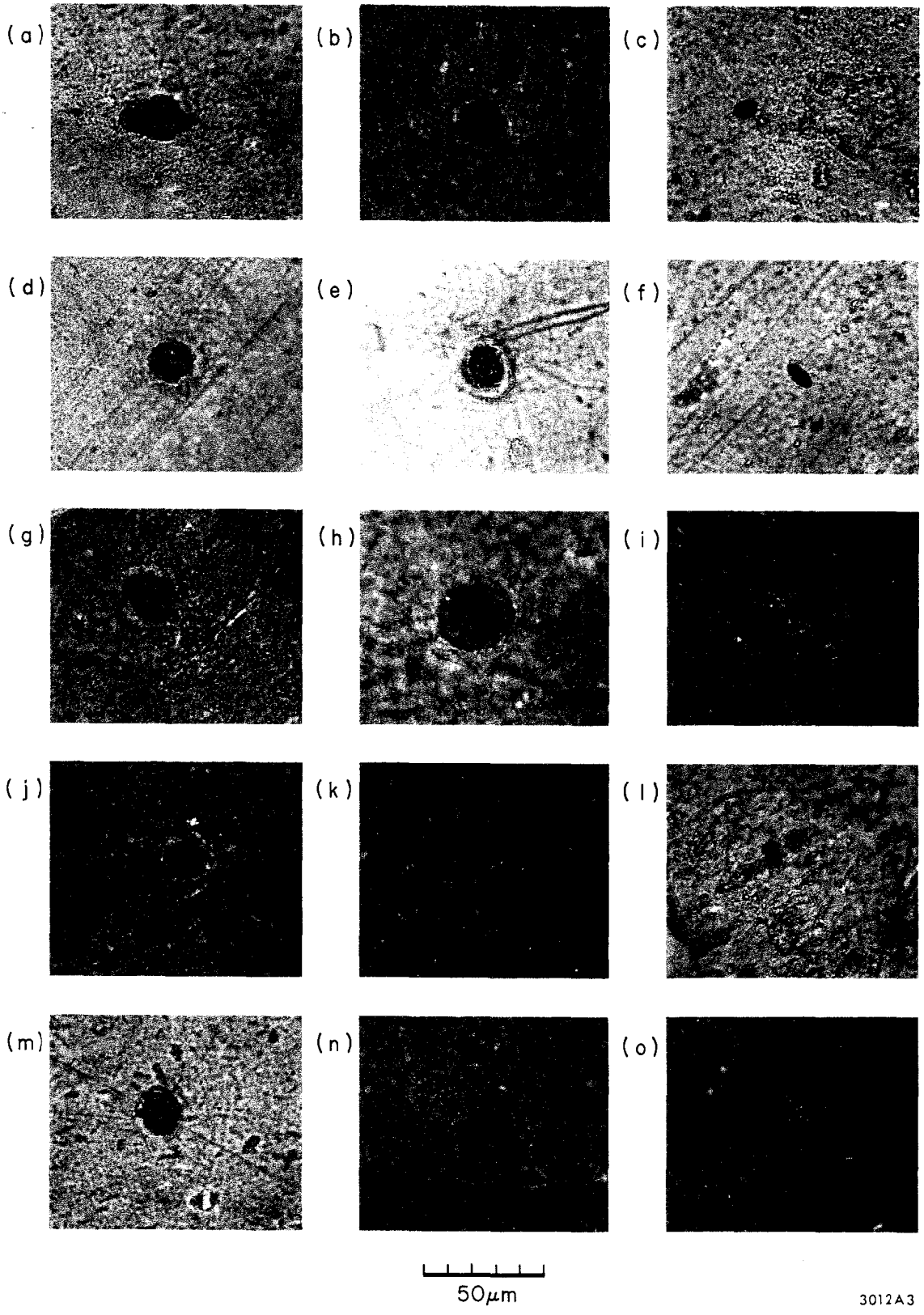

Fig. 2. Two-foil "fat" fission track events; and Cf and U calibration tracks (c, f, i, l, o) at 400X magnification.

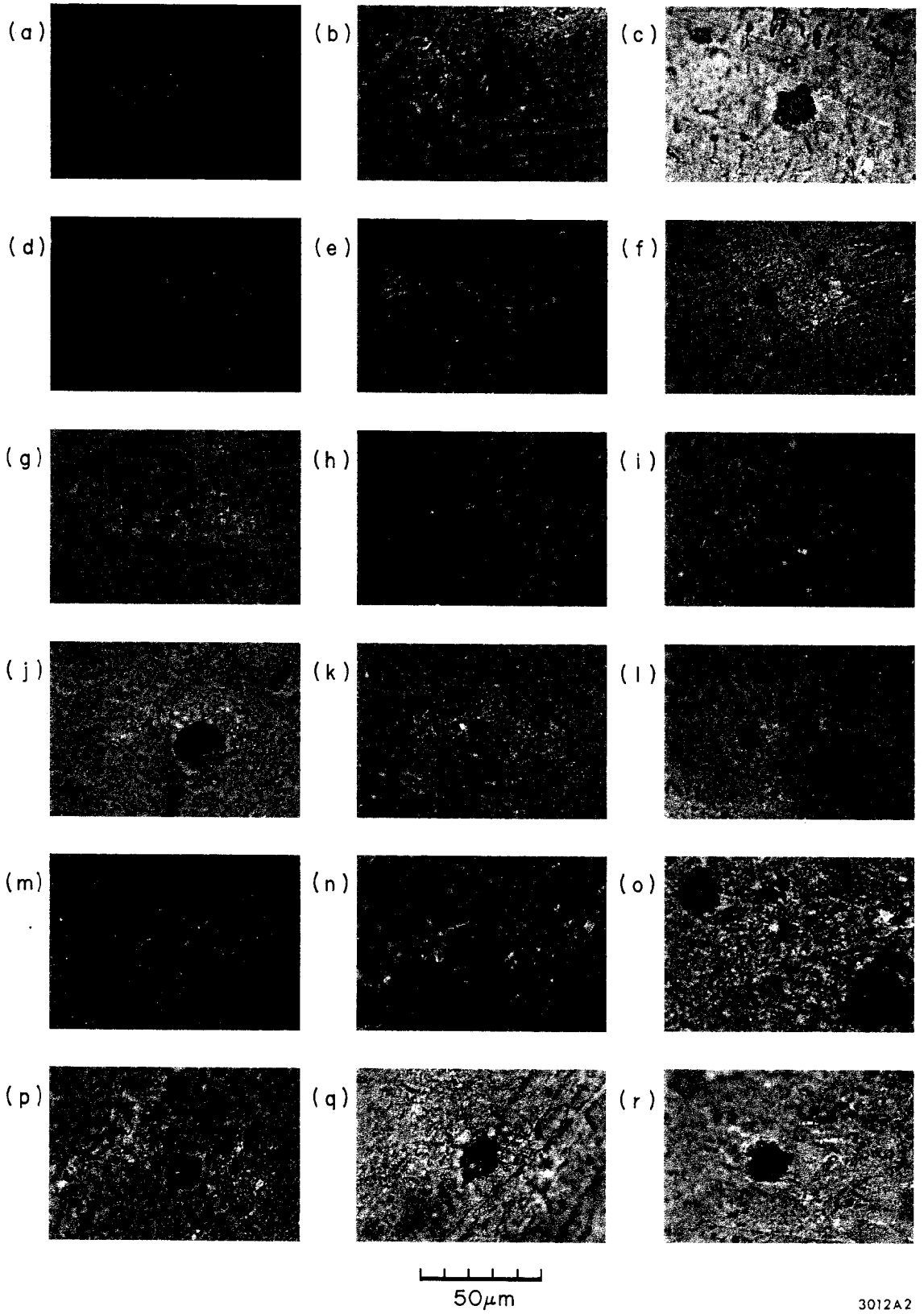

Fig. 3. Single-foil "fat" fission track events; and Cf and U calibration tracks (f, g, k, l) at 400X magnification.

The results for a total of 1538 days of exposure (i.e., the results presented as N_T in Fig. 1 plus an additional $2\frac{1}{2}$ years of new measurements) are given in the thermochromatogram of Fig. 4. The latter shows the distributions of fat tracks (N_{FT}) and regular tracks separately. The detection efficiency for fat tracks was assumed to be $E_T = 1.0$, i.e., only the fat tracks that penetrated the foil and were detected are used in Fig. 4.

Figure 4 shows further that fat and regular tracks originated only from source Nos. 6 through 11 (between 525°C to 680°C). At the lower temperatures (525°C and 650°C) they appeared from these sources primarily after 659 days of exposure. A reasonable explanation for this kind of growth is that the fractions at 525, 650, and also 680°C contain some mother element which by radioactive decay is transmuted to a daughter element(s) that fissions and creates the fat tracks.

The thermochromatogram from 5 ml of fraction F on anionite is given in Fig. 5. This graph demonstrates again that fission activity was elutriated in the first fractions with 9M and 8M HCl (just before hafnium), separated far from uranium (elutriated with 3M or 0.6M HCl). The basic difference between the fractions given in Fig. 5 to those shown in Fig. 4 is that the anionite-separated fractions do not contain a large portion of the fat tracks: only 4 fat tracks and 21 regular tracks were observed for the total of 1380 days of measurements. However, chemically both the fraction Nos. 6 through 11 in Fig. 4 and Nos. 1, 2 and 3 in Fig. 5 correspond to strongly basic cations. Besides the element causing the fat tracks, the anion exchange fraction Nos. 2 and 3 in Fig. 5 could contain other less strongly basic cations, which could be absent in the fractions shown in Fig. 4 (using dry chemistry).

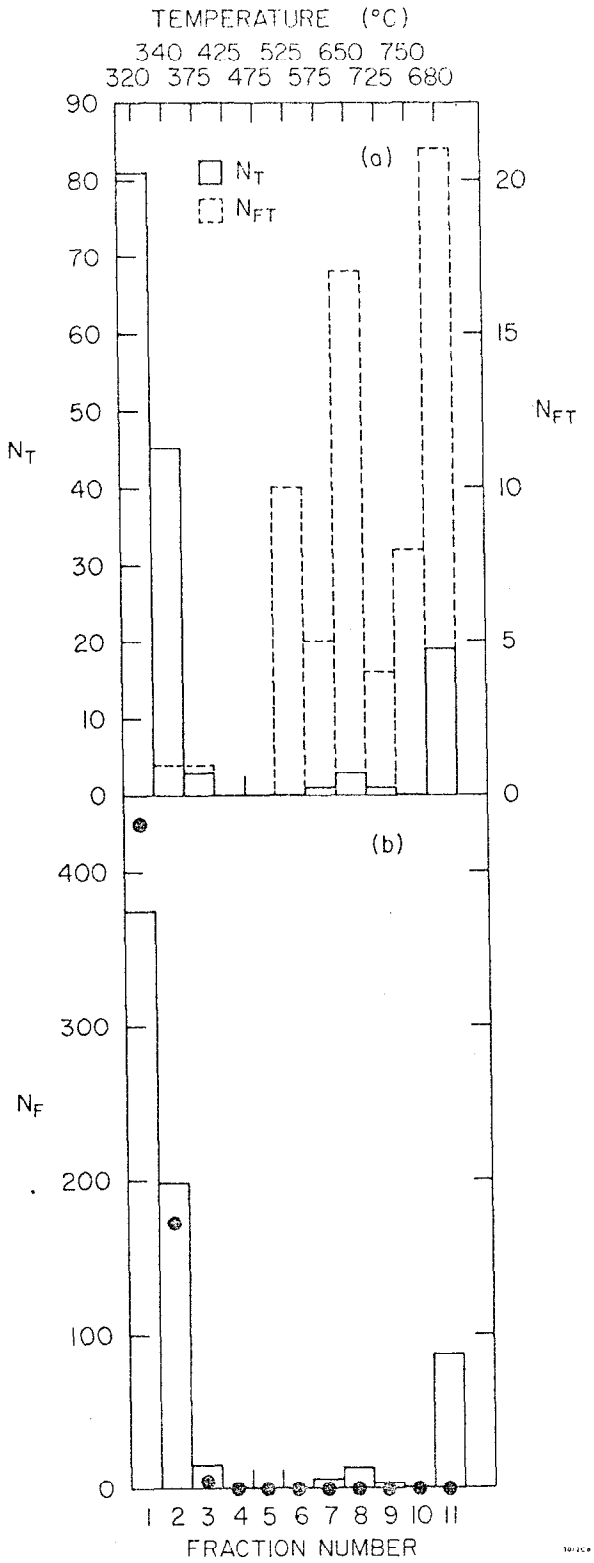

Fig. 4. Thermochromatogram for 1538 days exposure: (a) histogram N_T for regular tracks and histogram N_{FT} for fat tracks; (b) calculated number of fission events N_F from N_T in (a) represented by the histogram, and calculated fission events from natural uranium (points).

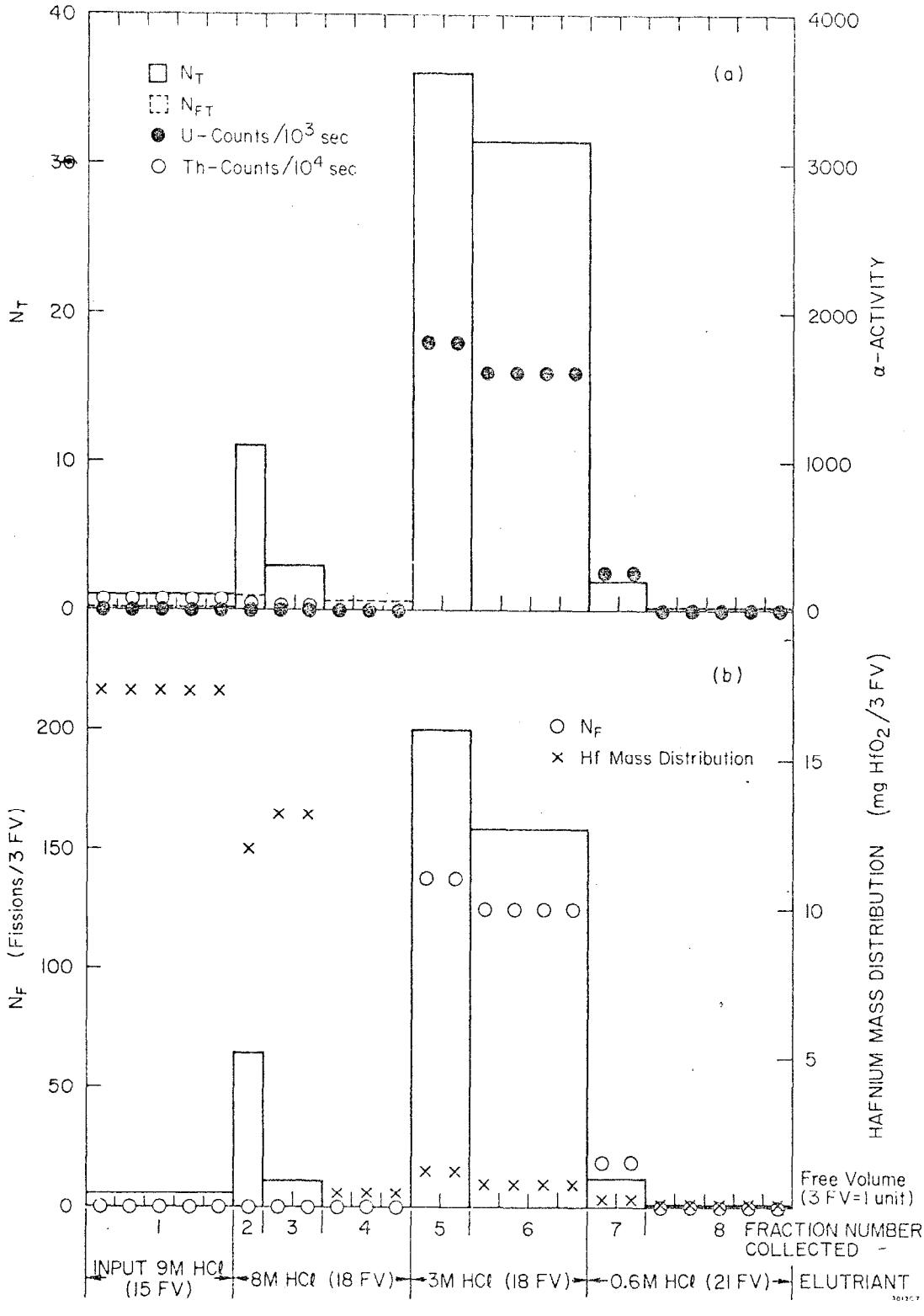

Fig. 5. Thermochromatogram for 1380 days exposure to 5 ml of fraction F, separated on anionite resin: histograms for N_T and N_F (expressed in units of "3 free volumes").

In the 11 measurements of fraction Nos. 1 through 11 in Fig. 4, only 5 background fat tracks were observed on mylar foil page No. 2 (i.e., five tracks were observed which resemble the fat tracks on mylar foil page No. 1 and which are not clear-cut cases of holes from cracks or other man-made artifacts on the foils). Thus, the 63 fat tracks presented in Fig. 4 could include a maximum of 5 fat tracks attributable to background; two of the fat tracks from source Nos. 2 and 3 of Fig. 4 can be such background events.

The 9 mylar foil measurements for each fraction Nos. 1 to 8 resulted in only 4 fat tracks which could be identified with a high degree of confidence and which are added to Fig. 5. However, in two out of the nine mylar foil exposures used for Fig. 5, an additional 4 fat tracks were observed from source No. 1 and a total of 3 fat tracks together from source Nos. 4, 5 and 6. Additionally, a large background was observed on mylar foil page No. 2 for each of these two exposures; 7 to 9 of these tracks somewhat resembled the fat tracks. Because of this large background and associated uncertainty, these 7 fat tracks were not included in Fig. 5. None of the other 7 exposures included in Fig. 5 showed any fat-track background on mylar page No. 2. Furthermore, none of the exposures used in these figures (11 for Fig. 4 and 9 for Fig. 5) showed any regular fission background on the mylar pages No. 2. The experiment represented by Fig. 5 was repeated simultaneously as a parallel experiment with an input of 1.5 ml of fraction F. The results of 9 mylar foil exposures were similar to those given in Fig. 5. A total of 7 regular fission tracks and 1 fat fission track were detected during 1380 days of exposure to 9M and 6M HCl fractions; this compares to 20 tracks found in these fractions using an input of 5 ml of fraction F and represented in Fig. 5(a).

The fat track fission activity as a function of time which is present in fraction Nos. 6 through 11 (see Fig. 4) is plotted in Fig. 6. Similarly, Fig. 7 presents and compares the regular fission activity from Fig. 4 to that found in the first three fractions of Fig. 5.

The statistics for the data plotted in Fig. 6 are low and no decay curves were drawn. For easier reading, the corresponding points were connected by straight lines. However, some preliminary conclusions can be drawn from the data in Fig. 6:

(1) The 525°C fraction (No. 6) generated no tracks during the first 475 days of measurement; all the observed fission activity has appeared only since this time. Chemically, the elements in this fraction resemble rare earths, actinides or Pu^{IV};

(2) the $\geq$680°C fraction (Nos. 11, 10 and 9) shows an activity which might be constant or could grow initially and then decay (with a possible half life of $T_{\frac{1}{2}} \sim$ 500 days). Chemically, the elements in this fraction could correspond to strongly-bivalent cations or bivalent actinides;

(3) the fractions taken at 575 to 650°C (Nos. 7 and 8) demonstrated initially an activity with a very high decay rate; i.e., with short half life, see the first point -o- showing a calculated fission rate of 125 fissions/250 days. This normalization to 250 days was done to make this data comparable to the other data presented in Fig. 6. Actually detected were only 8 fat tracks/16 days with one fragment passing both foils and observed during the interval between the 12th and 28th day after separation. After the initial 16 days of measurement no additional fat tracks were observed in the following 459 days (period covered by three mylar exposures). Some 500 days after separation the fat-track activity appeared to grow again and the equilibrium fission rate was probably reached.

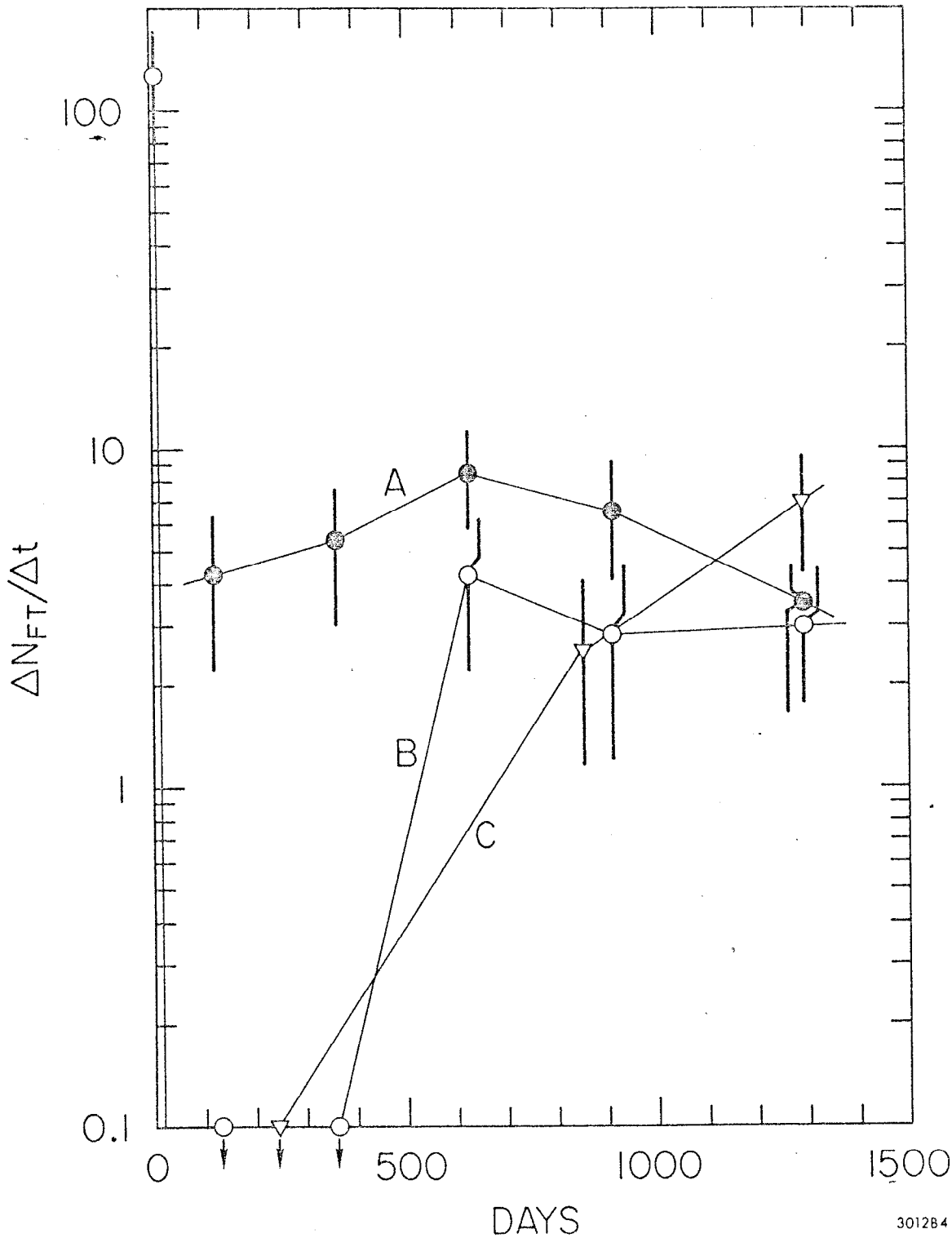

Fig. 6. Decay of "fat" track fission activity $\Delta N_F/\Delta t$. (A) Fraction Nos. 9, 10 and 11: deposited at $\geq 680^{o}C$, $\Delta N_{FT}/250$ days. (B) Fraction Nos. 7 and 8: deposited at 575-650°C, $\Delta N_{FT}/250$ days. (C) Fraction No. 6: deposited at 525°C, $\Delta N_{FT}/500$ days.

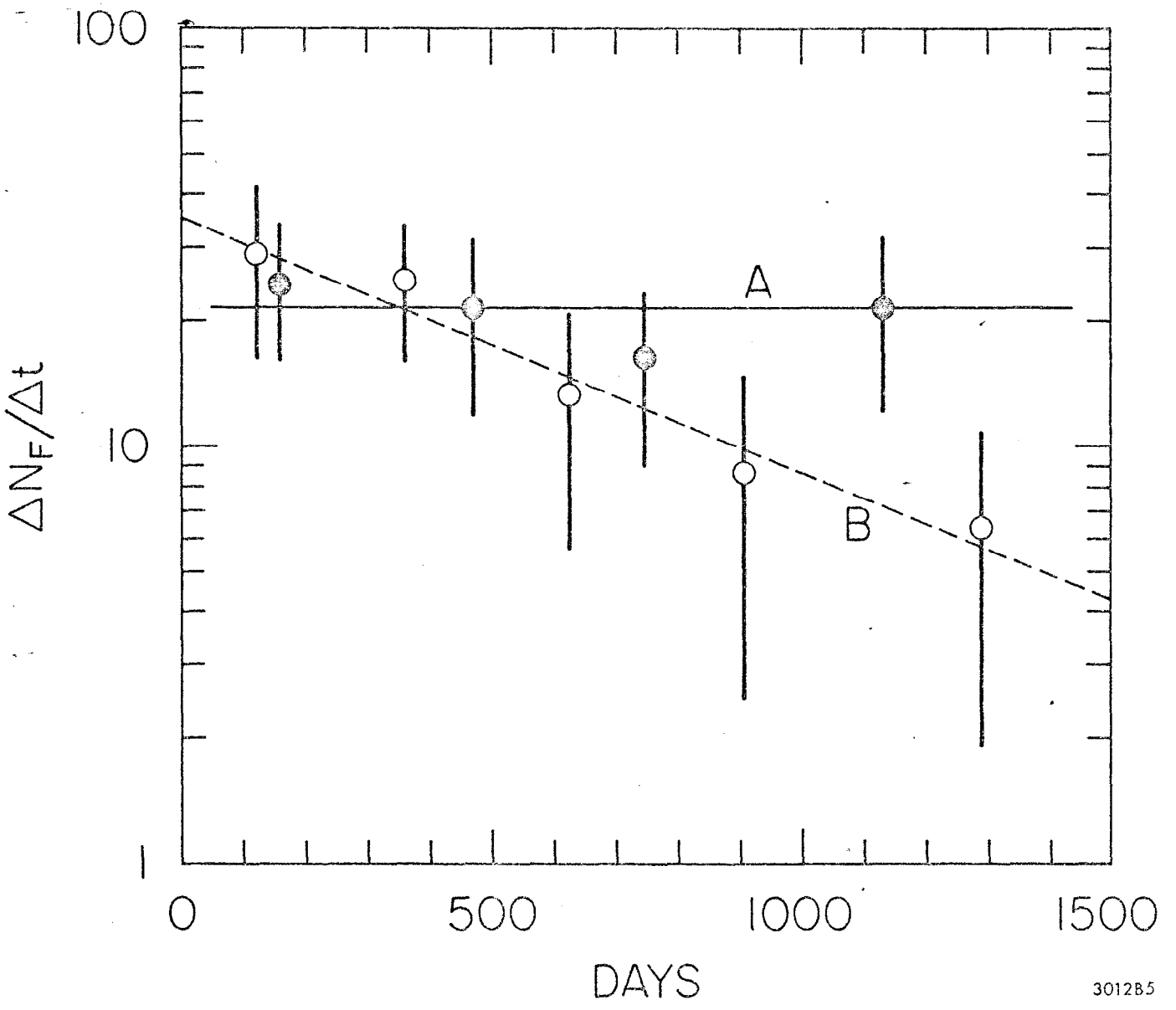

Fig. 7. Decay of regular fission activity $\Delta N_F/\Delta t$. (A) Fraction Nos. 1, 2 and 3: $\Delta N_F/250$ days. (B) Fraction Nos. 9, 10 and 11: $\Delta N_F/250$ days.

During the last 1000 days the fission rate was either constant or very slowly decaying. If the first point -o- is accepted as a statistical fluctuation and the 8 observed fat tracks are assigned to the first three mylar foil exposures (242 days total), then the following 233 days of exposure still give a value of zero on the curve denoted by -o- in Fig. 6.

The conclusions reached in (1), (2) and (3) above can best be explained by the hypothesis that a chain of natural superheavy elements is observed which produces fat fission fragment tracks at its end. The 525°C fraction could well contain a mother element with a long half life from which the short living ($T_{\frac{1}{2}} \sim$ 1 year) daughter elements were separated in the two other fractions. The fraction (Nos. 7 and 8) initially decays rapidly and then grows slowly, and, perhaps, decays again. The last case could well be explained as a rapid decay of a short-lived, light daughter isotope followed by slower α-decay of a heavier daughter isotope of the same element, yielding after two β-decays again the same short-lived light isotope. The fraction (Nos. 11, 10 and 9) could contain another element from such a postulated decay chain. Better statistics are required to support the explanation given above and reach definite conclusions.

The regular fission activity from Fig. 5, plotted as a function of time in Fig. 7, is not decaying; it was constant at a level of approximately 22 fissions/250 days as isolated from 4g HfO_2 (22 fissions/kg-day). The other regular fission activity plotted in Fig. 7 from data of source Nos. 11 through 9 of Fig. 3 (deposited at temperatures $\geq 680^{o}$C) appears to be decaying with $T_{\frac{1}{2}} \sim 500$ days. However, within statistical errors the half-life for this activity could be anywhere from 250 to 2000 days. It should be noted that the error bars do not exclude the possibility that this curve, interpreted as regular fission activity, came from the same isotope which produced the growing and decaying fat track

activity (fraction Nos. 11, 10 and 9) as shown in Fig. 6. The initial activity after separation for this decay curve is approximately 35 fissions/250 days as isolated from 50 g HfO_2 (2.8 fissions/kg-day). The regular fission activity as plotted in Fig. 7 could be explained in two ways: either it is a contamination with Cf and/or Cm isotopes, for example, from nuclear weapon test fallout, or it is due to spontaneously (or in-flight) fissioning isotopes in the region $92 \leq Z \leq 106$; the latter would have originated from a long alpha-decay chain or by asymmetric fission of a superheavy element. The regular fission fragment tracks mixed in among the fat tracks could also be explained as resulting from the light fission fragment created in strongly asymmetric fission of a superheavy element.

If the absolute number of fissions observed in source Nos. 6 through 11 during the last 502 days exposure are compared to the total amount of processed HfO_2 (50 g), then the following ratio is obtained: 1 fat track/25 days in 50 g of HfO_2 (assuming $E_T = 1.0$ for fat tracks) or 0.8 fat fission tracks/(kg-day) of HfO_2. Similarly, the fission effect in fraction Nos. 1 through 4 in Fig. 4 was: 4 fat tracks and 21 regular tracks during 1380 days of exposure to separation of ~4 g HfO_2 (1/12.5 of solution after second crystallization of hafnium oxychloride). This also corresponds to ~0.7 fat fission tracks/(kg-day) and ~3.8 regular fission tracks/(kg-day).

It can be seen that the element producing the fat tracks was nearly evenly distributed between the solution and the hafnium oxychloride during their foil precipitation. Assuming that the fat fission tracks are due to the presence of some superheavy element and accepting a half-life of approximately 10^9 years for this element, then the concentration of the superheavy element in this HfO_2 should be $\sim 2 \times 10^{-13}$ g/g (by addition of the effect of fat tracks from Figs. 4 and 5 and recalculated for 50 g HfO_2).

4. PRELIMINARY ESTIMATION OF A AND Z OF "FAT" TRACK FISSION FRAGMENTS

It can be assumed that the track diameter D is proportional to the leaching rate V_t; further that V_t is proportional to the ionization effect in a plastic, I, and to the ionization loss dE/dx according to the measurements of the leaching rate in lexan [23]:

$$k_1 D = V_t = B\left[I(\beta, Z^*)\right]^{1.8} \tag{1}$$

$$I(\beta, Z^*) = k_2 \frac{dE}{dx}(\beta, Z^*) \tag{2}$$

where k_1, B and k_2 are proportionality constants, $\beta = v/c$ = ion velocity, c = velocity of light, and Z^* = electronic charge of the ion with Z and A. The ionization loss dE/dx in lexan was further calculated [23] according to the Bethe-Bloch formula, which can be written in the following form:

$$I(\beta, Z^*) = 10^{-4} \frac{Z^{*2}}{\beta^2} \left\{ \ln\left(\frac{\beta^2}{1-\beta^2}\right) + K - \beta^2 - \delta(\beta) \right\} \tag{3}$$

where K = 62 [23], $\delta(\beta)$ for lexan, and Z^* was calculated according to an approximation formula in [23]. This paper is limited to the use of formulas (1) and (2) and to the range of the fat tracks.

The results from the last and longest exposure are presented in Fig. 8. Plotted are the track diameters, D, for 20 observed fat tracks; also given are regular uranium fission tracks for calibration. They are from U-sources mounted to the left and right from the fat tracks region on the same mylar foil. The uranium calibration was carried out during the total exposure time (502 days) and yielded approximately the same results: the uranium fission tracks have a width around 2 divisions on the microscope (5.4 μm) as compared to 3.5 to 6.5 divisions (9.5 to 17.5 μm) for the fat tracks. The two tracks passing through

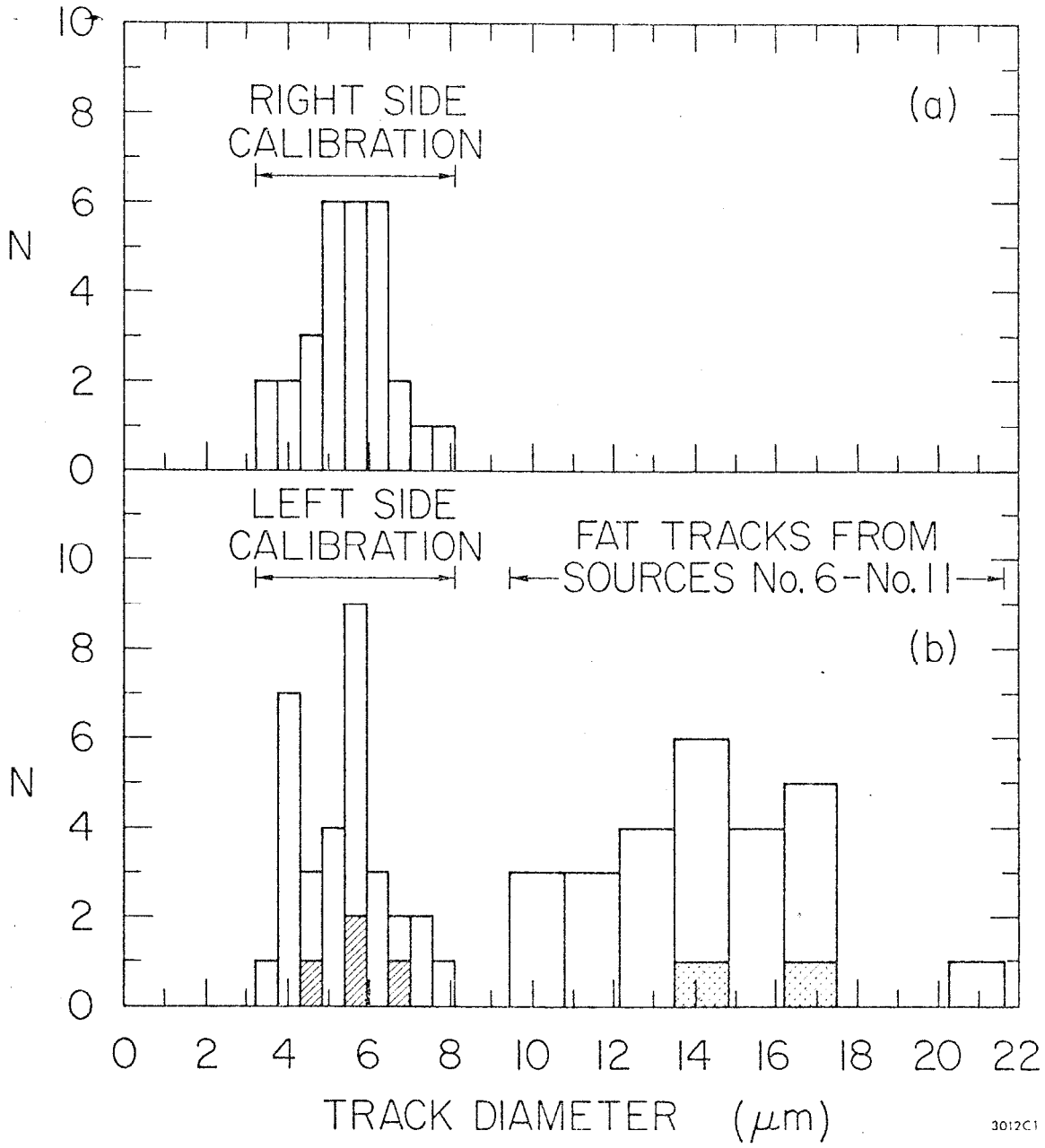

Fig. 8. Track diameter of regular and "fat" fission activity for 502 days exposure. N = number of tracks observed. Shaded areas in "left side calibration" represent regular fission tracks from source Nos. 6-11; cross-hatched areas in "fat tracks region" represent two-foil events. Double tracks are included as two separate tracks.

both foils in this exposure are 5.2 and 6.3 divisions (14 and 17 μm), respectively (marked in Fig. 8 by cross-hatched area).

The fact that the uranium calibration fission tracks from either side of the heavy tracks region are the same assures that there was no local overdevelopment. An additional proof comes from the presence of 4 regular tracks between the fat tracks (marked by shaded area in Fig. 8). Equal exposure time for the uranium calibration sources and the material which produced the fat tracks assured that both types of tracks were aged in the mylar foil for the same length of time.

Semiempirical tables [24] were used to estimate the Z and A of the fission fragments which generated the fat tracks, together with the following experimental information:

The diameter of the fat tracks, D, is 2 to 3 times larger than the mean diameter produced by uranium fission fragments (see Fig. 8 and also microscope photographs in Figs. 2 and 3) and their range, R, is 26 to 32 μm in mylar (from the first ten tracks in Fig. 2 which were due to fragments passing through two 13 μm thick mylar foils). The fat tracks which do not pass through both mylar foils have a range at least 1.5 times the thickness of the 13 μm of mylar, $R = 2.80$ mg/cm^2/foil. The track thickness, which is on the average 2 to 3 times larger than that from regular uranium fission tracks, corresponds to an ionization loss, dE/dx, that is according to Eqs. (1) and (2) 1.47 to 1.84 times larger than the average dE/dx from uranium fission fragments. Figure 9 presents data plotted from [24] and Table I gives ranges R (in mg/cm^2) and values for dE/dx (in MeV/mg/cm^2) in mylar for average light and heavy uranium fission fragments, $U_L = {}^{96}Sr$, $U_H = {}^{140}Xe$, approximated with data for ${}^{88}Sr$ and ${}^{132}Xe$ from [24]. It can be seen that the initial dE/dx is largest for heavy fragments; however, dE/dx

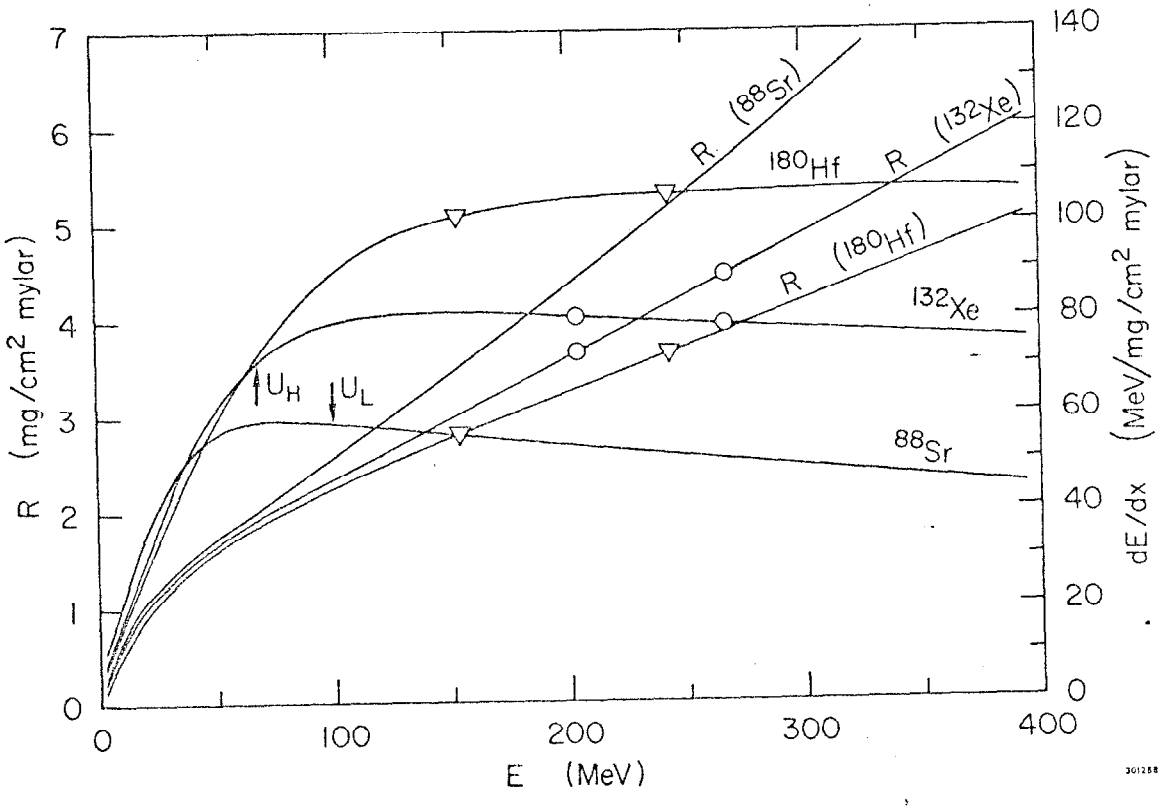

Fig. 9. Range and ionization loss curves in mylar from [24] for ^{88}Sr, ^{132}Xe and ^{180}Hf.

Table I. Energy, ionization loss and range for light and heavy uranium fission fragments in mylar; comparison of "fat" track fragments X_1 and X_2 to fission fragments exhibiting similar characteristics. (The maximum range of 4.45 mg/cm^2 corresponds to 32 μm and is a rough estimate obtained from angle measurements of some of the fat tracks.)

Ion Identification	E MeV	$\frac{dE}{dx}$ (0 μm) MeV/mg/cm^2	$\frac{dE}{dx}$ (6 μm) MeV/mg/cm^2	$\frac{dE}{dx}$ (13 μm) MeV/mg/cm^2	ΔE MeV/13 μm mylar	Range, R mg/cm^2
$U_L = {}^{96}Sr$	99.7					
${}^{88}Sr$	99.7	57.5	56	21.5	88.7	2.57
$U_H = {}^{140}Xe$	68.3					
${}^{132}Xe$	68.3	71.0	36	6.6	66.7	1.93
X_1		84.6	84.6		130	3.64 to 4.45
X_2		105.8	105.8		163	2.80 to 3.64
o ${}^{132}Xe$	204	80.2	81	67.3	144	3.64
o ${}^{132}Xe$	267	79	82.2	80.8	144	4.45
▽ ${}^{180}Hf$	153	101.5	77.5	31.5	130	2.80
▽ ${}^{180}Hf$	243	106	101.5	70.1	179	3.64

decreases rapidly and after such heavy fragments penetrated 13 μm of mylar, dE/dx is close to zero. Quite to the contrary, the dE/dx for light fragments remains substantial along the total path length of 13 μm in mylar. Consequently, in mylar the light fragments are observed leaving almost cylindrical holes. The heavy fragments, on the other hand, will produce a thinner hole with a short (~3 μm long) and somewhat wider entrance port (observed as a conical hole). The etching of a track with 6M NaOH is the combined effect of the chemical reaction and the diffusion of NaOH and chemical products of such a reaction in cylindrical geometry. From practical experience it is known that initially the hole is etched as a double-conical hole connected through a thin neck; as the process progresses, the hole often becomes completely cylindrical, although dE/dx decreases almost a factor of three even for light fragments along the 13 μm long path in mylar (see Table I). It can therefore be assumed that the total width of the etched cylindrical track is approximately proportional to the total energy loss ΔE in the first 13μm of mylar. It will be largest for lighter tracks, namely $\Delta E = 89$ MeV (see Table I) as compared to the heavier tracks which show $\Delta E = 67$ MeV.

Next, the fat tracks are compared to the wider cylindrical tracks from uranium fission fragments and it is assumed that the latter correspond to fragment ^{96}Sr. Using dE/dx values for ^{88}Sr as given in [24] (see Fig. 9) and a factor of 1.47 or 1.84, the dE/dx of the fat tracks X_1 and X_2 can be calculated to be 84.6 and 105.8 MeV/mg/cm^2 in mylar (see Table I); moreover, using the ^{88}Sr data given in this table for ΔE in 13 μm of mylar, the ΔE for the fat tracks is 130 and 163 MeV (for those fat tracks which are 2 to 3 times wider, respectively).

A comparison of the values of R, dE/dx and ΔE for X_1 and X_2 to fission fragments exhibiting similar characteristics (given in Fig. 9) yields the last

four lines of Table I. It can be seen that the observed fat tracks in this preliminary estimate correspond well to fission fragments with energies in the region of 150 to 270 MeV and with atomic numbers $54 \leq Z \leq 72$. This region of Z would agree with fragments from fission of an element with $Z \geq 120$. The fission fragments which produced the fat tracks in this investigation can thus best be explained as fragments from fissioning of a superheavy element.

The estimation of Z and energy of the fragments which produced the fat tracks is only preliminary. A calibration with heavy ions of Kr and Xe of different energies is necessary to verify the validity of Eq. (1) for mylar; the exponent of 1.8 as found for lexan [23] might be slightly different. Such a calibration could also substantiate the assumption that $D^{1/1.8}$ of a hole is proportional to ΔE in all mylar foils. Furthermore, the data from the tables [24] will have to be corrected for the difference in mass of ions to the real mass of the fission fragments (see $U_L = {}^{96}Sr$; data in [24] are for ${}^{88}Sr$, etc.). These corrections could change the energy and Z-assignment of the fat track fragments.

However, such corrections would not change the general conclusions reached herein, namely that the fat tracks are the result of spontaneous fissioning of a superheavy element (or elements) yielding heavy fission fragments with an energy substantially larger than those resulting from fission of uranium or californium. The second support for this conclusion is derived from the presence of 6 double track cases (three of which are shown in Fig. 3) from a total of 20 events found in the last exposure. These double tracks could well correspond to triple fission events (if confirmed by coincidence measurements). This would be in accord with theoretical predictions [25].

It should be noted that more recent theoretical predictions [12] call for islands of stability in the far-superheavy region around $Z = 164$ and $Z = 154$ in

addition to the earlier predicted island around element 114; the predicted half-lives are long enough that such far-superheavy elements could survive in nature. The Z = 154 element is eka-Rf (eka-eka-Hf). If this element were to exist, it would probably be present in Hf-minerals. However, Hf-minerals usually also contain Th, U and rare earths which could carry with Z = 122, 124 and 126 (or superactinide series) elements if they existed in nature.

5. CONCLUSIONS

Unusual radioactivity was observed in technical grade HfO_2. After some preliminary enrichment this activity can be separated in a thermochromatographic tube at the high temperature end (680°C); it can also be separated on anionite in the fraction washed with 9 to 8M HCl. The 680°C fraction produced unusually fat tracks in mylar with a range of at least 26 μm. Similar fat tracks also appeared in the lower temperature fractions (at 650 and 525°C). The fat track activity in the 525 and 650°C started to grow strongly only 500 days after separation and up to the limit of this observation (1538 days after separation). This indicates the presence of some separated mother and daughter elements in those thermochromatographic positions.

Because the tracks are two to three times as wide as tracks usually produced by uranium fission fragments, they cannot be caused by Cf-contamination. Some of the fat tracks could well be explained as ternary fissions.

The results presented herein can best be explained by the hypothesis that the fat track spontaneously-fissioning activities belong to some natural decay chain of superheavy elements, heavier than the Z = 114 region. The observed effect originally followed Hf and was isolated in the thermochromatographic position of Pu or lanthanides. This indicates that elements in the regions of Z = 154 and/or Z = 126 could be present in hafnium minerals.

If such a chain of superheavy elements exists in nature, it should have a long-lived first member (with $\geq 10^8$ half-life) with decreasing half-lives of daughter-members of lower Z, until Z reaches the next lower magic number. Members of lower Z than that of the mother element should partially or completely decay by spontaneous fission, which is generally predicted to have a high probability for ternary fission. There should be different elements in such a chain, some decaying and some growing in different fractions as a function of time after chemical separation.

The authors feel that the results presented herein are preliminary and need to be repeated on a larger scale with improved statistics. Only such a large scale effort can confirm and identify all the existing members and fission products of the postulated superheavy element chain. Furthermore, the authors hope that the evidence presented in this paper will stimulate systematic studies of spontaneously-fissioning elements contained in minerals which are used in the industrial production of Hf and Zr as well as Th and rare earths, or their compounds. Such studies should concentrate on several independent detection techniques for high-energy fission events. Further work is in progress.

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FOOTNOTES

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