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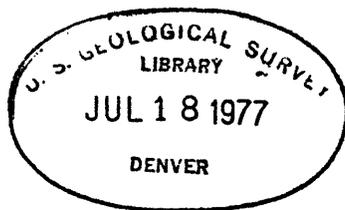
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Assay for uranium and determination of  
disequilibrium by means of in situ high-resolution  
gamma-ray spectrometry

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## Abstract

Two sealed sondes, using germanium gamma-ray detectors cooled by melting propane, have been field tested to depths of 79 m in water-filled boreholes at the Pawnee Uranium Mine in Bee Co., Texas. When used as total-count devices, the sondes are comparable in logging speed and counting rate with conventional scintillation detectors for locating zones of high radioactivity. When used with a multichannel analyzer, the sondes are detectors with such high resolution that individual lines from the complex spectra of the uranium and thorium series can be distinguished. Gamma rays from each group of the uranium series can be measured in ore zones permitting determination of the state of equilibrium at each measurement point. Series of 10-minute spectra taken at 0.3- to 0.6-m intervals in several holes showed zones where maxima from the uranium group and from the  $^{222}\text{Rn}$  group were displaced relative to each other. Apparent excesses of  $^{230}\text{Th}$  at some locations suggest that uranium-group concentrations at those locations were severalfold greater some tens of kiloyears ago. At the current state of development a 10-minute count yields a sensitivity of about 80 ppm  $\text{U}_3\text{O}_8$ . Data reduction could in practice be accomplished in about 5 minutes. The result is practically unaffected by disequilibrium or radon contamination. In comparison with core assay, high-resolution spectrometry samples a larger volume; avoids problems due to incomplete core recovery, loss of friable material to drilling fluids, and errors in depth and marking; and permits use of less expensive drilling methods. Because gamma rays from the radionuclides are accumulated simultaneously, it also avoids the problems inherent in trying to correlate logs made in separate runs with different equipment.

Continuous-motion delayed-gamma activation by a 163- $\mu\text{g}$   $^{252}\text{Cf}$  neutron source attached to the sonde yielded poor sensitivity. A better neutron-activation method, in which the sonde is moved in steps so as to place the detector at the previous activation point, could not be evaluated because of equipment failure.

## Introduction

In-borehole assay of uranium deposits has been done by measurement of gamma radiation since the early days of exploration. The Geiger-Müller detectors first used do not at all permit identification of the radionuclides from which the radiations are detected. The scintillation detectors of later and present design, although having some ability to distinguish a few of the more energetic gamma rays from uranium-series decay products in the  $^{222}\text{Rn}$  group (see Figure 1), cannot resolve the relatively weak and generally less energetic gamma rays from uranium itself and from those immediate decay products which can be expected to be in radioactive equilibrium with uranium under natural conditions. In practice, radiometric logging of uranium deposits is done by counting all gamma rays above an arbitrary, "threshold" energy without regard to the source of the radiation. If geologic phenomena such as ground-water motion and redox changes have caused partial separation of the groups of uranium series decay products because of their disparate chemical and physical behavior, the radiometric assay may be erroneously high or low. If significant concentrations of other radioactive nuclides, particularly thorium and its decay products, are present, the radiometric assay is erroneously high. As a consequence, the uranium exploration company often resorts to core drilling and chemical assay, despite the higher drilling cost, the delay in obtaining the results, the errors caused by incomplete core recovery, and the possibility of mix-up of samples.

We describe here the use in test boreholes of semiconductor radiation detectors having the ability to distinguish the gamma and X- radiations of the individual radionuclides. The semiconductor is a single germanium crystal that has been depleted of charge carriers either by their

immobilization by diffusing lithium through the crystal ("Ge(Li)") or by their removal by sophisticated purification techniques ("intrinsic" or "IG"). In order to reduce the electrical effect of thermally induced atomic vibration, the detector must be operated near the temperature of boiling nitrogen (77 K, -196°C). Because it is difficult to expel the nitrogen vapor at constant pressure at varying depth under water, we cool the germanium crystal with melting propane (85 K, whose expansion during melting poses no significant problem. For the tests reported here we used a medium-sized coaxial Ge(Li) crystal useful for gamma rays of energies greater than about 140 keV and a 500-mm<sup>2</sup> planar IG crystal useful for X rays and gamma rays in the range 5 to 800 keV. The crystals are housed in individual sondes 7.3 cm in diameter and about 1.5 m long, including the borehole electronics sections. Details of the sondes have been published (Tanner et al., 1971, 1972; Boynton, 1975; Senftle et al., 1976).

The tests were to evaluate the usefulness of the sondes in several ways: (1) as total-count detectors in conventional logging to determine zones of significant mineralization quickly; (2) as high-resolution detectors, to enable in situ assay for uranium by specific measurement of one of the two immediate, short-lived <sup>238</sup>U-decay products, <sup>234</sup>Th or <sup>234m</sup>Pa, which should be in equilibrium with <sup>238</sup>U under natural conditions; (3) as high-resolution detectors, to determine the state of equilibrium among uranium and its decay products, thereby providing information about the emplacement of the uranium and a guide to ore; and (4) as high-resolution detectors, to enable assay of uranium by activation by neutrons from <sup>252</sup>Cf.

The logging experiments described below were undertaken in cooperation with the U.S. Bureau of Mines at the Intercontinental Energy Company's uranium deposit near Pawnee, Bee County, Texas, during the period 12-27 October 1976.

### Total-count, conventional logging tests

The low-energy sonde, housing the IG planar detector, was used for continuous-motion conventional logging in holes nos. 4 and 8 (Figures 2 and 3, respectively). Figure 2 shows a conventional scintillation log (solid line) with the IG log normalized to the same maximum and superimposed (dotted line). For the IG logs the electronics were set to accept pulses from gamma rays and X rays of greater than 5-keV energy. The actual counting rates at the maxima were 5500 and 4500 counts per second, respectively, for the scintillation and the IG detectors.

The high-energy sonde, housing the Ge(Li) detector, was used for continuous-motion conventional logging in hole 7 (Figure 4). Because the thick zirconium alloy case of the high-energy sonde strongly absorbs the X- and low-energy gamma rays, the counting rate from the high-energy sonde was only 24 percent as great as that from the scintillation detector. Use of a thinner case and lower atomic number material for it would result in more nearly equal counting rates.

The counting rates of the high-resolution detectors demonstrate that they are effective for rapid evaluation of boreholes. By choice of detector volume, case material and thickness, and energy discrimination level, the total-count performance of the high-resolution detector could be made to match the typical scintillation detector. Because the log's definition of anomalous zones and the logging speed permissible are determined only by the counting rate and the time constant (or dwell period) used, there is no inherent difference in the total-count capabilities of the two types of detector.

## In situ assay for uranium by natural radioactivity

### X rays and gamma rays from uranium and its immediate decay products

Except for a weak gamma ray of about 48 keV attributed to it,  $^{238}\text{U}$  does not emit gamma rays observable in uranium-bearing material of ore grade. Uranium X rays are prominent in high-resolution spectra but assay by their measurement is complicated because they arise by two means: X-ray fluorescence from all uranium isotopes, excited by the ambient photon radiation, and X-ray fluorescence from  $^{234}\text{U}$ , excited by internal conversion of the gamma rays emitted by  $^{234\text{m}}\text{Pa}$  and  $^{234}\text{Pa}$  during their decay to  $^{234}\text{U}$ . Although the internally-excited X rays should be in proportion to the concentration of  $^{238}\text{U}$ , the X rays produced by external excitation should be approximately proportional to the square of the uranium concentration, because the intensity of the exciting radiation, if due primarily to the uranium-series decay, is itself proportional to the uranium concentration. Both of the two best uranium X rays are also subject to interference: the  $\text{K}\alpha_1$  X ray at 98.4 keV is reinforced by the 98.4-keV double-escape photopeak from the prominent 1120.4-keV line of  $^{214}\text{Bi}$ , in the  $^{222}\text{Rn}$  group; and the  $\text{K}\alpha_2$  X ray (94.7 keV) is not well-resolved from the Th  $\text{K}\alpha_1$  X ray (93.3 keV) or from the  $^{234}\text{Th}$  doublet at about 92.6 keV.

The first decay product of  $^{238}\text{U}$  is  $^{234}\text{Th}$ , whose 24.1-day half life is so short as to make unlikely a significant disturbance of radioactive equilibrium between it and its parent uranium in a solid deposit. (Solution mining could, of course, disrupt the equilibrium in a shorter period.) This expected equilibrium between  $^{234}\text{Th}$  and its parent is the basis for assay of uranium by natural gamma radiation.  $^{234}\text{Th}$  decays to an excited isomer,  $^{234\text{m}}\text{Pa}$ , 99.87 percent of which decays with a 1.17-minute half life to  $^{234}\text{U}$  (Ellis, 1970). The remaining 0.13 percent decays to the

ground state of  $^{234}\text{Pa}$ , but is not important to the present study because of its minor abundance. The very short half life of  $^{234\text{m}}\text{Pa}$  makes it as suitable as  $^{234}\text{Th}$  for assay of  $^{238}\text{U}$ .

As a result of literature study, measurements of laboratory standard samples, and tests in our laboratory borehole facility, we concluded earlier that the most suitable natural gamma ray to use is the 63.3-keV gamma ray from  $^{234}\text{Th}$  (Senftle et al., 1976; Moxham and Tanner, in press). Besides the X rays, other gamma rays thought to be less suitable but worth attention are a 92.6-keV doublet from  $^{234}\text{Th}$  and 766.4-keV and 1001.4-keV gamma rays from  $^{234\text{m}}\text{Pa}$ . All these radiations could be evaluated by the present tests.

The 92.6-keV doublet from  $^{234}\text{Th}$  has been suggested as a basis for uranium analysis by scintillation spectrometry (Richard et al., 1970). When what appears to be a 92.6-keV peak in a scintillation spectrum is examined with knowledge of a high-resolution spectrum in the same energy range, it is seen that the X rays actually dominate the spectrum. Even high-resolution spectrometry cannot resolve the 92.6-keV gamma-ray doublet from the 93.3-keV Th  $K\alpha_1$  X ray; because of the variable interference from the X ray, we conclude that it is a poorer choice for assay than is the 63.3-keV gamma ray from the same isotope.

The 766.4-keV gamma ray from  $^{234\text{m}}\text{Pa}$  is subject to strong interference from a gamma ray of nearly identical energy from  $^{211}\text{Pb}$  and is also less intense than the interference-free 1001.4-keV gamma ray.

Brodzinski and Wogman (1976) found from some experiments in a simulated borehole that the 1001.4-keV gamma ray could be used to analyze 0.029-percent uranium ore, using a 26-percent-efficient germanium detector, with a statistical uncertainty of 27 percent in 1 minute or 12 percent in 5 minutes.

Only the low-energy sonde is capable of measuring the X rays and the 63.3-keV and 92.6-keV gamma rays in the complex radiation environment of a borehole, because excessive scattering and attenuation of the low-energy radiations take place in the housing of the high-energy sonde. Both sondes are useful for gamma rays of energy greater than about 140 keV, the high-energy sonde being progressively better with greater energies because its larger volume entails a greater probability of detection and consequently better counting statistics. The high-energy sonde is, therefore, the instrument of choice for measurement of the 766.4-keV and 1001.4-keV gamma rays.

As expected, the 63.3-keV photopeak from  $^{234}\text{Th}$  gave the best combination of counting rate and unambiguity of the various radiations considered above. The usefulness of the 1001.4-keV photopeak from  $^{234\text{m}}\text{Pa}$  very much exceeded expectations. Despite a nearly tenfold lesser intensity than that of the 63.3-keV line (Ellis, 1970), the greater penetrating power of the more energetic 1001.4-keV gamma ray resulted in a photopeak that was about 85 percent as large, because a larger volume of wall rock was sampled and a larger detector volume was feasible.

$^{235}\text{U}$ , which exists in a nearly universal ratio of 1:137 to  $^{238}\text{U}$ , and its first decay product,  $^{231}\text{Th}$ , emit gamma rays. Neither nuclide is a good prospect for uranium assay, however, owing to the minor isotopic abundance of  $^{235}\text{U}$  and to interference with the few gamma rays of adequate intensity and energy. Those gamma rays of the  $^{235}\text{U}$  series detected in these tests are noted below in the section on disequilibrium studies.

### High-resolution logs for uranium assay

The high-resolution logs consist of series of 4096- or 8192 channel pulse-height spectra accumulated at discrete depths in the borehole, with the sonde held motionless, at depth intervals ranging from 8 cm to 1.2 m, for accumulation periods of 10 minutes. The spectra were recorded on magnetic cassettes for later interpretation by a 10-second routine and 2- to 3-minute printout performed by the minicomputer used for the spectrum acquisition. The algorithm used is a fixed-width, rectangular approximation of a peak that is applied as a weighting function, channel by channel and is stepped across the spectrum. The routine yields a reduced, smoothed spectrum of net peaks on a zero baseline (Senftle et al., 1976). The net peaks computed by the routine are typically about 70 percent of the actual peak areas and are those numbers appearing in the figures of this report.

High-resolution logs were constructed for the more interesting parts of holes numbers 7, 4, 1, and 8, which are nearly coplanar in a downdip direction. The high-energy sonde was used for logs of all four holes; because of a high-voltage circuit failure the low-energy sonde was used for a log in hole 4 only.

### Calibration

Standard boreholes for calibration of the high-resolution sondes were not available. Two different approaches were tried to relate the counting rates in selected photopeaks and the uranium concentrations at the corresponding depths: comparison with core scrapings analyzed fluorimetrically for uranium by the Bureau of Economic Geology of the University of Texas; and comparison of core samples and standard samples by gamma-ray spectrometry in our laboratory.

To obtain accurate depth control we used depth markings on tape on the sonde suspension cable. Figure 5 shows that our measurements in hole 4 (after correction to ground-level datum) agree closely in depth with the conventional gamma-ray log. The centroids of the main gamma-ray anomaly at 75.9 m differ by less than 0.01 m. In contrast, there is apparently a discrepancy of about 1.0 m between our logs and analyses based on cores from hole 4. Figure 6 presents the best correlation of our uranium analyses, based on the 1001.4-keV gamma ray from  $^{234}\text{mPa}$ , with the University of Texas' analyses of core scrapings. By this correlation 1.0 m should be added to the depths given for core analyses in hole 4 to reconcile them with either the conventional gamma-ray log or our high-resolution logging results.

The correlation of the 1001.4-keV gamma-ray data with the University of Texas' core analyses yields a maximum concentration of 0.325 percent  $\text{U}_3\text{O}_8$  at 76.7-m (251.5-ft) depth in hole 4. An alternative calibration method was to count a sealed split of core under standard conditions with high-resolution laboratory gamma-ray detectors and to compare the results with those on ERDA New Brunswick Laboratory standard uranium ore samples. Having determined the uranium concentration in the core sample, we calculated the coefficient needed to convert counts in the 1001.4-keV photopeak from the borehole measurement to the  $\text{U}_3\text{O}_8$  concentration in the core sample at the corresponding depth (75.4 m; 247.5 ft). This conversion was used for all uranium concentrations reported here (except for the correlation with the fluorimetric analyses, Figure 6) that were based on the 1001.4-keV photopeak. In like manner, we calibrated for equivalent uranium based on the 1120.4-keV photopeak from  $^{214}\text{Bi}$ . The results for both ore zones of hole 4 are shown in Figure 7. Calibration by gamma-ray spectrometry yielded

values 9 percent lower than by comparison with the fluorimetric analyses. In view of the larger sampling volume and more complete sampling by gamma-ray spectrometry and of the normal analytical error of the fluorimetric analysis, the difference is probably not significant.

An estimate of the sensitivity of the assay follows from the results and the calibration. The data reduction technique used forces to zero any results that do not pass a statistical test for significance at a selectable number of standard deviations. Five of the measurements of the 1001.4-keV photopeak passed a 1-s.d. test but failed a 2-s.d. test. The average U<sub>3</sub>O<sub>8</sub> concentration at the corresponding stations was about 80 ppm, which is inferred to be the sensitivity using the 1001.4-keV peak and a 10-minute counting period.

#### Disequilibrium determinations from in-situ spectrometry

High-resolution, in-situ spectrometry of the natural gamma rays from the uranium series offers the unique advantage of being able to measure disequilibrium at a point in a borehole with a single detector. The appropriate photopeaks are measured in the same time and depth intervals, avoiding uncertainties in depth control and the zone of sampling. Within a volume that contains the <sup>238</sup>U series in radioactive equilibrium, each member of the series has the same number of atoms decaying per unit time. Literature compilations give the number of gamma rays of each energy to be expected per decay. Within uranium ore at equilibrium the population of gamma rays emitted should be in the same relative proportions as the absolute intensities given in the literature. However, the effect of increasing depth of penetration with increasing gamma-ray energy, particularly in the

cylindrical geometry of the borehole, is to increase the volume sampled. An opposite but not generally balancing effect is caused by the decreasing probability with increasing energy that the detector will absorb a gamma ray and fully convert its energy to an electrical pulse. We have sought to minimize errors due to these and other effects by determining the relative gamma-ray intensities empirically in cylindrical geometry. One calibration model is a plastic bucket with an annular space of 6 cm inner radius, 15 cm outer radius, and 18 cm height, filled with New Brunswick Laboratory standard pitchblende diluted with sand to 0.118 percent  $U_3O_8$ . Another calibration model is a plywood barrel with an annular space of 6 cm inner radius, 38 cm outer radius, and 0.7 m height, filled with a uranium ore of incompletely known characteristics. Although the barrel is large enough to contain the volume effectively sampled by all the radiations of interest, the uncertainty about the state of equilibrium and the heterogeneity of its ore limit the reliability of results obtained from it. The bucket contains a more definitely known and homogeneous ore but is somewhat smaller than the volume effectively sampled by the gamma rays of 186-keV and greater energy. Additional relative-intensity data were available by comparison of core splits 4-245 and 4-252 with standard uranium samples in a well-defined laboratory setup.

Figures 8 and 9, respectively, show logs of  $^{238}U$ - and  $^{235}U$ - series variation with depth in hole 4. A preliminary attempt has been made to calibrate each log in units of percent equivalent  $U_3O_8$ , using a reconciliation of results from the calibration models and from the core splits. On the right side of each figure is shown the log of the 1460-keV gamma ray intensity from  $^{40}K$ . The abrupt step below 75.9 m (249 ft) correlates with an increase in the resistivity log and with the indication of monmorillonitic mudstone on the core log.

Figure 8 shows logs of photopeaks representing different decay groups in the  $^{238}\text{U}$  series. The uranium group is represented by the 63.3-keV gamma ray of  $^{234}\text{Th}$ ,  $^{230}\text{Th}$  is represented by its 67.7-keV gamma ray, the radon group is represented by the 241.9-keV gamma ray of  $^{214}\text{Pb}$ , and the  $^{210}\text{Pb}$  group is represented by the 46.5-keV gamma ray of  $^{210}\text{Pb}$ .  $^{226}\text{Ra}$  is not unambiguously represented because its only gamma radiation of adequate intensity, at 186.0 keV, has comparable interference from  $^{235}\text{U}$ .

Figure 9 shows logs of photopeaks representing the isotope  $^{235}\text{U}$  and the single group comprising the rest of the  $^{235}\text{U}$  series, the  $^{231}\text{Pa}$  group. The isotope  $^{235}\text{U}$  itself emits gamma rays, the strongest of which are at 186 and 144 keV. Unfortunately, both have interferences: the 186-keV gamma ray of  $^{226}\text{Ra}$  and the 144-keV gamma ray of  $^{223}\text{Ra}$  prevent straightforward interpretation of the data. Because the ratio  $^{235}\text{U}/^{238}\text{U}$  is practically constant in uranium ores (Senftle et al., 1957), it is preferable to infer the  $^{235}\text{U}$  concentration from the more readily and accurately measured concentration of  $^{238}\text{U}$ . We therefore take the  $^{234\text{m}}\text{Pa}$  and  $^{234}\text{Th}$  measurements to be the best indicators of the relative concentrations of  $^{235}\text{U}$ , as well as of  $^{238}\text{U}$ , and include them in Figure 9. All the numerous gamma rays emitted by members of the  $^{231}\text{Pa}$  group are too weak for accurate analysis for the counting period used; the most intense are at 236.0 keV from  $^{227}\text{Th}$  and at 269.6 keV from  $^{223}\text{Ra}$ . Both are subject to interference from members of the thorium series: 238.6 keV from  $^{212}\text{Pb}$  and 270.5 keV from  $^{228}\text{Ac}$ . The 236.0-keV gamma ray is the stronger and is well enough separated from the 238.6-keV gamma ray to make the thorium-series interference unimportant. Gamma rays from  $^{211}\text{Pb}$  (405 and 427 keV) were also observed in the borehole spectra but were too weak for quantitative treatment.

Figures 8 and 9 both show that the uranium isotopes heading the two series are present in excess with respect to  $^{226}\text{Ra}$  and the  $^{222}\text{Rn}$  group at 74.8-m (245-ft) depth. Figure 8 also shows  $^{238}\text{U}$  to be deficient at 72.7 (238.5-ft) and 78-m (256-ft) depths. In between, at 76.0-m (249.5-ft) depth,  $^{230}\text{Th}$ , with its 80-kiloyear half life, and  $^{223}\text{Ra}$ , controlled by the 34.3-kiloyear half life of  $^{231}\text{Pa}$ , are deficient in comparison with both their long-lived uranium precursors and the shorter-lived decay products of the  $^{238}\text{U}$  series. Thorium and protactinium form very insoluble compounds and are immobile in comparison with uranium, radium, and radon. The deficiency of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  at the 76.0-m depth can be explained only by movement of uranium isotopes,  $^{226}\text{Ra}$  and the  $^{222}\text{Rn}$  group into that location within the last period of the order of 10 kiloyears.

Figure 8 shows maxima of the  $^{230}\text{Th}$  67.7-keV gamma ray at 74.5 m (244.5 ft) and at 76.7 m (251.5 ft). At those locations the ratio of the 63.3-keV to 67.7-keV gamma-ray intensities from  $^{234}\text{Th}$  and  $^{230}\text{Th}$  is about 2:1. At equilibrium the ratio of absolute intensities is 14.25:1. Because the 67.7-keV gamma ray has slightly greater penetrating power, the ratio of intensities detected in borehole geometry is substantially smaller; we have measured the ratio to be 7:1 in the bucket model and between 5.4:1 and 7.1:1 in the barrel model. By comparison with core splits the ratio is 5.6:1. It appears that  $^{230}\text{Th}$  occurs in two-to-three-fold excess of equilibrium at the two locations, and in excess of equilibrium at most locations measured. If true, the concentration of  $^{234}\text{U}$  and almost certainly of  $^{238}\text{U}$  and  $^{235}\text{U}$  was greater at those locations some tens of kiloyears ago. Coupling this lessening of concentration of the uranium group toward the upper and lower boundaries of the ore zone in hole 4 with enrichment of the uranium group at the middle and lower middle of the zone, we infer that some process has

been working to redistribute the radio-nuclides over a period of the past 10 to 100 kiloyears. From the data from only one hole penetrating ore of sufficient grade to give good statistics for the weaker gamma rays, we cannot discriminate between vertical redistribution such as might result from water-table fluctuations at the ore horizon, and horizontal redistribution such as might result from changes in path of the major ground-water movement.

In the three other holes investigated the uranium-series mineralization is of much lower grade. The counting rates for the gamma rays used to measure  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ -group concentrations were too low to permit considerations like those above. However, the counting rates for the gamma rays representing the uranium and  $^{222}\text{Rn}$  groups were adequate to establish the pattern of disequilibrium between the two groups and to suggest the trend of their movement over the most recent period comparable with the half life of  $^{226}\text{Ra}$  (1.6 kiloyears). Figure 10 presents, in cross-section form, a plot of  $\text{U}_3\text{O}_8$  concentration as inferred from the 1001.4-keV gamma ray of  $^{234\text{m}}\text{Pa}$ , of the uranium-equivalent  $^{214}\text{Bi}$  concentration, and of the equilibrium ratio ( $\text{U}/e^{214}\text{Bi}$ ). The figure is drawn to scale with no vertical exaggeration. A horizontal layer above 64-m depth is barren and has been omitted. At the time of investigation the top of the water table was at about 44-m depth. Ground-water flow should be downdip, to the right in the figure. On the basis of conventional gamma-ray logs and core study, W. E. Galloway (Texas Bureau of Economic Geology, written communication, 1976) has described the (lower) ore body as "... an almost classic roll with well-developed wings updip ...." The wings are evident at hole 7. Fine stippling at each hole denotes zones where uranium is present in excess of equilibrium; open rectangles to the left of the vertical

denote zones where  $e^{214}\text{Bi}$  is present in excess. Coarse stippling denotes the inferred extension of the excess-uranium zones between holes; crosshatching denotes the inferred pattern of excess  $^{222}\text{Rn}$ -group activity. The  $^{222}\text{Rn}$  group is evidently dispersed above and below the ore body and in the downdip direction, partly due to the well-known mobility of the radon isotopes, but partly due to the mobility of  $^{226}\text{Ra}$ . Because there is some ambiguity in assignment of counts in the 186-keV photopeak between  $^{235}\text{U}$  and  $^{226}\text{Ra}$ , as mentioned above, it is not possible to determine the uranium-equivalent  $^{226}\text{Ra}$  accurately. However, in hole 4, the combination of  $^{235}\text{U}$  and  $^{226}\text{Ra}$  is deficient with respect to the  $^{222}\text{Rn}$  group at the uppermost four and lowest three measurement points of the lower ore zone. The  $^{210}\text{Pb}$  group, which results from decay of the  $^{222}\text{Rn}$  group, shows much less departure from equilibrium and suggests that the apparent dispersion of the  $^{222}\text{Rn}$  group is due in part to perturbations caused by drilling.

In-situ assay for uranium by  
delayed-gamma-ray neutron activation

Neutron activation of  $^{238}\text{U}$  yields  $^{239}\text{U}$ , which decays with a half life of 23.54 minutes and emits a gamma ray at 74.67 keV that has adequate intensity for assay in the field (Philbin and Senftle, 1971). Unfortunately, the X rays of bismuth (74.81 keV) and lead (74.96 keV) strongly interfere with the 74.67-keV gamma ray from  $^{239}\text{U}$ . In a well-shielded fixed geometry, Philbin and Senftle were able to reduce this interference by using 20-minute irradiation time followed by a 5-minute counting time; uranium concentrations down to 0.01 percent could be determined. By keeping the counting time short, the X-ray contribution was minimized.

Continuous-motion neutron activation in a borehole implies equal irradiation and counting periods, and consequently of questionable value for the assay of low grade uranium ores. However, as the  $^{252}\text{Cf}$  source was stronger than that used by Philbin and Senftle and the sample size in the borehole was larger, a test was made in hole 4 with a 163- $\mu\text{g}$  ( $3.77 \times 10^8$  n/s)  $^{252}\text{Cf}$  source attached 1.40 m below the detector of the low-energy sonde. The assembly was lowered at a rate of 23 mm/s (4.6 ft/min) from 60.5 m to 78.3 m, while pulse-height spectra were being recorded in accumulation periods of 60 seconds. The ratio of the net peak at 74.6-74.8 keV to the net peak at 77.1 keV is shown for the lower ore zone in Figure 11. Although the effect of the uranium activation is evident, the results indicate a poor signal-to-noise ratio and poor sensitivity using continuous motion.

In order to improve the neutron-activation technique, it is necessary to increase the activation by using a stronger neutron source or a longer activation time or to decrease the X-ray contribution by

using a shorter counting time. Although field use of  $^{252}\text{Cf}$  sources an order of magnitude stronger is considered practicable, we believe that it is preferable to make the counting time short compared with the irradiation time. The irradiation time can be lengthened and the counting time shortened by moving the sonde in steps corresponding to the distance between source and detector, the sonde being held motionless during the irradiation period. Counting at the site of the previous activation is done during a brief interval after the step and avoids buildup of the continuum and of the interfering X rays. Our plans to evaluate this "stepwise activation" technique were aborted by electronic failure of the low-energy sonde. A subsequent simulation was made in our laboratory borehole facility. With the same source and with the repaired sonde in an annulus 75 cm high having a 10-cm bore and a 28-cm radial thickness filled with an ore of about 0.25 percent  $\text{U}_3\text{O}_8$ , we counted for 2 minutes before and after activation for 25 minutes. The ratio of the 74.7-keV net peak to the 77.1-keV net peak was 0.99 before the activation and 6.13 afterwards. On the basis of statistical errors only, we infer a sensitivity of roughly 60 ppm  $\text{U}_3\text{O}_8$  under these conditions. As other counting errors are involved, we feel that this sensitivity may be difficult to realize and that further field tests should be made before application is made at such low concentrations of uranium. However, at higher concentrations the neutron activation may be practically applied as it is substantially unaffected by such drastic recent disruptions of the  $^{238}\text{U}$ - $^{234\text{m}}\text{Pa}$  equilibrium as would be caused by solution mining.

## Conclusions

For assay of uranium in deposits whose equilibrium has been disturbed by leaching within the preceding several months, a stepwise neutron-activation, delayed-gamma technique using a high-resolution detector optimized for low energies is suitable to a sensitivity of the order of 100 ppm  $U_3O_8$  when a  $4 \times 10^8$  n/s  $^{252}Cf$  source irradiates a station for 25 minutes and the resulting activity of  $^{239}U$  is counted promptly for 2 minutes. The stepwise technique has the disadvantages of requiring a neutron source, of needing accurate positioning of the detector at the location previously irradiated, and of not permitting arbitrarily close spacing of data points on the same run. Continuous-motion neutron-activation, delayed-gamma logging is not feasible without very strong sources; that is, of the order of  $10^{10}$  n/s.

For assay of uranium in deposits that have not been leached within the preceding several months, high-resolution gamma-ray spectrometry of the natural radioactivity of the deposit yields good sensitivity, free from the influences of disequilibrium, radon contamination, and thorium. A routine cycle of 10 minutes of measurement and 5 minutes of data reduction and movement to the next station should be practicable and should yield a sensitivity of about 80 ppm  $U_3O_8$ . The high-resolution sonde may operated in a total-count, continuous-motion mode to achieve the same results as conventional scintillation logging at comparable speeds.

In comparison with core assay, high-resolution spectrometry samples a larger volume; avoids problems due to incomplete core recovery, loss of friable material to drilling fluids, and errors in depth and marking; and permits use of less expensive drilling methods. Because gamma rays from

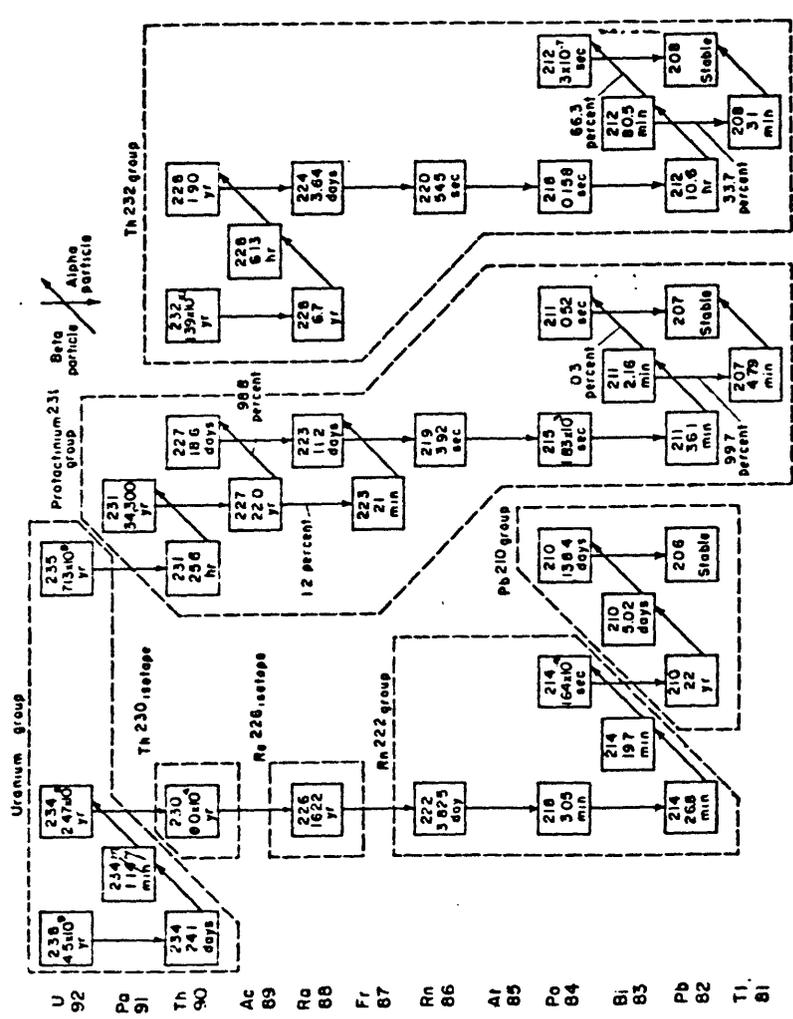
the radionuclides are accumulated simultaneously, it also avoids the problems inherent in trying to correlate logs made in separate runs with different equipment.

## Acknowledgments

We thank the Intercontinental Energy Corporation for access to the boreholes studied and for facilities made available at the site and Daryl R. Tweeton, U. S. Bureau of Mines, for initiating the investigation. Joseph A. Baicker, Peter Ryge, Micha Harchol, and Leonard Goldman, Princeton Gamma-Tech, Inc., have been most helpful in development and optimization of the borehole sondes. This work was supported in part by the Twin Cities Mining Research Center of the U. S. Bureau of Mines.

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Classification of natural radioisotopes into groups, showing atomic numbers, half-life periods, and modes of decay.

From Rosholt, 1959

Figure 1. The natural radioactive series

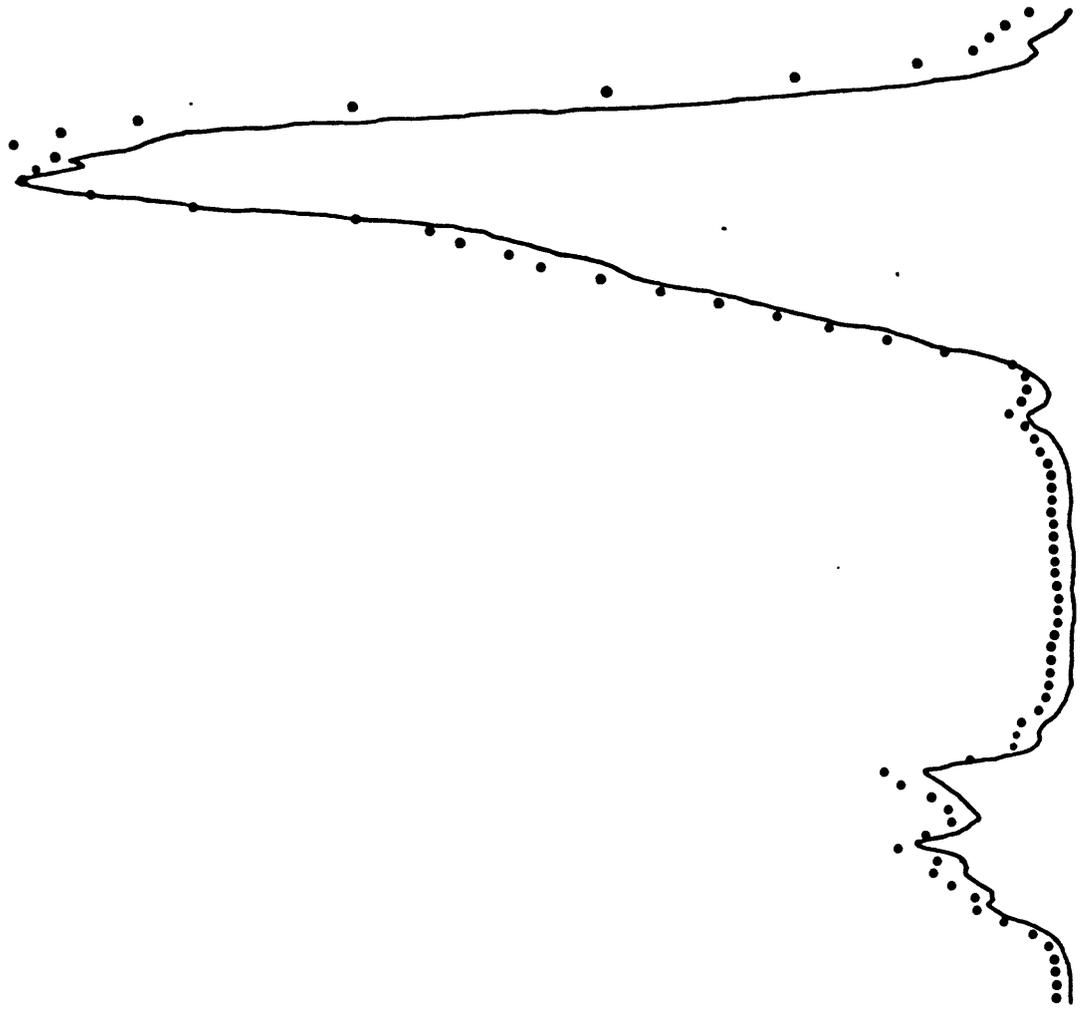


Fig. 2. Comparison of continuous-motion, total count logs made with high resolution detector (dots) and conventional scintillation detector (solid line).

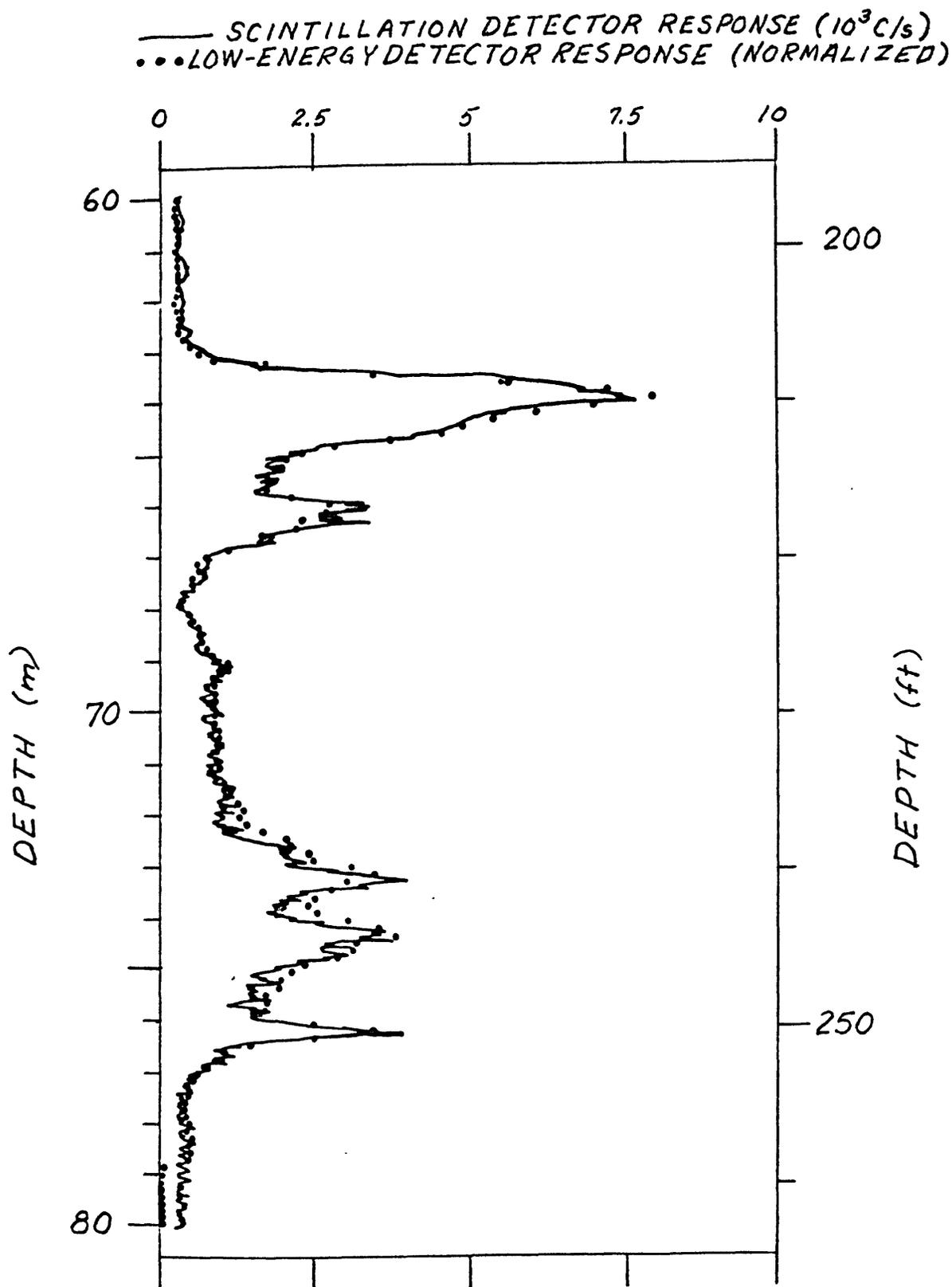


Fig 3. Comparison of continuous-motion, total-count logs made with scintillation detector ascending and low-energy detector descending. (Hole 8)

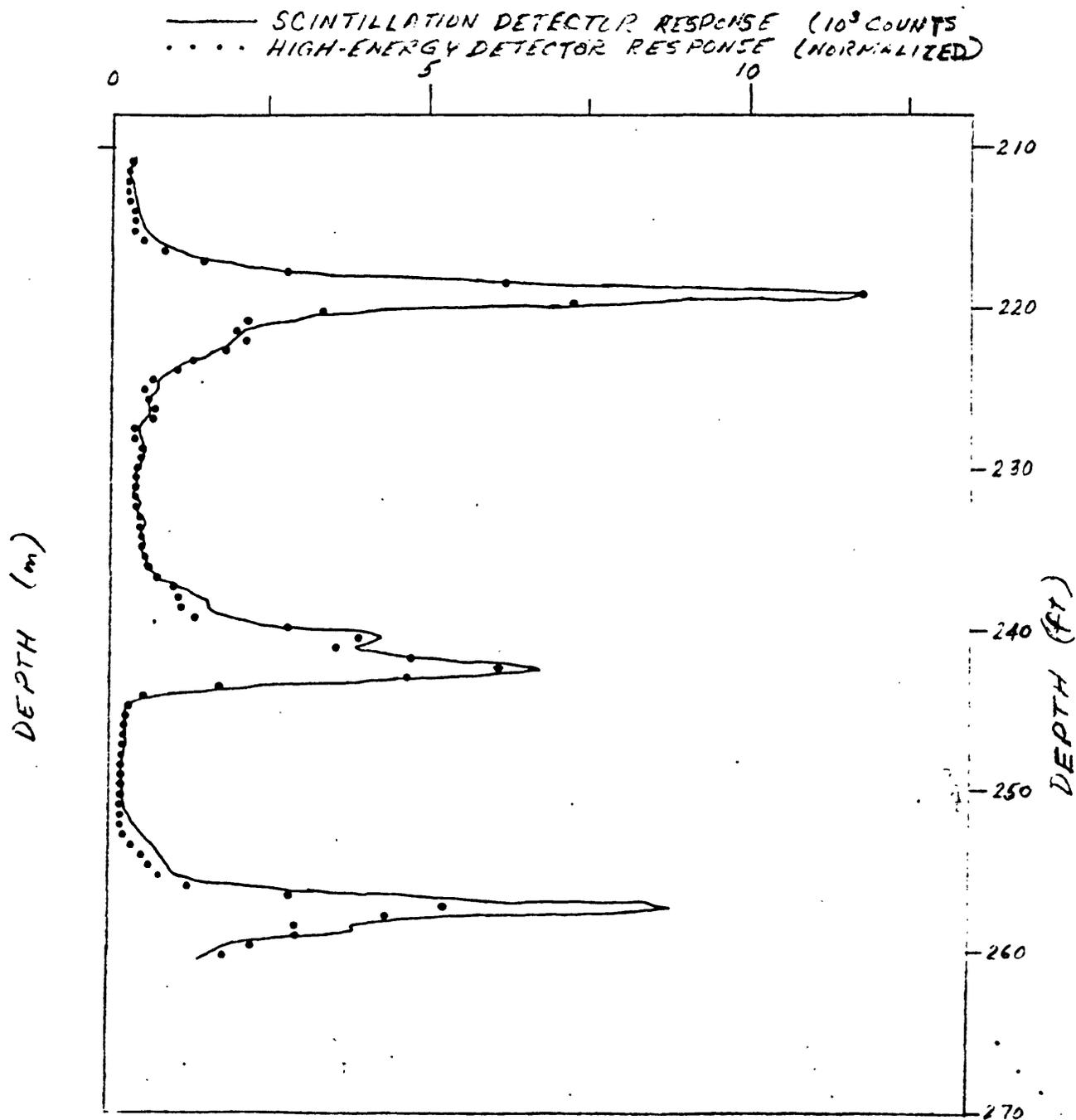


Fig. 4 Comparison of continuous-motion, total-count logs made with scintillation detector ascending and high-energy sonde descending.

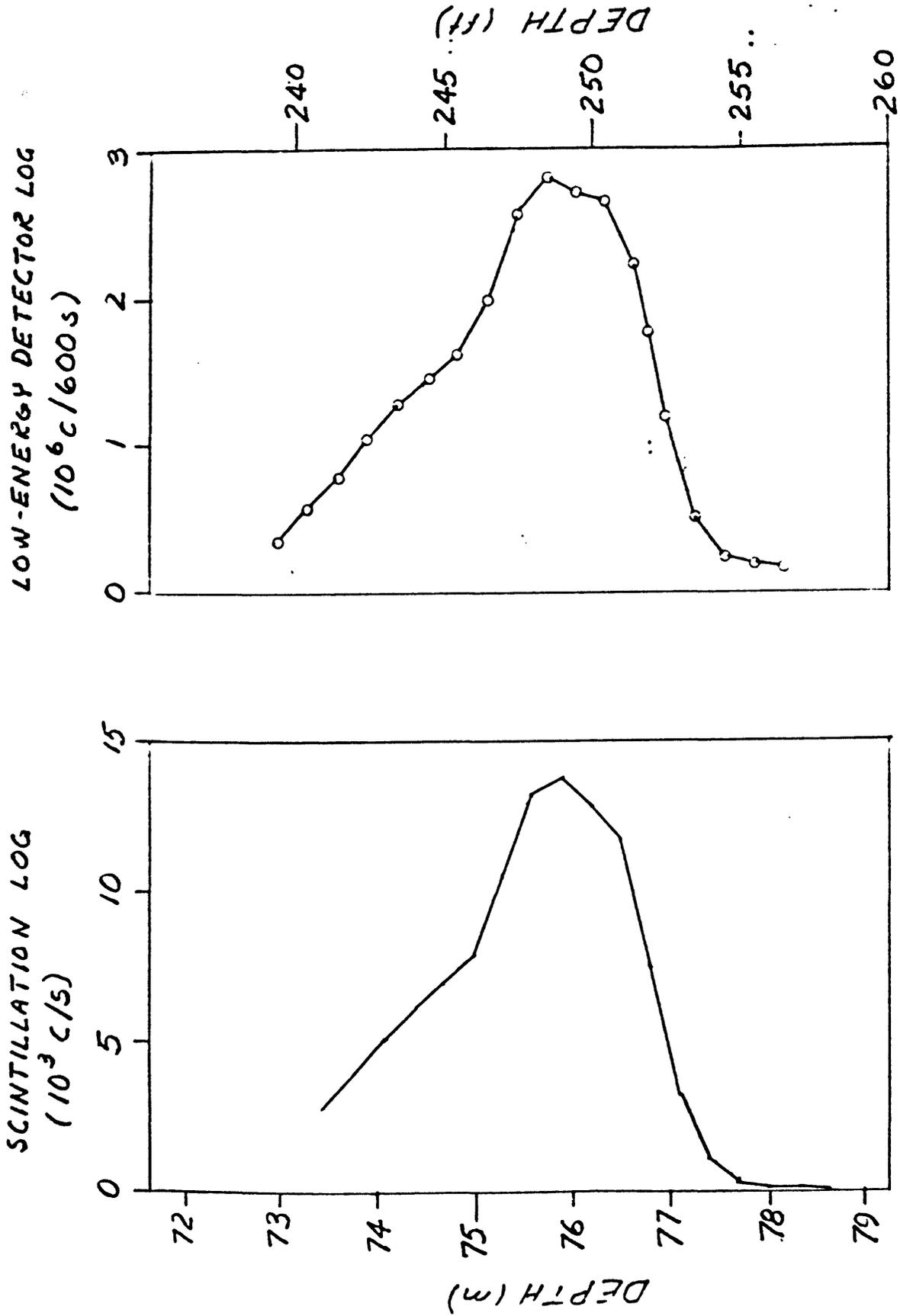


Fig. 5. Comparison of service-company gamma-ray log made with scintillation detector and gamma-ray log made with low-energy germanium detector in 600-second counts at stations shown by circles. The comparison shows close agreement in depth control. For this figure, all counts in the high-resolution spectrum were summed to give the total count at each station. (Hole 4)

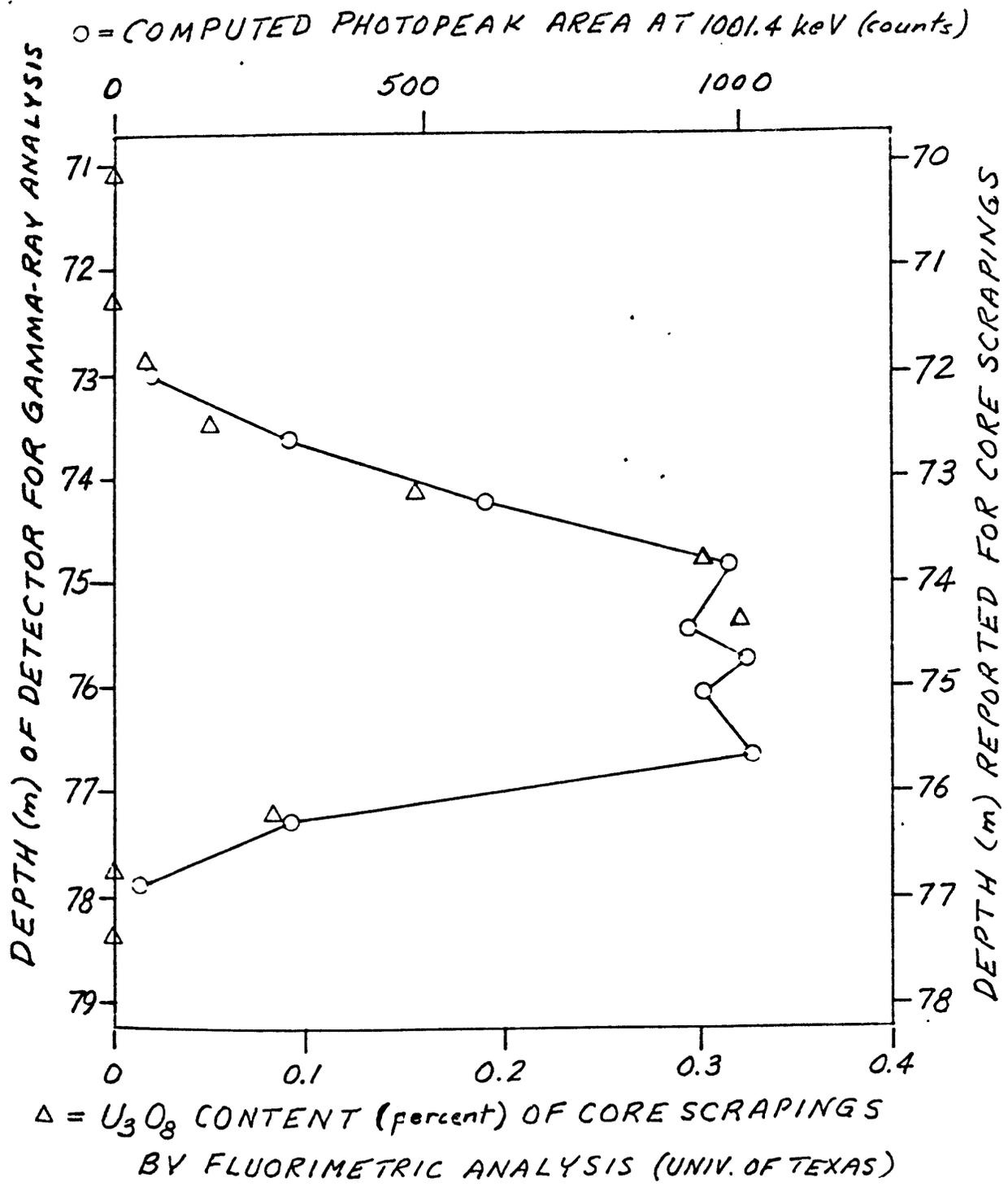


Fig. 6. Reconciliation of log of uranium, as inferred from 1001.4-keV gamma-ray intensity from <sup>234m</sup>Pa and measured with the high-energy sonde in 600-second counts, with uranium content of core scrapings as determined fluorimetrically by the Bureau of Economic Geology of the University of Texas. The gamma-ray log has been normalized on the abscissa and displaced vertically to achieve a best fit with the core analyses. The gamma-ray log is represented by joined circles and the left depth scale; the core log is represented by triangles and the right depth scale. Depths reported for the core scrapings are, by this reconciliation, 1.00 m shallower than those inferred from the gamma-ray log. (Hole 4)

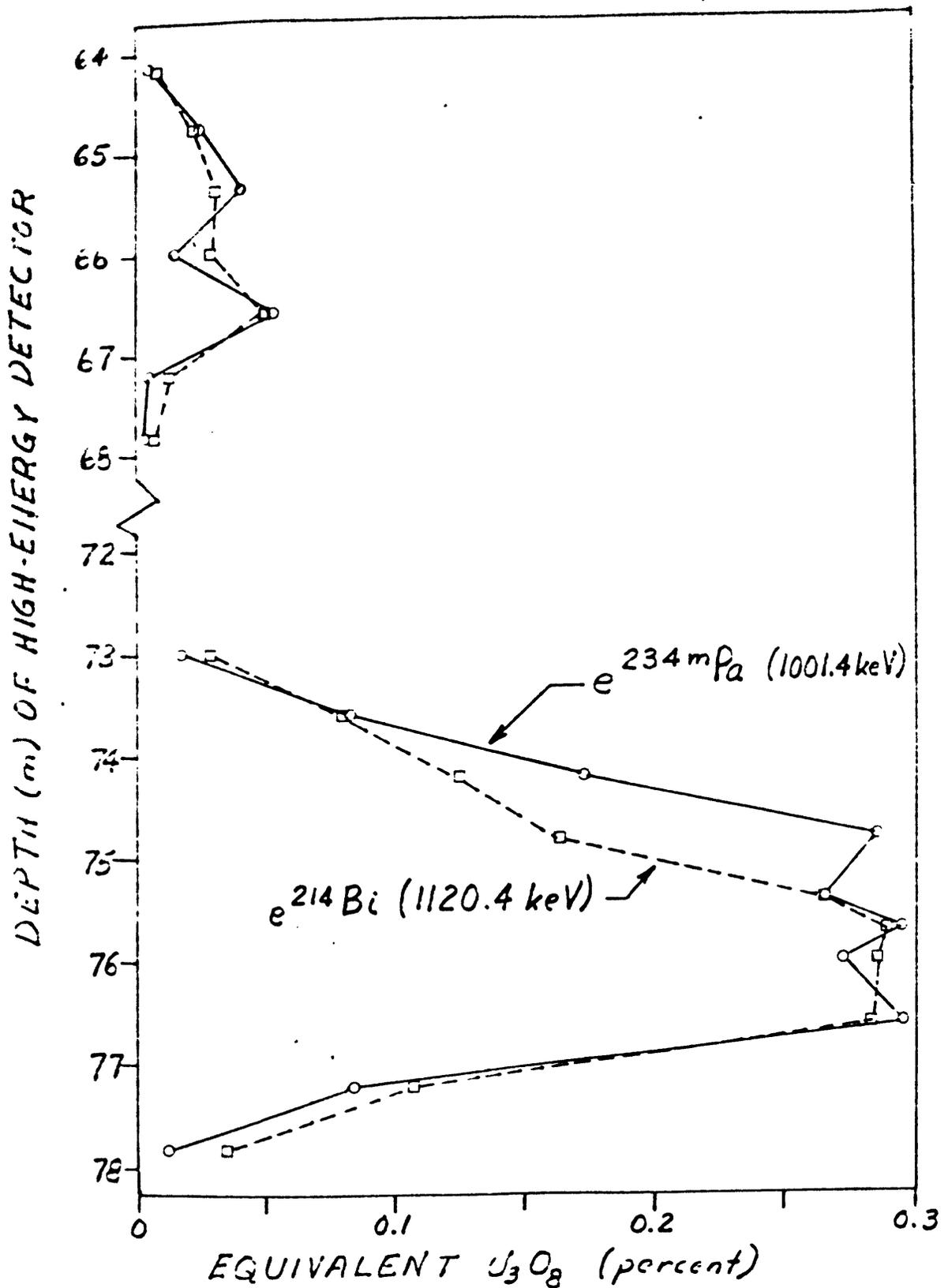


Fig. 7. Logs of the computed peak areas of the 1001.4-keV gamma ray from  $^{234m}Pa$  (circles) and of the 1120.4-keV gamma ray from  $^{214}Bi$  (squares) measured concurrently during 600-second counts at stations in the upper and lower ore zones of hole 4. The points have been adjusted to correspond with the uranium concentrations they would be equivalent to if radioactive equilibrium prevailed. The state of equilibrium and uranium concentration at the 75.44-m level are assumed to be the same as those determined by laboratory gamma-ray spectrometry on sealed core scrapings (USBM 4-245) most nearly corresponding to the 75.44-m level, according to the reconciliation in Figure 6.

NET AREA OF 63.3-keV PEAK (Relative units)

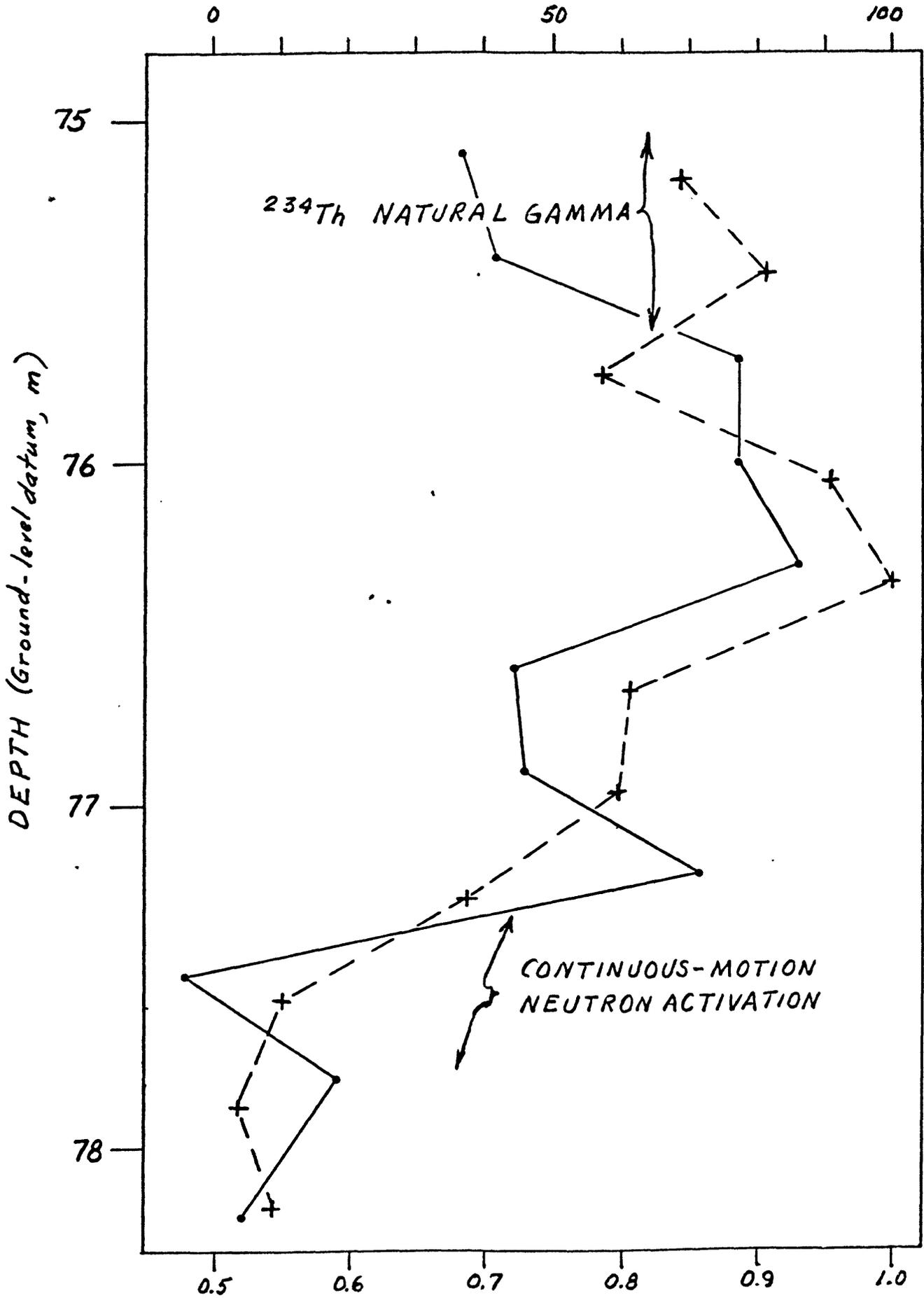


FIG. 11 Comparison of natural gamma-ray and neutron-activation logs for lower part of hole 4.

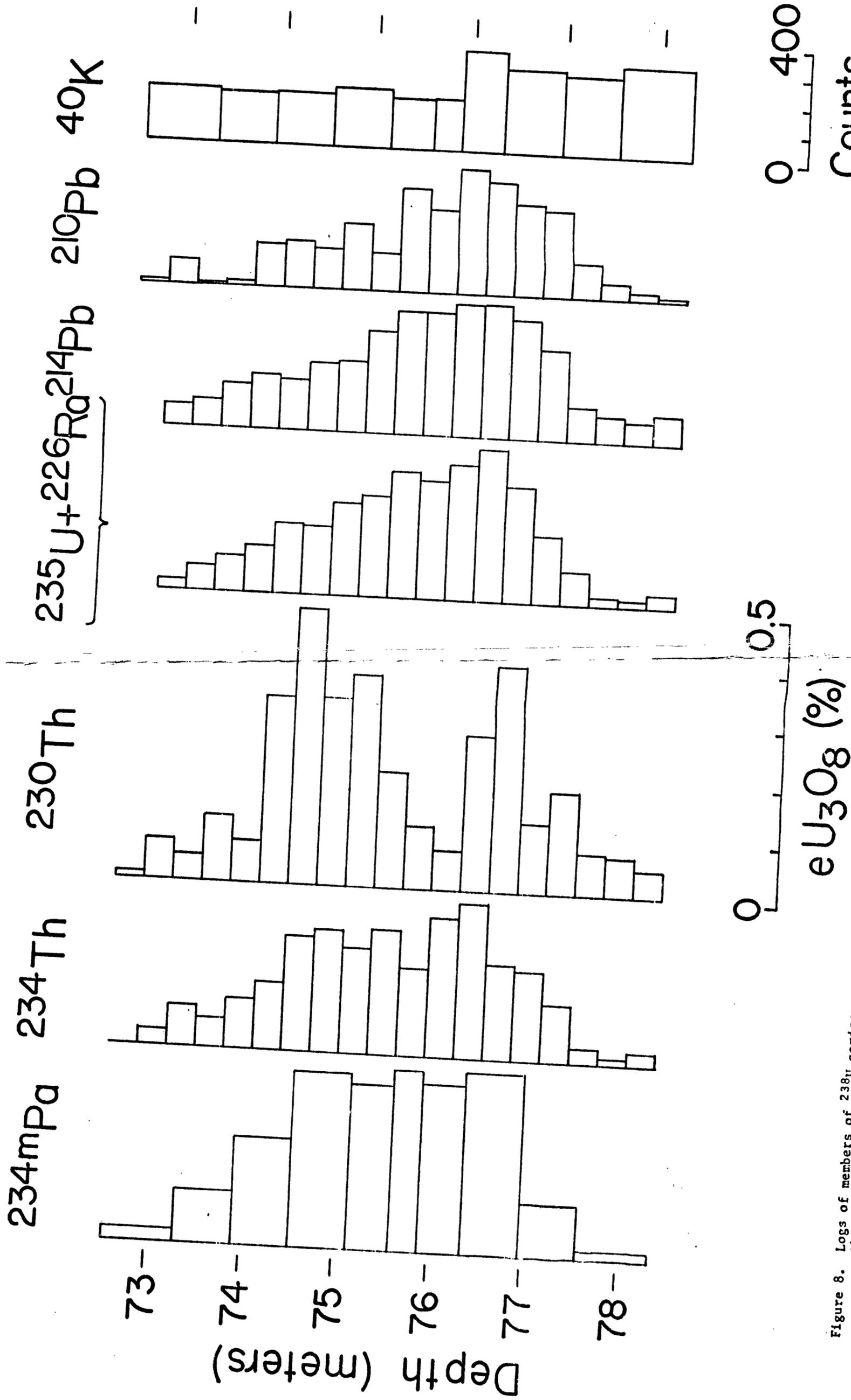


Figure 8. Logs of members of <sup>238</sup>U series representative of groups in the series. The log of <sup>40</sup>K is representative of potassium. (Hole 4)

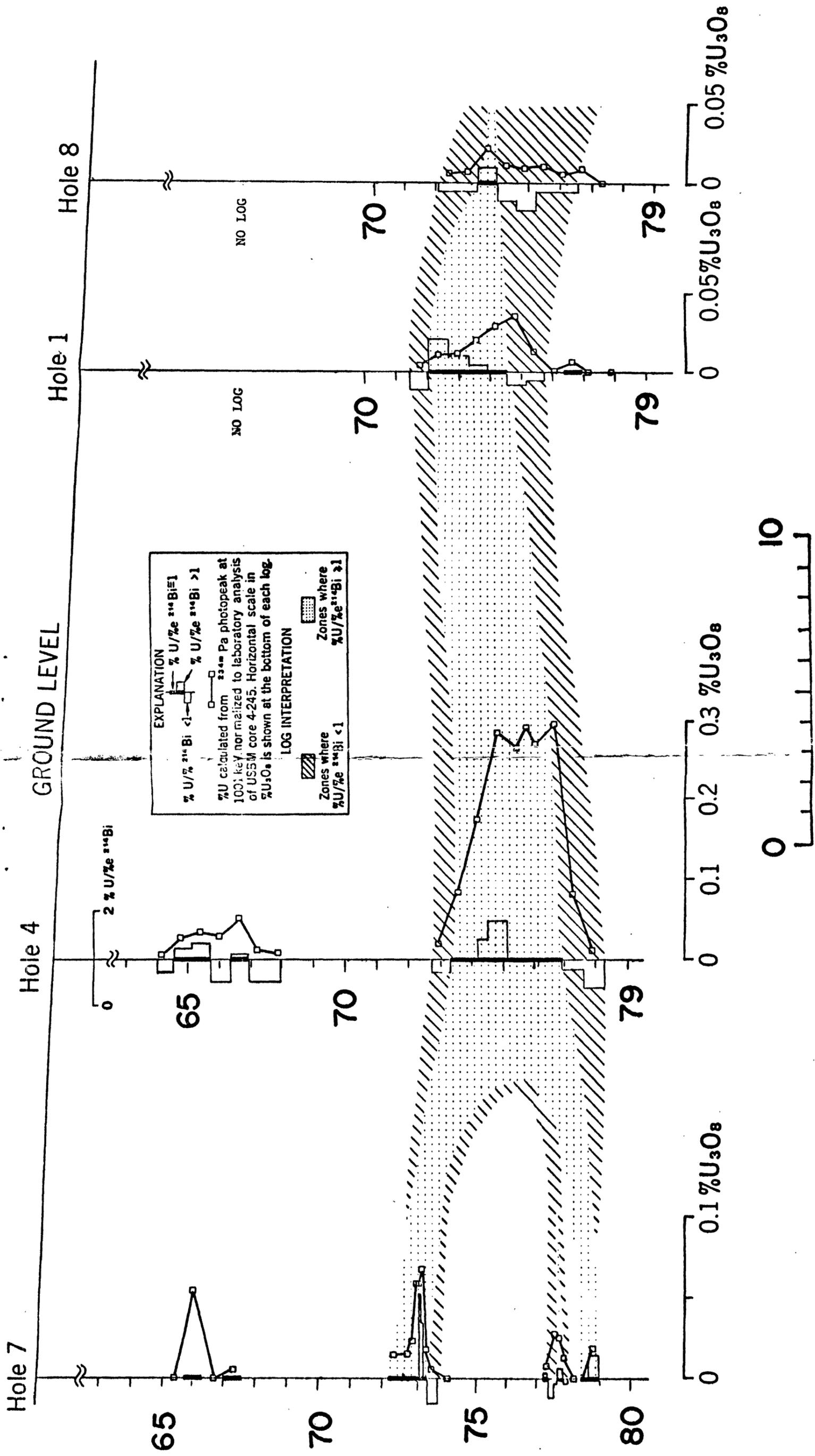


Figure 10. Cross section showing logs of uranium and equilibrium ratios,  $U/e^{214}\text{Bi}$ , and inferred pattern of ore and disequilibrium at Pawnee Mine.

Scale (meters)

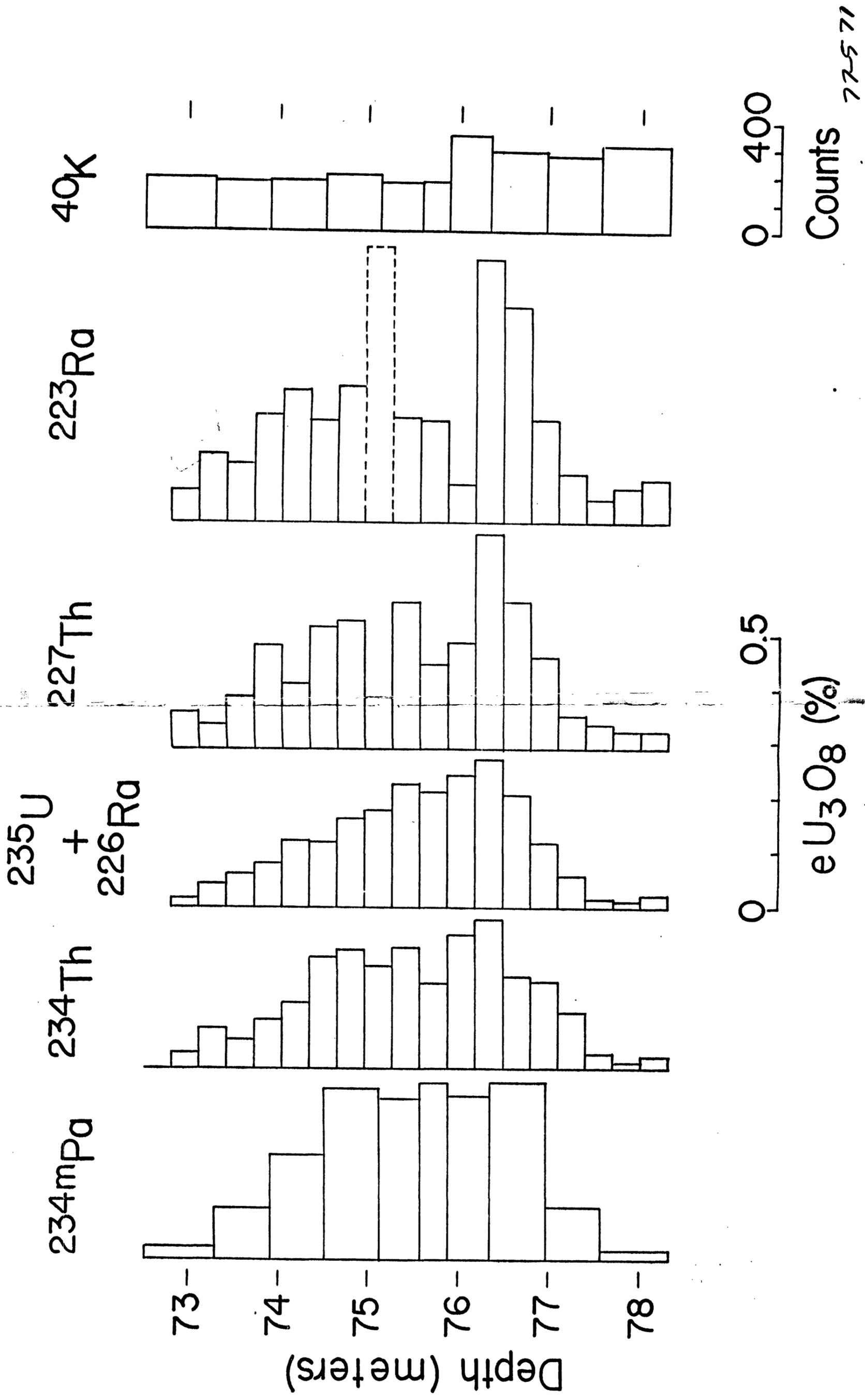


Figure 9. Logs of numbers of <sup>226</sup>U and <sup>235</sup>U series and of <sup>40</sup>K. The log of <sup>235</sup>U is better inferred from the two logs at left.