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RADIOACTIVE DISEQUILIBRIUM DETERMINATIONS

Part 1: Determination of radioactive disequilibrium in uranium ores by alpha-spectrometry

P.G. KILLEEN
C.M. CARMICHAEL

Part 2: Radioactive disequilibrium investigations, Elliot Lake area, Ontario

L. OSTRIHANSKY

Energy, Mines and
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FOREWORD

The Geological Survey of Canada has a long history of scientific investigations relating to the discovery and measurement of natural radioactivity.

When an expanded research and development program involving the field and airborne use of gamma-ray spectrometry commenced in 1967, the possibility that extensive surface disequilibrium might seriously affect the usefulness of spectrometry measurements was very much in mind.

Disequilibrium is obviously of prime concern in the normal situation where a measurement of ^{214}Bi abundance is used as an indirect measure of uranium content. Preliminary field investigations made in 1966 and 1967 in areas containing various forms of uranium mineralization at the surface confirmed quite clearly that there is a strong positive correlation between count rate due to ^{214}Bi, and uranium content. This was sufficient to justify the continued development of field methods based on gamma-ray spectrometry. Nevertheless it was considered desirable to investigate the disequilibrium problem in greater detail, and two independent studies were initiated, both focussing on material from the Elliot Lake area. One study was conducted by P. G. Killeen, and was commenced whilst he was an assistant with the Geological Survey. The other was undertaken by Dr. L. Ostrihansky during tenure of a Post Doctoral Fellowship.

The first paper in this publication, by Dr. P. G. Killeen and Professor C. M. Carmichael, reports work which largely concentrated on developing a technique for disequilibrium determination by alpha-spectrometry. The second paper by Dr. Ostrihansky, reports work which used both solid state Ge(Li) and NaI(Tl) detectors to undertake detailed gamma-spectrometric studies of short cores from Elliot Lake. Both studies encountered considerable problems with the analytical methods selected, and most of the efforts of the investigators were devoted to establishing their techniques. Neither was wholly successful in this respect since neither method can be applied to rocks containing average amounts of the radioelements.

The papers published here are a record of what has been tried, and what has been achieved, and as such should be a valuable guide to future investigators. Improved methods capable of being applied at ordinary levels of soil and rock radioelement concentration still need to be developed, with the intention of making more numerous systematic studies of the general type reported here by Dr. Ostrihansky. Our ability to extract significant information from measurements of surface radioactivity is dependent upon having the fullest possible knowledge of the extent and variety of disequilibrium effects in different situations.

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PART 1: DETERMINATION OF RADIOACTIVE DISEQUILIBRIUM IN URANIUM ORES BY ALPHA-SPECTROMETRY

P.G. Killeen and C.M. Carmichael

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Abstract

The natural radiation from rocks and minerals is primarily from ^{40}K *and the* ^{238}U *and* ^{232}Th *radioactive decay series. This is composed of alpha particles of 23 different energies, along with beta and gamma radiation.*

Although the analysis of rocks for uranium content by gamma-ray spectrometry is a rapid and efficient method, it depends on the crucial assumption that the ^{238}U *decay series is in radioactive equilibrium. An* α*-spectrometric method of detecting the presence of disequilibrium in the* ^{238}U *decay series has been developed. A silicon semi-conductor detector and a 1024 channel pulse height analyzer were used to obtain alpha particle energy spectra of uraniferous rocks and minerals. "Infinitely thick" sources were used to avoid the problems involved in preparation of "infinitely thin" sources. The method involves the generation of theoretical energy distributions for infinitely thick sources. Complete theoretical spectra were computed for comparison with experimentally obtained alpha particle energy spectra of rocks and minerals. The presence and extent of disequilibrium in the* ^{238}U *decay series in a rock is determined from the residual spectrum obtained by subtracting a fitted theoretical spectrum from the measured spectrum of a rock.*

Résumé

Le rayonnement naturel émanant des roches et des minéraux provient principalement ^{40}K *et des familles radioactives de l'uranium (*^{238}U*) et du thorium (*^{232}Th*). Ce rayonnement comporte des particules alpha de 23 énergies différentes, ainsi que des rayonnements bêta et gamma.*

Bien que l'analyse des roches en vue de la détermination de leur teneur en uranium par la spectrométrie aux rayons gamma soit une méthode rapide et efficace, elle repose sur l'hypothèse cruciale que la famille de l'uranium (^{238}U*) est en équilibre radioactif. Les auteurs ont mis au point une méthode permettant de déceler la présence de déséquilibre dans la famille de l'uranium, par la spectrométrie à rayons alpha. Ils utilisent un détecteur semiconducteur au silicium et un analyseur à canaux multibles (1024) d'impulsions d'amplitude pour obtenir le spectre d'énergie des particules alpha de minéraux et de roches uranifères. Ils utilisent des sources "infiniment épaisses" pour éviter les problèmes que pose la préparation des sources "infiniment minces". Cette méthode exige que l'on détermine d'abord les fonctions de distribution d'énergie théoriques dans le cas de sources infiniment épaisses. Des spectres complets théoriques ont été calculés et comparés à des spectres d'énergie des particules alpha obtenus expérimentalement pour des roches et des minéraux. La présence et l'importance du déséquilibre dans la famille de l'uranium, dans une roche donnée, sont déterminées à partir du spectre résiduel obtenu en soustrayant un spectre théorique approprié du spectre d'une roche, mesuré expérimentalement.*

PART 1: DETERMINATION OF RADIOACTIVE DISEQUILIBRIUM IN URANIUM ORES BY ALPHA-SPECTROMETRY

INTRODUCTION

The most commonly used method of analysis for uranium and thorium in geologic materials is that of gamma-ray spectrometry. The method involves the counting of gamma rays of energies usually chosen as 1.76 Mev and 2.62 Mev for the uranium and thorium analyses respectively. These gamma radiations are actually produced by daughter products Bismuth-214 in the ^{238}U decay series and Thallium-208 in the ^{232}Th decay series as shown in Figure 1.1. The gamma-ray count rate is then used to compute the amount of parent, assuming there is a relationship between the amount of daughter and parent. This assumption is more precisely defined by stating that the radioactive decay series is assumed to be in a state of secular equilibrium.

Radioactive Equilibrium

A radioactive decay series such as that for ^{238}U is said to be in a state of secular equilibrium when the number of atoms of each daughter in the series being produced is equal to the number of atoms of that daughter being lost by radioactive decay. The laws of radioactive decay have been discussed in numerous textbooks (eg. Arya, 1968).

The rate of loss by decay is proportional to the amount of radioelement present, i.e.

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \tag{1}$$

where N_1 = the amount of element N_1

λ_1 = the decay constant for the element N_1

then the rate of decay of the daughter of N_1 is given by the difference between its loss rate and its production rate from its parent, i.e.

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \tag{2}$$

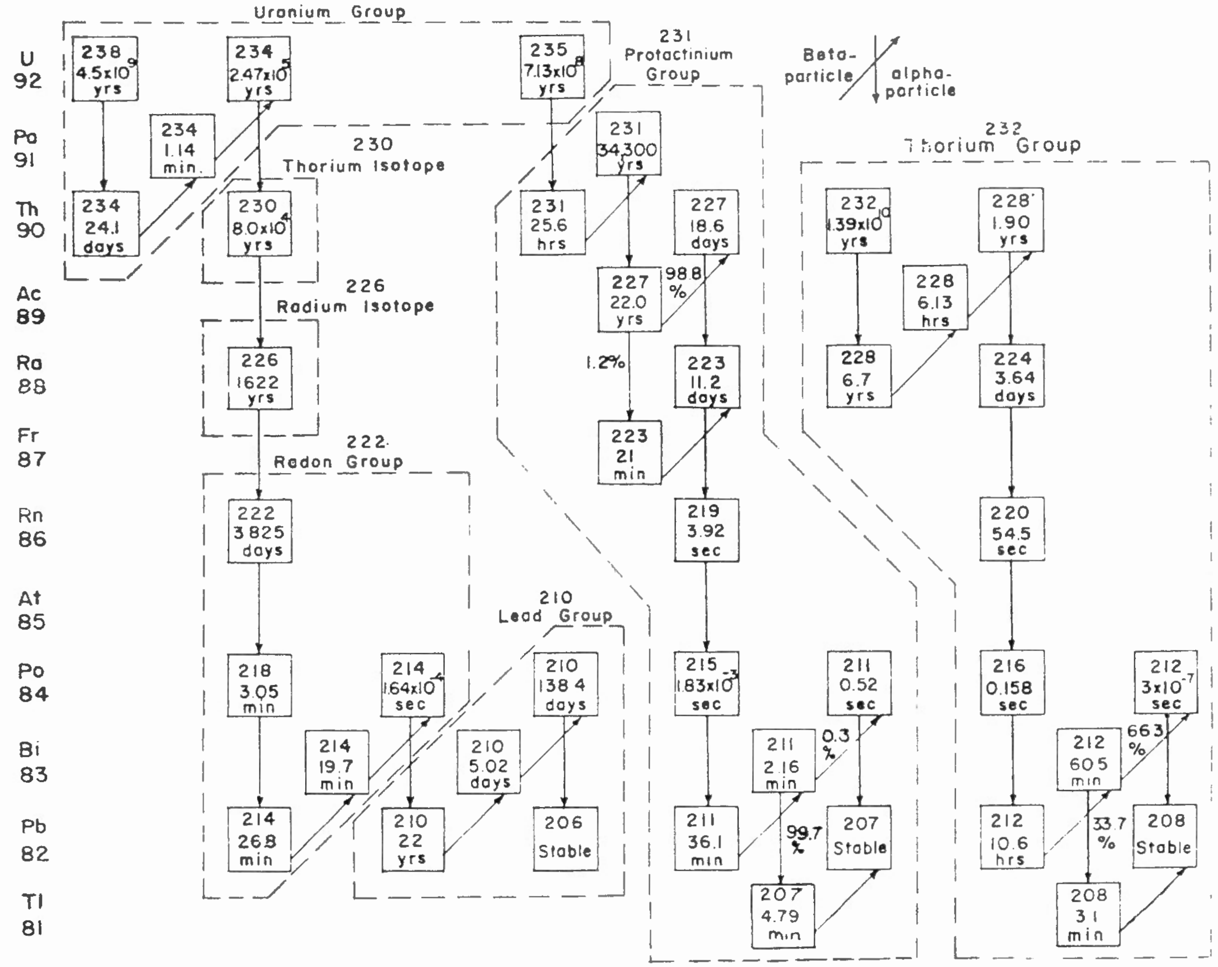

Figure 1.1. The natural radioactive decay series (after Rosholt, 1958).

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It can be shown that after a long period of time the amount of daughter is constant. Its rate of production from parent is equal to its rate of loss by its own decay. This is then a state of secular equilibrium.

For a radioactive decay series, secular equilibrium implies that

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \ldots . \lambda_n N_n \qquad (3)$$

The question then becomes whether the assumption of secular equilibrium, required for analysis by gamma-ray spectrometric techniques, is valid for the geologic material being analyzed for its uranium or thorium content.

If one or more of the daughter products has been lost by any process other than radioactive decay, then equation (3) is not satisfied. Since each daughter product is a different chemical element, they will behave differently in the same environment. For example, Radon-222 in the ^{238}U decay series is a gas, and it could possibly be lost to the decay system during its 3. 8-day half-life. The chemical solubility of radium and uranium and thorium isotopes also differ, and preferential leaching of isotopes is another possibility.

The ^{232}Th decay series can be safely assumed to be in radioactive equilibrium since the largest half-life of all the daughters in the series is 6. 7 years, that of Radium-228. Thus even if the series were disturbed by a metamorphic event, it would cause only temporary disequilibrium, and would in geological terms be 'instantly' returned to equilibrium.

The ^{238}U decay series, on the other hand, contains daughters with half-lives which are of appreciable length even geologically such as ^{234}U with half-life equal to 250 000 years and ^{230}Th with a half-life of 80 000 years. A disturbance resulting in loss of a daughter would not quickly be restored to equilibrium. The assumption of equilibrium of the ^{232}Th series is also supported by the fact that Radon-220 has a half-life of 54. 5 seconds, not long enough for it to escape, while the ^{238}U series produces Radon-222 with a half-life of 3. 82 days, a significant time in which it could possibly escape. The assumption of thorium series equilibrium is further supported in the literature by Mero (1960).

Previous Investigations

Mero (1960) described a method determining the presence of equilibrium by the use of gamma-ray spectrometry, involving comparison of gamma count rates at 0. 190 Mev and 0. 240 Mev. Coquema *et al.* (1963) described a combination radiochemical analysis and alpha, beta and gamma counting technique used to study radioactive disequilibrium and its relation to geochronology. Richardson (1964) studied drill cores of Conway granite of New Hampshire with a radiochemical separation, electro-deposition, and thin-source alpha spectrometric analysis. The top 15 feet were deficient in ^{234}U, an example of isotopic fractionation of uranium in nature. Somayajulu *et al.* (1966) reported on the disequilibrium observed in the ^{238}U series of basalt samples from Hawaii, Japan and Iwo Jima. Their technique was a combination of radiochemical separation and mass spectrometry. Rosholt (1954, 1957) described quantitative radiochemical methods for determining the sources of natural radioactivity.

Rosholt (1958) subdivided the ^{238}U decay series into five distinct groups for equilibrium studies. These consist of the uranium group, ^{230}Th alone, ^{226}Ra alone, the ^{222}Rn group, and the ^{210}Pb group (*see* Fig. 1. 1). The uranium group contains ^{238}U and its immediate daughters up to and including ^{214}Po. The ^{210}Pb group contains the remaining daughters in the series. When the relative abundances of each group are known, the extent of disequilibrium is completely defined. Each group can be assumed to be in equilibrium as a unit, but disequilibrium may exist between groups.

Rosholt (1959) discussed the geochemical processes affecting ore deposits and their relation to radioactive disequilibrium. His studies indicated that six basic types of disequilibrium can occur in present-day radioactive deposits. These are summarized by Ostrihansky (this publ., Pt. 2).

Rosholt (1960) described four different types of uranium migration in sandstone-type ore deposits. In another paper Rosholt and Dooley (1960) described the radiochemical analysis technique which they improved since the early work of Rosholt (1954). Rosholt (1961a), Robinson and Rosholt (1961) and Rosholt (1961b) elaborated on uranium migration in sandstones as studied above, and were able to relate the amount of disequilibrium to the apparent date of migration. Rosholt *et al.* (1963) described isotopic fractionation of uranium in some sandstones with a range of from 40 per cent excess ^{234}U to 40 per cent deficient ^{234}U. The surprising result of ^{234}U being leached preferentially to ^{238}U is considered due in part to changes in oxidation states. Isotopic disequilibrium was also found by Pierce and Rosholt (1961) in uranium-bearing asphaltite nodules in dolomite. Dooley *et al.* (1964) reported radioactive disequilibrium in roll features of the uranium deposits of Shirley Basin, Wyoming, using Rosholt's technique. They found the uranium contained ^{230}Th in excess of the amount required for equilibrium with ^{234}U.

Fractionation of uranium isotopes and daughter products in weathered granite and uranium-bearing sandstone has been reported in the Wind River Basin of Wyoming (Rosholt *et al.*, 1964). Ratios of ^{235}U/^{234}U and of ^{234}U/^{238}U were determined with a mass spectrometer. Rosholt *et al.* (1965a) studied ^{234}U/^{238}U ratios in Wyoming and in Colorado uranium ores and found deficiencies of ^{234}U from 40 to 60 per cent. The date of migration of the ^{234}U in the above mentioned areas was determined to be at least 100 000 years (Rosholt, *et al.*, 1965b). Rosholt and Ferreira (1965) found ^{234}U deficiencies of 7 to 29 per cent in samples from the Wentz mine in Wyoming, in relation to the water table.

Objectives

The problem of radioactive disequilibrium in the ^{238}U decay series has been studied primarily by elaborate and tedious radiochemical analysis techniques

TABLE 1.1

Statistics for Alpha Particle Decay of ^{238}U and ^{232}Th

^{238}U DECAY SERIES IN EQUILIBRIUM

Energy (Mev)	Per cent	Decay Order	Isotope	Half-Life	Range in Air (cm)
4.20	77.0	1.0	U238	4.51 x 10^{9}Y	2.65
4.15	23.0	1.0	U238	4.51 x 10^{9}Y	2.65
4.80	72.0	2.0	U234	2.47 x 10^{5}Y	3.21
4.75	28.0	2.0	U234	2.47 x 10^{5}Y	3.21
4.70	76.0	3.0	Th230	8.00 x 10^{4}Y	3.09
4.65	24.0	3.0	Th230	8.00 x 10^{4}Y	3.09
4.85	94.6	4.0	Ra226	1622 Y	3.26
4.60	5.4	4.0	Ra226	1622 Y	3.00
5.50	100.0	5.0	Rn222	3.83 Day	4.05
6.00	100.0	6.0	Po218	3.05 Min	4.66
7.70	100.0	7.0	Po214	1.6 x 10^{-4}Sec	6.91
5.30	100.0	8.0	Po210	138.4 Day	3.84

^{232}Th DECAY SERIES IN EQUILIBRIUM

Energy (Mev)	Per cent	Decay Order	Isotope	Half-Life	Range in Air (cm)
4.01	77.0	1.0	Th232	1.41 x 10^{10}Y	2.10
3.95	23.0	1.0	Th232	1.41 x 10^{10}Y	2.10
5.42	71.0	2.0	Th228	1.91 Y	3.95
5.34	28.0	2.0	Th228	1.91 Y	3.95
5.68	94.5	3.0	Ra224	3.64 Day	4.28
5.45	5.5	3.0	Ra224	3.64 Day	4.00
6.28	100.0	4.0	Rn220	55.0 Sec	5.00
6.78	100.0	5.0	Po216	0.15 Sec	5.64
6.09	9.8	6.0	Bi212	60.6 Min	4.73
6.04	24.9	6.0	Bi212	60.6 Min	4.73
8.78	64.0	7.0	Po212	3.0 x 10^{-7}Sec	8.57

involving combinations of mass spectrometric isotope ratio determinations, and more recently, thin-source alpha particle spectrometric analysis of some of the radiochemically separated isotopes. Another promising method made possible with the development of high resolution lithium drifted germanium detectors involves counting gamma-rays of low energies (Lewis, 1974; Ostrihansky, this publ.).

Since most techniques involve elaborate, time consuming sample preparation, with the consequent possibility of introducing disequilibrium, the present objective was to develop a technique for detecting the presence of disequilibrium which minimized sample preparation time. The characteristic energies of the alpha particles were to be utilized in alpha spectrometry with a large silicon semi-conductor detector, which provides very good energy resolution. Ideally, the method should not only detect the presence of disequilibrium in a rock sample, but also identify any radioelement which is the cause of the disequilibrium.

Theoretical Alpha Particle Spectra

A study of the energy spectra of alpha particles emitted by radioisotopes of the ^{238}U decay series along with the ^{235}U series and the ^{232}Th series which are associated with it, requires such knowledge as the peak energies, peak intensities or activities, order of decay and half-lives of all isotopes in the series. Most of these data are available in 'Table of Isotopes' compiled by Lederer *et al.* (1968). Table 1.1 lists the pertinent data for the ^{238}U series, and the ^{232}Th series for radioactive equilibrium conditions. The energies are given in Mev, and intensity is in relative percentages where the number of decays of parent element represents 100 per cent. The range in air is measured in centimetres and is taken from Nogami and Hurley (1948). The ^{235}U component in the alpha spectrum is negligible compared to the ^{238}U component since $^{238}U/^{235}U = 137.8$ (Hyde *et al.*, 1964). Since most rocks contain thorium along with uranium, the thorium series data are important. The Th/U in most rocks in the lithosphere is about 4.0 (Adams, 1962).

The relative activities of the series are also important. The specific activities given by Hyde *et al.* (1964) are:

1 mg of pure natural Uranium with isotopes in proper ratios emit 1501 alphas per minute	^{238}U =	733.6 dpm
	^{234}U =	733.6 dpm
	^{235}U =	33.7 dpm

The specific activity for ^{232}Th is 246 dis/min/mg (Hyde *et al.*, 1964). Thus the ^{232}Th series is roughly one third as active as the ^{238}U series, but in an average rock the amount of thorium is roughly 4 times that of uranium so the contributions are comparable.

A theoretical alpha particle energy spectrum combining both the ^{238}U and ^{232}Th series is shown in Figure 1.2. This spectrum represents that expected for a sample with a Th/U ratio = 3.5. Here the parent ^{238}U is taken as 100 per cent and all isotopes of both series are relative to the ^{238}U.

The highest peaks in Figure 1.2 (nos. 20 and 21) are from the ^{232}Th series as expected since the ratio of activities of $^{238}U/^{232}Th$ is 733.6/246.0 and the Th/U ratio is 3.5, slightly larger than the activity ratio. The thorium component of the alpha spectrum of a uranium ore sample would be much less than that shown in Figure 1.2. Most uranium ore contains a certain amount of thorium, but the average ratio for rocks mentioned above does not hold for the anomalous conditions of an

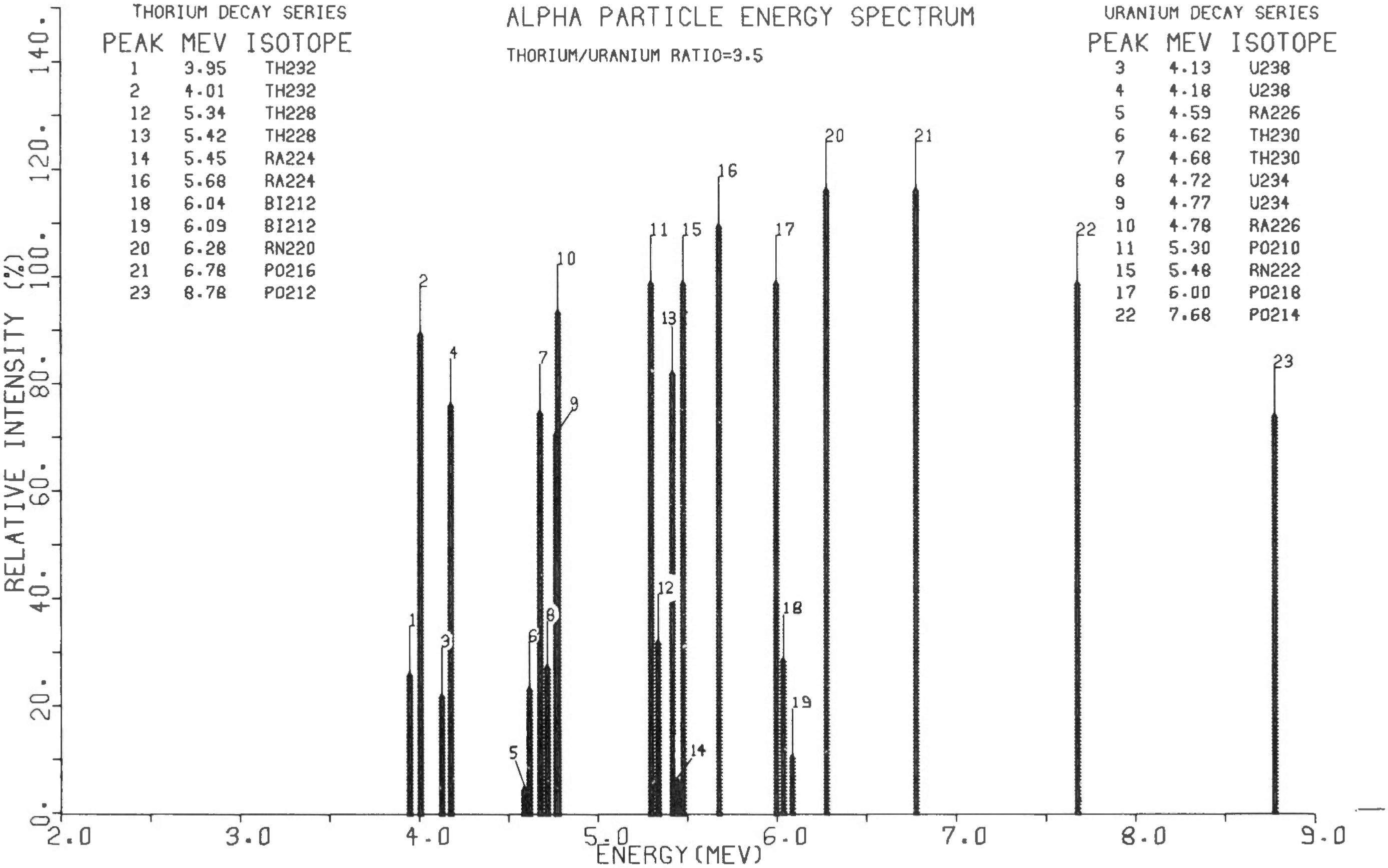

Figure 1.2. A theoretical alpha particle energy spectrum. Peaks number 3 and 4 from ^{238}U sum to 100 per cent. The other peak intensities are computed relative to the ^{238}U intensity.

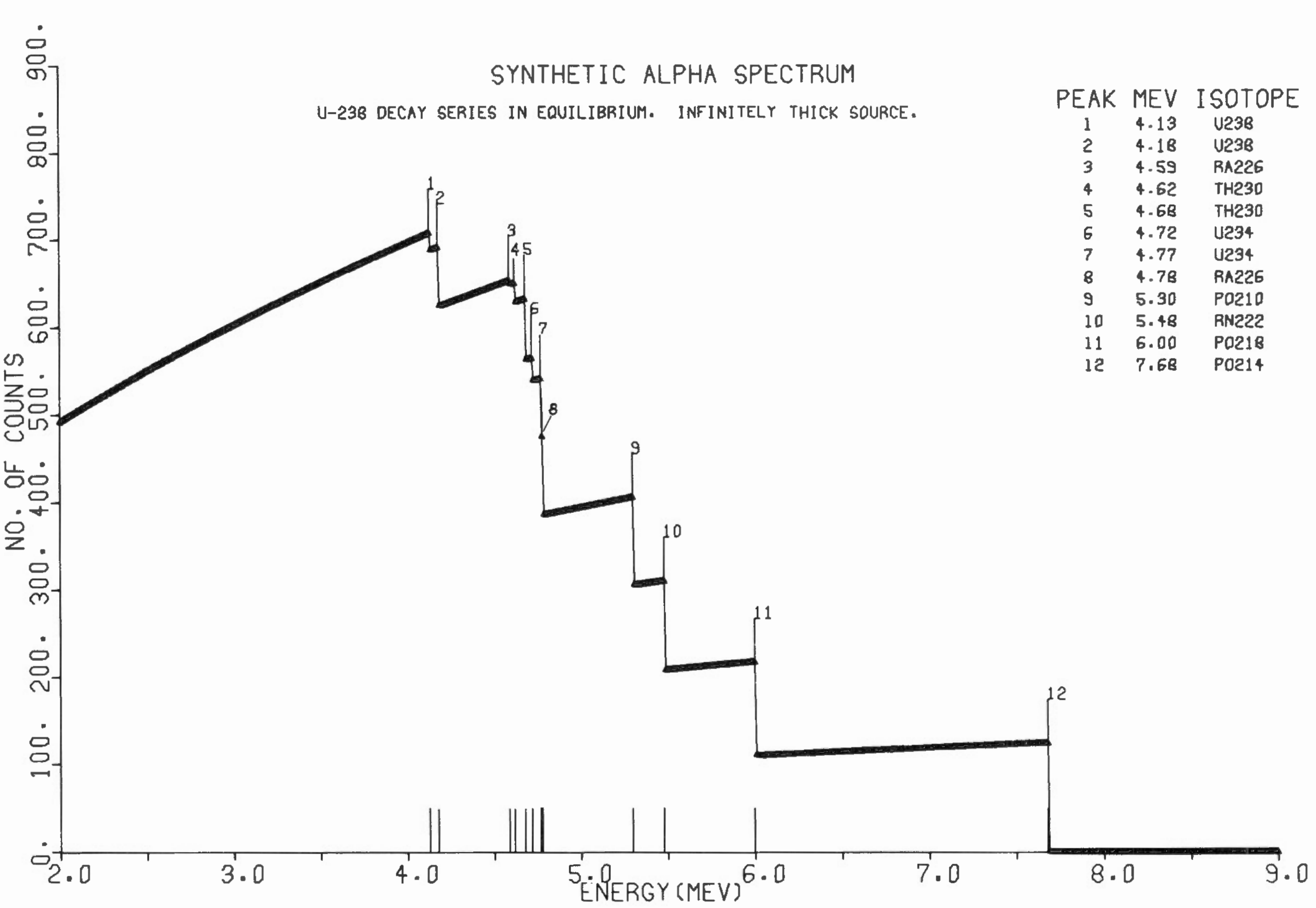

Figure 1.3. A synthetic alpha particle energy spectrum from an infinitely thick source for the ^{238}U decay series in radioactive equilibrium.

orebody. Having discussed the theoretical alpha particle energy spectrum, the effects of absorption and the actual experimentally measured spectrum must be considered.

The interaction of alpha particles with matter causes a loss in energy which is related to the amount of material through which the alpha particle travels. For any given material, and a given initial energy for the alpha particle there is a particular range or mean free path. The range-energy relationship for alpha particles originally formulated by Geiger in 1910 as a range-velocity relation is described by Glasstone (1967) as:

$$R = 3.09\, E^{3/2} \qquad (4)$$

where R = range in air in centimetres, and E = energy in Mev. The Geiger formula is applicable only for alpha particles with ranges from 3 to 7 cm of air, equivalent to 4.0 Mev to 8.0 Mev energies. An approximate expression for range of alpha particles in solids is given by the Bragg-Kleeman relation (Lapp and Andrews, 1963).

Thin-Source Alpha Particle Spectrometry

The shape of the energy distribution of a mono-energetic alpha particle being emitted from a source will be dependent upon the amount of material through which it passes. From equation (4) it can be seen that there is a given range for the given alpha particle energy. If the thickness of the source layer through which it travels is greater than the range of the alpha particle, it will not be emitted from the source at all, but will be totally absorbed. For source thickness less than the range of alpha particles, it will be emitted but with an energy less than its initial energy. In a homogeneous distribution of alpha emitters in the source, the alphas originating at the surface of a sample in a vacuum chamber are unaffected and are able to reach the detector with no energy loss. As a result, a continuous distribution of alpha energies from zero up to the initial energy of emission, are recorded. This complex 'tail' of energy distribution will have a shape that is dependent on the source thickness. To simplify the determination of the alpha particle energy, and

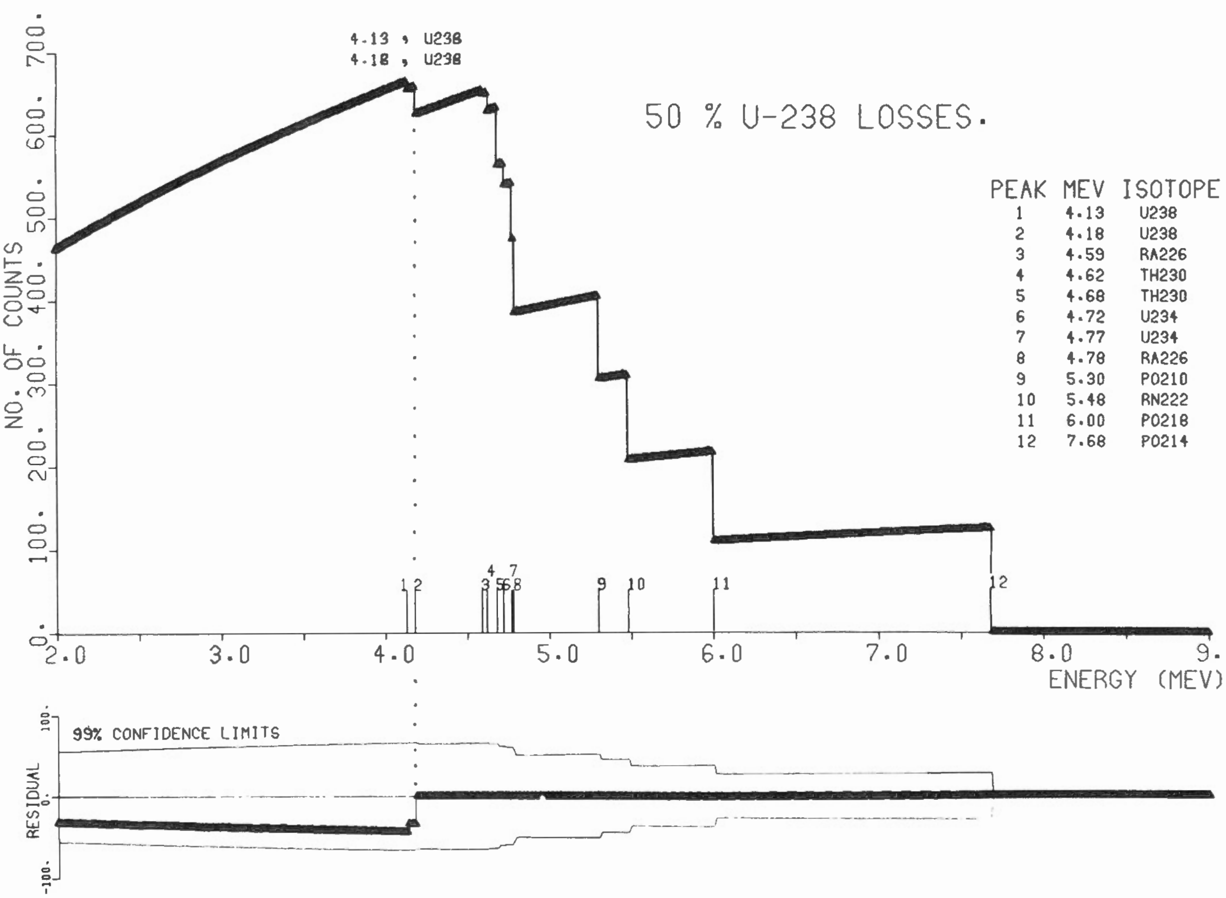

Figure 1.4. A synthetic alpha particle energy spectrum for the ^{238}U decay series with a 50 per cent loss of ^{238}U. The disequilibrium is indicated by the residual spectrum at the bottom.

amount of radioelement in the source, an 'infinitely' thin source would be desirable. This would approach the theoretical 'spike'-shaped energy spectra shown in Figure 1.2. Unfortunately, for comparison and quantitative analysis, the thickness of the 'infinitely' thin source must be reproducible and uniform. Methods such as vacuum sublimation from a hot filament, electro-spraying and electrodeposition are a few of the source preparation techniques.

The source preparation in all thin-source alpha spectrometry is rather elaborate, and the loss of short lived daughters in preparation could be a problem in studying the state of radioactive equilibrium of the sample. In addition the count rate from thin sources is usually very low due to the very small amount of sample involved.

Thick-Source Alpha Particle Spectrometry

Although thick sources have the advantage of a minimum of source preparation, they have not been widely used because of the effect of the energy distribution at energies lower than the initial peak energy of the alpha particle. Before the development of high resolution instrumentation, thick sources were utilized in counting the total alpha activity of the decay series, with no discrimination between the various particle energies (Evans, 1934; Finney and Evans, 1935; Keevil and Grasham, 1943). Chudacek (1958) derived an expression for the energy spectrum of alpha particles emitted from sources of varying thicknesses. It was found that the distribution given by Chudacek (1958) is more applicable to results from a spectrometer of extremely poor resolution.

Another expression for the differential energy alpha spectrum from an infinitely thick source was derived by Graeffe and Nurmia (1961). Although the resulting spectrum computed for an entire decay series was better than that mentioned above, it did not fit the experimental spectra within satisfactory limits.

Abrosimov and Kocharov (1962) derived the shape of the energy distribution of alpha particles for varying source thickness. Application of their theory to the particular geometry and detecting system used for this study, led to the development of energy distributions for the entire ^{238}U and ^{232}Th decay series which closely matched the experimental results. The general formula for computing the number of alpha counts (dN) in an energy range (dE) of the energy distribution is given by: (Abrosimov and Kocharov, 1962):

$$\frac{dN}{dE} = \frac{N_o A n}{4h} E^{n-1} \qquad (5)$$

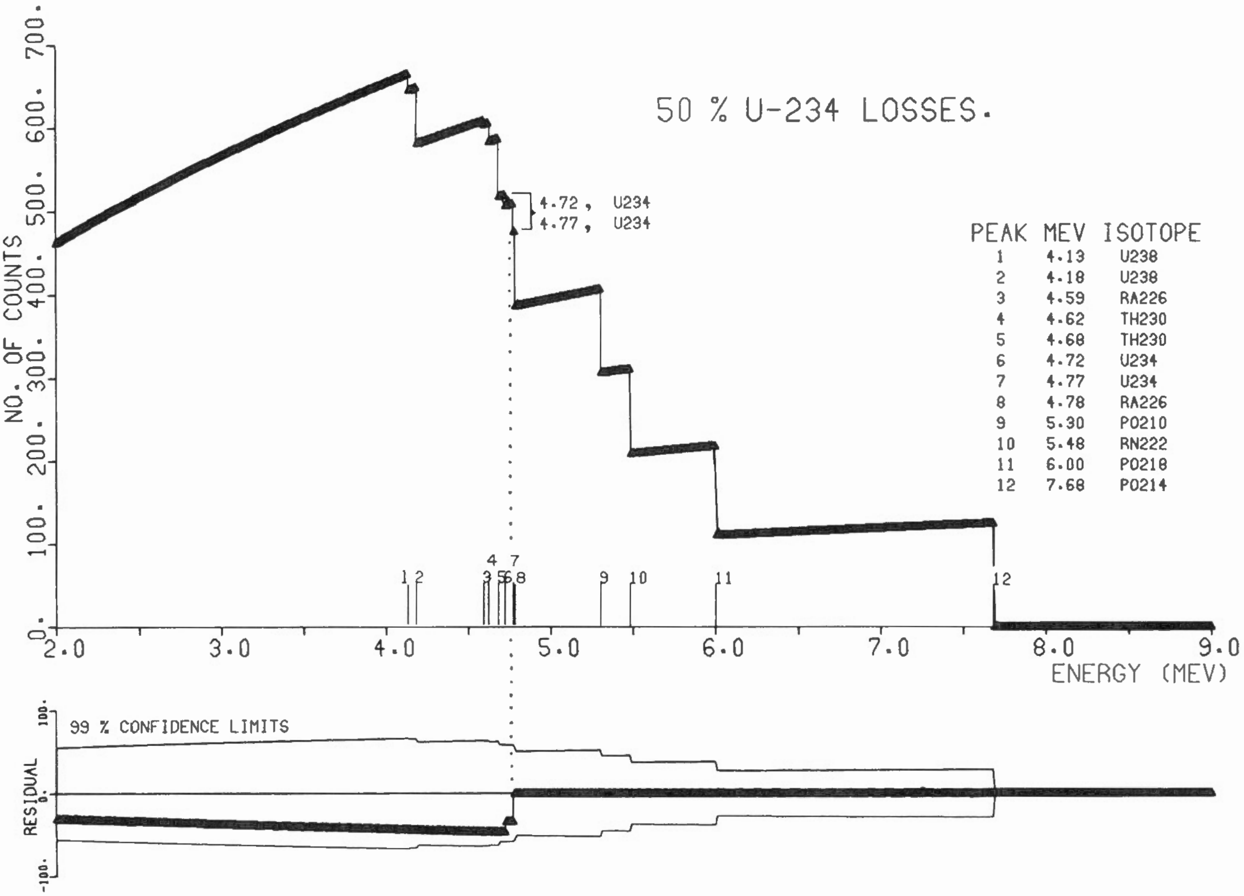

Figure 1.5. A synthetic alpha particle energy spectrum for the ^{238}U decay series with a 50 per cent loss of ^{234}U. The residual spectrum indicates disequilibrium at the location of peaks 6 and 7.

The equation depends upon a knowledge of the number of alpha particles emitted by the entire source per unit time (N_o), the thickness of the source (h), and the constant of proportionality (A) from the range-energy equation:

$$R = AE^n \tag{6}$$

where R = the range of the alpha particle in air and n is a constant equal to approximately 1.5 depending upon the effective atomic number of the source material (Glasstone, 1967). The derivation of the thick-source energy distribution for an entire decay series based upon equation (5) is given in the appendix. Modifications to the shape of infinitely thick-source alpha spectra caused by inhomogeneous distribution of emitters in the sample have been discussed by Kolenkow (1968) and Kolenkow and Manly (1967).

Figure 1.3 illustrates a synthetic alpha particle spectrum composed of the accumulated energy distributions for the entire ^{238}U decay series in radioactive equilibrium for an infinitely thick source. The spectrum was computed assuming a peak count of 125 counts in the energy channel containing the initial energy of the 7.68 Mev Polonium-214 alpha peak and a value of 1.5 was used for n. The energy increment used is 10 Kev, the same as that used for the experimental spectra. Thus the envelope of the distributions in the figure shows the same as that from a pulse height analyzer over 700 channels from 2.0 Mev to 9.0 Mev with 10 Kev per channel.

Elimination of the ^{232}Th Series Contribution to a 'Rock Spectrum'

In order to study the ^{238}U decay series for the presence of radioactive equilibrium, the contributions of the ^{232}Th series to the spectrum, if present, must be removed. A large number of Pitchblende uranium ores do not contain appreciable thorium and this is not a problem, but in general thorium is associated with uranium. Since we can assume the ^{232}Th series to be in equilibrium, it should be possible to match the ^{232}Th contribution in the 'rock spectrum' (i.e. the spectrum with both Th series and U series components) to the synthetic equilibrium alpha spectrum of the ^{232}Th series. Subtracting the synthetic spectrum will leave the ^{238}U series as a residual. This can be accomplished by fitting the 'rock spectrum' to the synthetic ^{232}Th spectrum at the highest energy peak of the ^{232}Th series (8.7 Mev, ^{212}Po). In this portion of the spectrum the ^{238}U series is absent, and will not present a problem. Since the 'rock spectrum' contains the statistical scatter of counting, fitting it to the synthetic spectrum is accomplished using the entire portion of the 8.78 Mev ^{212}Po peak energy distribution from 8.78 Mev down to 6.78 Mev (the highest ^{238}U series peak). The least squares criterion is used in determining the best fit. This determines the normalization factor by which the 'rock spectrum' must be multiplied to match it to the synthetic spectrum. It was found that the technique of removing the thorium series spectrum from the rock spectrum was satisfactory. It required only that a statistically significant number of counts were obtained in the ^{212}Po peak for a good least squares fit to be made with the theoretical thorium series spectrum.

Determination of the Presence of Disequilibrium in a ^{238}U Alpha Spectrum

Consider the ^{238}U series residual spectrum after removal of ^{232}Th series components as described above, or the ^{238}U series spectrum obtained from a rock with no thorium, to be in radioactive equilibrium. Then, fitting the synthetic ^{238}U series alpha spectrum to the highest energy peak in the series and subtracting the synthetic spectrum should give a residual spectrum which simply reflects the statistical scatter present in the experimental spectrum, fluctuating about a value of zero.

If the experimental or rock spectrum were not in equilibrium it would show a departure from this scatter about the zero residual, and would reflect the location in the decay series and degree of disequilibrium. From previous equilibrium studies using radiochemical and other techniques, carried out on various radioactive ores, several common types of disequilibrium have been observed, along with a few relatively rare types (Rosholt, 1958). A study of the theoretical results of the application of the present technique to these characteristic cases described by other workers would give an insight into what to expect as a residual spectrum for each case.

Application of the Technique to Theoretical Spectra

Subtraction of the synthetic spectrum from the experimentally obtained 'rock spectrum' was adopted as the standard technique, mainly because it resulted in a positive residual spectrum if the 'rock spectrum' contained additional components not contained in the synthetic spectrum. If the 'rock spectrum' did not contain a particular peak that was in the synthetic spectrum, it showed as a negative residual, indicating a deficiency in the 'rock spectrum'. So in effect, positive and negative residuals indicated excesses and deficiencies respectively, in the 'rock spectrum'.

The total count in each channel of the alpha energy spectrum determines the standard deviation for that portion of the spectrum. Since counting statistics are Poisson distributed, one standard deviation equals the square root of the count. The 99 per cent confidence limits equals 2.58 times the standard deviation. In all analyses of the state of equilibrium of samples under consideration, the residual spectrum is displayed with the 99 per cent confidence limits above and below the zero residual line. This allows one to determine whether a particular positive or negative residual can be relied upon to be a valid indication of disequilibrium or a result of statistical scatter. The following examples illustrating the expected residual spectra for some theoretical cases of disequilibrium will clarify the method of interpretation of the experimentally obtained spectrum and residuals.

Figure 1.4 shows a theoretical case of disequilibrium wherein the ^{238}U isotope has suffered a 50 per cent loss. The example is considered to represent one in which recent leaching of uranium took place, the time being relatively short, and the remainder of the series is in equilibrium with the original amount of ^{238}U that was present. This could occur in nature since the first alpha emitting daughter below ^{238}U is ^{234}U with a half-life of 250 000 years. The residual spectrum shown at the bottom of Figure 1.4 is zero in the region where the theoretical equilibrium spectrum coincides with the theoretical disequilibrium spectrum. Below 4.18 Mev (the location of the ^{238}U peak) the residual spectrum is negative, indicating a ^{238}U deficiency.

Another more realistic case is that of preferential leaching of ^{234}U (Richardson, 1964). A theoretical example of this case with 50 per cent ^{234}U is shown in Figure 1.5. This example is again considered an 'instant' loss in geologic time. The 80 000 year half-life of the ^{230}Th below it supports the bottom of the series without significant decrease in activity for several thousand years. The result is similar to the previous case, in that the negative residual which occurs at the position of ^{234}U in the alpha spectrum, indicates a ^{234}U deficiency. A loss of ^{230}Th would be distinguishable from the loss of ^{234}U in theory, but in practice would require a detector of higher resolution than that used in this study, and with thick sources might even prove impossible, due to the similar energies involved.

One particularly interesting case to consider is that of disequilibrium introduced in the laboratory during sample preparation time. Figure 1.6 shows this case which results in a large positive residual at the low energy end of the spectrum. The residual departs from zero at the location of the 5.30 Mev ^{210}Po peak. If the radon loss had occurred in the sample while it was *in situ*, the residual would depart from zero at the ^{226}Ra peak location at 4.78 Mev instead. The reason for this is that disequilibrium introduced by ^{222}Rn loss in the laboratory would result in a similar loss of ^{218}Po (6.00 Mev) and ^{214}Po (7.68 Mev), which are the immediate daughters of ^{222}Rn with half-lives of 3.05 minutes and 160 milliseconds respectively. The last alpha emitter in the decay series, ^{210}Po (5.30 Mev) would be supported by Lead-210 with $T_{\frac{1}{2}} = 22$ years. Thus ^{210}Po would retain the same activity level during the laboratory measurements as if it were in equilibrium with the top members of the series. Thus the positive residual would occur at 5.30 Mev, showing the "excess" of ^{210}Po relative to the ^{222}Rn, ^{218}Po, and ^{214}Po. In the case of ^{222}Rn loss in the field, it would probably have occurred at a time appreciably greater than several half-lives

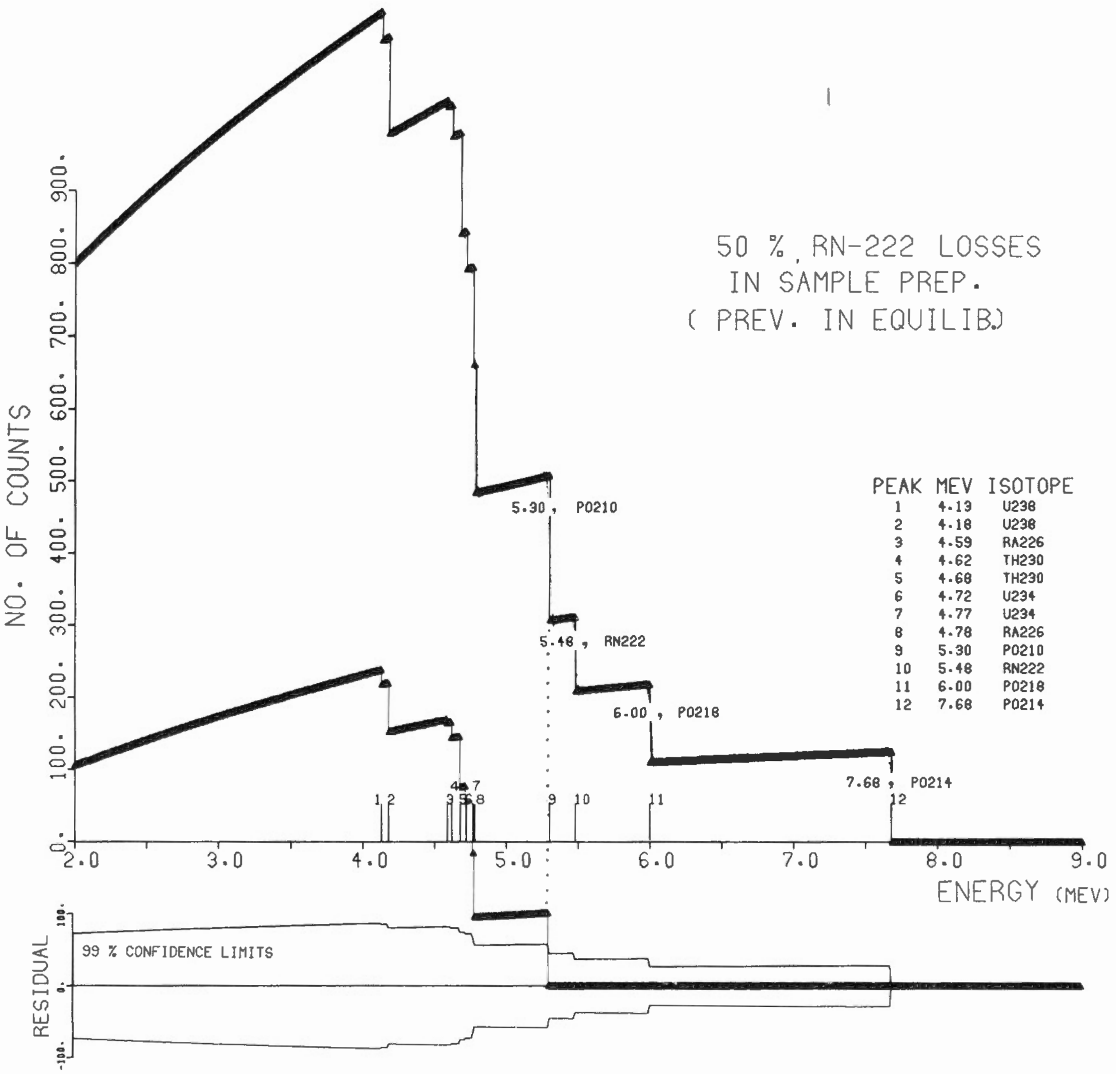

Figure 1.6. A synthetic alpha particle energy spectrum for the ^{238}U decay series with a 50 per cent loss of ^{222}Rn. The loss occurred during sample preparation since the residual spectrum indicates disequilibrium at ^{210}Po.

of Lead-210/22 years, and the ^{222}Rn loss would be reflected in the ^{210}Po peak. Thus the residual would depart from zero at 4.78 Mev, the ^{226}Ra peak, which would represent the lowest daughter still in equilibrium with the upper members of the decay series.

Other less straightforward cases of multiple losses have been computed as an aid in interpretation of the residual spectra (Killeen, 1971).

Instrumentation

A silicon semiconductor detector was used in conjunction with a Nuclear Data 1024-channel pulse height analyzer to obtain the alpha particle spectra. The detector and sample were enclosed in a vacuum chamber. The detector with an active area of 950 mm^2 was mounted in the top of the vacuum chamber, sensitive side downward. The manufacturer's (Ortec Inc.) alpha resolution measurement is the full width half maximum (FWHM) of a 5.5 Mev thin Am-241 alpha source spectrum line. The manufacturer's guaranteed alpha resolution was 70 Kev, FWHM, but by actual measurement was 54.4 Kev, FWHM.

Preliminary Experiments

Before this technique for detecting disequilibrium could be generally applied to any rock sample, the effect of variation of experimental parameters had to be determined. In order to simulate variations in concentrations of the radioelements, a number of synthetic rocks were produced by mixing pure silica sand with epoxy and known amounts of U_3O_8 powder. This permitted a control over the U_3O_8 concentrations

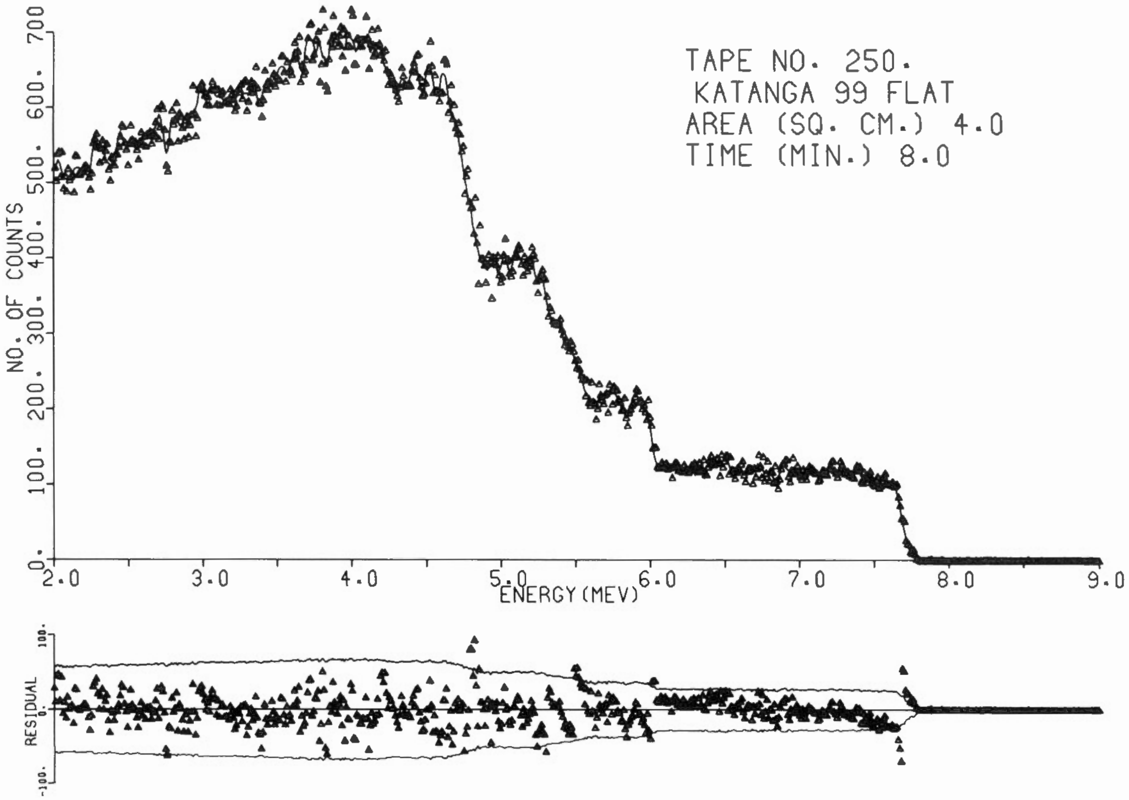

Figure 1. 7. Alpha particle energy spectrum of a pitchblende sample. The residual spectrum shows the statistical scattering about the zero residual line, indicating the sample is in radioactive equilibrium.

which would not be possible with real rock samples. The synthetic rocks were prepared and allowed to harden in glass petri dishes, which gave them a thickness of about half an inch. When the mixture had hardened, the surface was ground flat to expose a fresh surface of the synthetic rock. The surface area was approximately 65 square centimetres.

A series of experiments were conducted varying the source area, concentration, and source-detector separation, in order to determine the effect on the energy distribution of the alpha spectra. No significant changes were measured for source-detector distances from 1. 0 to 4. 5 cm, or for source areas of 1 sq. cm to 65 sq. cm, and source concentrations of 1 per cent to 50 per cent U_3O_8 content.

In practice the source-detector distance was kept constant at 2. 0 cm and the source area was determined by the sample size and size of the vacuum chamber, 65 cm^2 being the largest possible area. The sample preparation consisted of cutting the rock to produce a flat surface (not polished) for counting. Since the prepared samples were irregular in shape, a thin lead foil sheet with a circular hole was placed in contact with the sample. The size of the circular hole was made as large as possible, without exposing the edge of the sample. Thus all samples were essentially circular, planar, infinitely thick sources.

Limitations of the Present Study

1. Energy Resolution of the System

An inherent limitation of the alpha spectrometric method is the inability to distinguish between radioactive isotopes having alphas of energies too close to be resolved by the spectrometer. With the resolution of the detector used in this study the 4. 77 Mev ^{234}U peak cannot be resolved from the 4. 78 Mev ^{226}Ra peak, and the 4. 68 Mev ^{230}Th peak cannot be distinguished from the 4. 72 Mev ^{234}U peak. When a rock contains thorium and its decay series, the possibility of more combinations of unresolvable peaks results. Some improvement might be possible with a detecting system of higher resolution, but at present this necessitates going to a smaller area detector, resulting in a decreased count rate, and increased counting times.

In the case of a group of say 3 peaks, the presence of disequilibrium can still be detected, but which of the isotopes is the cause may be indeterminate. However, a study of other isotopes in the series may indicate which isotope in the group is the most likely to be the cause of the disequilibrium.

2. Low Intensity Alpha Peaks

When a particular alpha decay results in alpha particles of either of two different energies, usually alphas of one energy occur much more often than the other. For example, ^{226}Ra emits an alpha of 4. 78 Mev 94 per cent of the time and a 4. 59 Mev alpha 6 per cent of the time. The 4. 59 Mev alpha peak will be of such low intensity that it may be undetectable, but any disequilibrium due to ^{226}Ra will show up in the high intensity peak.

3. Low Concentrations of Uranium in the Rock

A lower limit of detectability is also set by the uranium content of the rock. Since the volume of rock is extremely small (not more than 64 cm^2 area and less than 80 microns thick) the amount of uranium contributing alpha particles to the spectrum is extremely small. In practice it has been determined that a uranium content of less than 1 per cent U_3O_8 presents difficulties and a lower limit of about 0. 1 per cent U_3O_8 is set by the length of counting time possible without significant shift in the electronic parameters of the instrumentation.

4. Counting Times and System Stability

As mentioned above, after a certain amount of time the inherent drift in the measuring instruments prevents a good spectrum from being formed. The main problem is a slight shift in gain with time which causes a loss in resolution and broadening of the spectral peaks. A time of 72 hours was the maximum possible counting time to retain a useful spectrum.

Application of the Technique to Uranium ore Samples

The experimental spectra were first processed by a gain shifting program to align them with the theoretical spectra which were generated with 10 Kev per channel and the zero energy in channel zero. Since the value of n in the equation (5) generating the synthetic spectrum is a function of the effective atomic number of the source and has a value "close to 1. 5" (Lapp and Andrews, 1963), an iterative technique was developed to determine the best value of n. The best value was obtained when the residual from the fit of the experimental and synthetic spectra was a minimum. If the best value of n was found to lie between 1. 43 and 1. 57, the spectrum was arbitrarily assumed to be in equilibrium as the value of n is "close to 1. 5. Otherwise, the value of n was set to exactly 1. 50 and the computed residual spectrum indicated the location and amount of the disequilibrium in the decay series. The effect on the synthetic spectra of variation of the value of n was discussed by Killeen (1971). An increase in the value of n raises the proportion of counts in the energy distribution 'tail' and a decrease lowers the 'tail'. A small change in the value of n is most notable at lower energies by the cumulative effect on the 'tails' of several peaks.

Results for two samples, one found to be in radioactive equilibrium, and the other definitely in a 'state' of disequilibrium, illustrate the application of the method. Since the height of the synthetic spectrum is arbitrary, a value of 125 counts was chosen for the highest energy peak. The 'fit' determines the normalization factor by which the experimental spectrum is multiplied to bring it into alignment with this synthetic spectrum.

Counting times were determined as the time required to obtain a peak height of about 100 counts in the highest energy peak.

The first example shown in Figure 1. 7 is the alpha spectrum of a pitchblende sample originating from Katanga, Congo, obtained from the Royal Ontario Museum in Toronto. The sample surface was a fresh cut of area 4 sq. cm, and the counting time was 8 minutes. The normalization factor is 0. 981, and the iterated best value of n was 1. 5062. The residual is well within the confidence limits indicating the sample is in radioactive equilibrium.

An interesting effect shown by Figure 1. 7 is the large residual at the locations of several peaks in the spectrum. This is the result of subtracting the synthetic spectrum which has a sharp theoretical rise at each peak, while the experimental spectrum exhibits a gaussian rounding of the edges of the peaks due to a combination of high energy stragglers, and the finite resolution of the instrumentation. It would be possible to eliminate this effect by including a gaussian rounding effect in the theoretical spectrum at each peak location. However, it was decided to retain the sharp rise in the theoretical spectra since the shape of the residual gives an indication as to whether the correct gain shift for the experimental spectrum was used. An incorrect gain shift is indicated by the presence of asymmetric residuals at the peak locations. The result is best seen by observing the highest energy peak and its associated residual. These residuals at peaks quite often extend outside the confidence limits but are not related to the equilibrium state of the sample.

The second example shown in Figure 1. 8 is the alpha spectrum of a weathered sample or uraninite from Bolivia with surface area 8. 0 sq. cm, counting time 100 minutes, and normalization factor 0. 092. A fresh sample from the same location showed no disequilibrium. The weathered sample, however, shows a loss of ^{238}U, and one of the three daughters, ^{226}Ra, ^{230}Th, or ^{234}U in the multiple peak at 4. 7 Mev. The most likely interpretation is that ^{238}U and ^{234}U, being chemically similar were both lost. A rough quantitative estimate of the percentage losses can be obtained by comparing the magnitude of the residual ($\sim$ 150 counts) to the spectrum magnitude at say 4 Mev ($\sim$ 550 counts). Then the per cent loss will be approximately 150/(550 + 150) $\sim$ 20 per cent.

An interesting feature carried over from the sample which was counted immediately before this sample is the small peak at 6. 62 Mev due to Bismuth-211, supported by ^{211}Pb, a beta emitter with a 36-minute half-life. The previous sample had been extremely porous and an outgassing of radon in the vacuum chamber took place. The supply of ^{219}Rn was removed when the porous rock

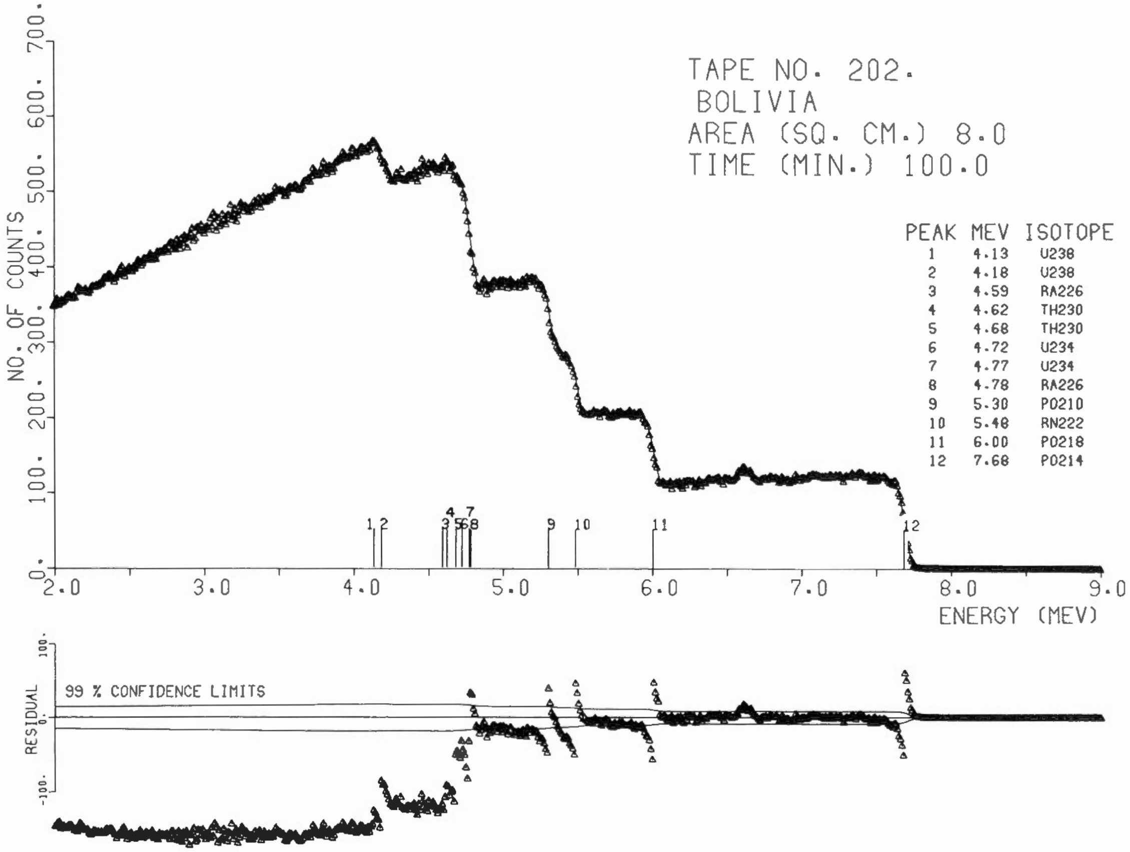

Figure 1.8. Alpha particle energy spectrum of a weathered sample of uraninite. Disequilibrium is indicated by the residual spectrum which shows negative values (losses).

was removed, but Radon 219 which had decayed in the chamber contaminated the chamber with daughter nuclides which plated on the walls and the detector. The ^{211}Pb continued to produce ^{211}Bi which emits the 6.62 Mev alpha particle as a short-lived contamination. The time between removal of the previous sample, and the start of counting was about 40 minutes, one half-life of ^{211}Pb. A repeat of this spectrum taken at a later date showed no sign of this small peak.

A qualitative external check was made using X-ray fluorescence studies of both the weathered and fresh portions of this sample of Bolivian Uraninite. The results supported the conclusions of uranium losses measured by the alpha spectrometric technique.

Summary and Conclusions

The present thick-source alpha particle spectrometric technique permits the detection of radioactive disequilibrium with a minimum of sample preparation time. It can further identify its location in the ^{238}U decay series within limitations which are partly instrumental, and should show some improvement with detectors of sufficiently high resolution.

To summarize, the equilibrium study involves the following steps for a sample containing both thorium and uranium:

a) Production of the experimental alpha particle spectrum from an infinitely thick source which is under investigation.

b) Computation of a synthetic equilibrium alpha spectrum for the Thorium-232 decay series.

c) Fitting the synthetic Thorium-232 equilibrium spectrum at the location of the highest energy peak (to eliminate interference of the ^{238}U series for the fit).

d) Subtraction of the synthetic Thorium-232 series spectrum. The residual is the alpha spectrum of the Uranium-238 series component.

e) Computation of a synthetic equilibrium alpha spectrum for the ^{238}U series.

f) Fitting the synthetic ^{238}U equilibrium spectrum to the uranium residual obtained above in (d). Again the fit is made at the highest energy peak.

g) Subtraction of the synthetic ^{238}U equilibrium spectrum. The residual spectrum represents the statistical scatter present in all radioactive counting results, and should fluctuate about a residual count value of zero.

h) The departure of any residual spectrum from zero indicates a state of disequilibrium since the experimental and theoretical spectra differ. The location in the residual spectrum where the departure from zero exists, indicates the location of the radioactive disequilibrium. Steps b, c, d can be eliminated if no thorium is present.

The method was applied to a variety of rock and mineral samples, nearly all comprising uranium ore from various parts of the world (Killeen, 1971). The samples ranged from badly weathered surface exposure to fresh samples obtained from underground in active uranium mines. Some of the results were almost 'text book' cases, while others required considerable explanation of peculiar behaviour. The out-gassing of radon and its contamination effect on the spectrum of some porous samples was also noted. The main limitation of the technique seems to be the low emission rate of alpha particles from some samples, necessitating counting times beyond that permissible to retain good energy resolution without incurring instrumental variation. This limit is probably about 0.1 per cent U_3O_8, the concentrations typical of Blind River conglomeratic uranium ore.

The subtraction of the Thorium-232 decay series component from the total alpha spectrum works well; the residual Uranium-238 spectrum being quite amenable to study by this technique, subject to the limitations of minimum concentration mentioned above.

The samples considered here illustrated a case of radioactive equilibrium, and one of definite disequilibrium. Disequilibrium was a result of losses of two or more nuclides in the ^{238}U decay series. The examples were representative of cases to be expected during routine application of the technique to uraniferous rocks and minerals. Sample preparation time averaged less than half an hour.

Discussion

The technique for detection and identification of radioactive disequilibrium developed here can be used to monitor the validity of gamma-ray spectrometric measurements in uranium mining and exploration. Further improvement in energy resolution would make it possible to do quantitative analyses of the disequilibrium samples, and leads to the possibility of computing the history of the sample with reference to the time of loss of the various daughter products (Rosholt, 1961a; Robinson and Rosholt, 1961). Advances in the 'state of the art' of semi-conductor detectors may result in the development of detectors combining high resolution with large area. Increasing the detecting surface area would permit analysis of samples with lower uranium content, leading to the general applicability of the technique to any geologic material. This would have special importance for ground follow-up studies in the field of remote sensing by airborne gamma-ray spectrometry, or 'airborne geochemistry' as it is sometimes called (Darnley and Grasty, 1971; Allan and Richardson, 1974). Definition of geologic units by airborne gamma-ray spectrometric analyses of thorium, uranium and potassium, and subsequent mapping of such ratios as Th/U or U/K assumes that the uranium is in equilibrium.

The problem of radioactive disequilibrium is minimized by the large sample volume examined by an airborne gamma-ray spectrometer. Ostrihansky (this publ.) for example, has shown that disequilibrium usually occurs on a small scale. Both parent and daughter isotopes, even if separated, would both be included in the field of view of an airborne spectrometer. The ground follow-up, however, usually involves collection of rock samples which may be out of equilibrium.

Random representative surface samples could be obtained for equilibrium analyses by this technique. Similarly, any *in situ* ground gamma-ray spectrometric survey for uranium (Killeen, 1966; Doig, 1968; Carson, 1970; Killeen and Carmichael, 1970, 1972; Charbonneau *et al.*, 1975) should have some of the survey area checked for equilibrium in the ^{238}U series to insure valid uranium analyses. Here again, the relatively large sample volume of an *in situ* analysis, compared to the volume of a hand specimen for laboratory analysis, tends to decrease the effect of any small scale disequilibrium.

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APPENDIX

The Theoretical Alpha Spectrum of an Entire Decay Series

Extending the relation (equation [5]) for the alpha particle energy distribution of a single radioisotope to include several isotopes of various initial energies and intensities is accomplished as follows:

The total count under a particular alpha particle energy distribution is the sum of all the counts of all energies below the maximum energy E max., i.e. the initial energy of the alpha particle:

$$\int_{0}^{E_{max}} dN = \int_{0}^{E_{max}} \frac{N_oAn}{4h} E^{n-1} dE \qquad [6]$$

$$N_{total} = \left[\frac{N_oAn}{4h}\right] \frac{E^n_{max}}{n} \qquad [7]$$

For a given peak we can arbitrarily determine its peak count rate but all others in the decay series will then have count rates relative to that chosen for the first peak, i.e. the relative total counts under the peak energy distributions will be determined by their relative intensities, and ranges in the rock.

Consider peak 1 (which can be any peak):

$$\frac{dN}{dE_{max1}} = \left[\frac{N_oAn}{4h}\right]_1 E^{n-1}_{max1} \qquad [8]$$

Integrating eqn. [8] in the same way as [6] we get:

$$N_{tot1} = \left[\frac{N_oAn}{4h}\right]_1 \frac{E^n_{max1}}{n} \qquad [9]$$

Solving for the constant in eqn. [8]:

$$\left[\frac{N_oAn}{4h}\right]_1 = \frac{\left[\frac{dN}{dE_{max1}}\right]}{\left[E^{n-1}_{max1}\right]} \qquad [10]$$

Since $\left[\frac{dN}{dE_{max1}}\right]$ is the count which we can arbitrarily choose in the largest energy increment (or channel in the case of a pulse height analyzer) containing the initial energy of the alpha particle (E_{max1}), we can solve for the constant on the left side of eqn. [10].

Then the entire distribution can be computed from eqn. [5]:

$$\frac{dN}{dE_i} = \left[\frac{N_oAn}{4h}\right]_1 E_i^{n-1} \qquad [11]$$

Now for the second peak we know that as in eqn. [9],

$$N_{tot2} = \left[\frac{N_oAn}{4h}\right]_2 \frac{E^n_{max2}}{n} \qquad [12]$$

Solving for the new constant in eqn. [12],

$$\left[\frac{N_oAn}{4h}\right]_2 = \frac{\left[N_{tot2}\right]}{\left[\frac{E^n_{max2}}{n}\right]} \qquad [13]$$

The ratio of the total count under the two energy distributions is now dependent on the relative ranges (since it is an infinitely thick source and we can count all alphas within a volume proportional to its range), percentages, and activity of each isotope:

$$\frac{N_{tot2}}{N_{tot1}} = \frac{\text{Range of 2}}{\text{Range of 1}} \times \frac{\text{\% of 2}}{\text{\% of 1}} \times \frac{\text{Activity of 2}}{\text{Activity of 1}}$$

$$= R_{21} \qquad [14]$$

Therefore substituting for N_{tot2} from eqn. [14] into eqn. [13]

$$\left[\frac{N_oAn}{4h}\right]_2 = \frac{\left[N_{tot2}\right]}{\left[\frac{E^n_{max2}}{n}\right]} = \frac{R_{21}\left[N_{tot1}\right] n}{\left[E^n_{max2}\right]}$$

and substituting for N_{tot1} from eqn. [9], we get:

$$= R_{21}\left[\frac{N_oAn}{4h}\right]_1 \cdot \frac{\left[E^n_{max1}\right]}{n} \cdot \frac{n}{\left[E^n_{max2}\right]}$$

$$= R_{21}\left[\frac{N_oAn}{4h}\right]_1 \left[\frac{E_{max1}}{E_{max2}}\right]^n \qquad [15]$$

Substituting this value in eqn. [5], the energy distribution for the second peak is then:

$$\frac{dN}{dE_i} = \left[\frac{N_oAn}{4h}\right]_2 E_i^{n-1}$$

$$= R_{21}\left[\frac{N_oAn}{4h}\right]_1 \left[\frac{E_{max1}}{E_{max2}}\right]^n E_i^{n-1} \qquad [16]$$

Similarly for a third peak:

$$\frac{dN}{dE_i} = R_{31}\left[\frac{N_oAn}{4h}\right]_1 \left[\frac{E_{max1}}{E_{max3}}\right]^n E_i^{n-1} \qquad [17]$$

Thus an entire decay series can be constructed with the correct relative peak heights and energy distributions, by summing the distribution of all the peaks of the series; the entire spectrum height being dependent only upon the count chosen for the peak channel of the first peak calculated. In practice the highest energy peak is the easiest peak for which to choose an arbitrary height since it stands out from the other peaks.

PART 2: RADIOACTIVE DISEQUILIBRIUM INVESTIGATIONS, ELLIOT LAKE AREA, ONTARIO

L. Ostrihansky

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PART 2: RADIOACTIVE DISEQUILIBRIUM INVESTIGATIONS, ELLIOT LAKE AREA, ONTARIO

Abstract

A method of investigating the state of radioactive equilibrium of the ^{238}U *decay series in uranium ores has been developed. The technique utilizes a Ge(Li) detector to measure parts of the low energy gamma-ray spectrum and a NaI(Tl) detector for high energies.*

Application of the method to rocks from the Elliot Lake uranium mining area shows a considerable degree of disequilibrium in surface samples. The degree of disequilibrium appears to relate to the levels of uranium concentration, and rapid changes in the state of equilibrium can occur over short distances.

Although measurements are suitable for uranium ores, considerable uncertainty is possible at lower concentration levels, primarily due to the inherent low sensitivity of the Ge(Li) detector.

Résumé

Une méthode de détermination de l'état d'équilibre radioactif de la famille de l'uranium a été mise au point pour étudier notamment les minerais d'uranium. Cette technique utilise un détecteur au Ge(Li) pour la région des faibles énergies du spectre de rayons gamma et un détecteur au NaI(Tl) pour les grandes énergies.

L'application de la méthode aux roches de la région des mines d'uranium du lac Elliot montre que le degré de déséquilibre est considérable dans les échantillons de surface. Ce degré de déséquilibre semble être en relation avec les concentrations en uranium et des variations brusques de l'état d'équilibre peuvent se produire sur de courtes distances.

Bien que ces mesures conviennent aux minerais d'uranium, il peut y avoir une grande incertitude pour des concentrations plus faibles, en raison surtout de la faible sensibilité du détecteur au Ge(Li).

Introduction

The natural radioactive decay series are supported by parent nuclides having half-lives comparable to the age of the earth. They are ^{238}U (half-life 4.51×10^9 years), ^{235}U (half-life 7.13×10^8 years) and ^{232}Th (half-life 1.39×10^{10} years) (*see* Appendix 4). However, in these natural decay series there exist daughter isotopes which also have sufficiently long half-lives that it is possible their equilibrium ratio to the parent isotope can be changed by physical and chemical processes in nature. These isotopes are:

^{234}U (half-life 2.48×10^5 years)
^{230}Th (half-life 7.52×10^4 years)
^{231}Pa (half-life 3.48×10^4 years)
^{226}Ra (half-life 1.62×10^3 years)

Some others of lesser importance (having shorter half-lives) are: ^{227}Ac (22 years), ^{210}Pb (19.4 years), ^{228}Ra (6.7 years) and ^{228}Th (1.91 years). The remaining isotopes have very short half-lives and are therefore always in radioactive equilibrium with their parents. One exception is ^{222}Rn with a short half-life (3.825 days) which can accumulate or escape from the rocks because of its special property as a gas.

The problem of radioactive disequilibrium is important in the case of uranium determinations made by gamma-ray spectrometry. Laboratory, in situ, and airborne gamma-ray spectrometer equipment commonly utilizes the measurement of the ^{214}Bi peak in the ^{238}U decay series to determine uranium concentrations in rocks. The technique thus relies on the assumption that the ^{238}U decay series is in radioactive equilibrium. The present work investigates a method for measurement of radioactive disequilibrium using some selected rock and soil samples collected from the Elliot Lake uranium mining area of Ontario. Most of the samples were collected from within two feet of the surface, since that is the layer of material which is analyzed by *in situ* and airborne λ-ray spectrometric surveys.

^{234}U

The discovery of disequilibrium between ^{234}U and ^{238}U was surprising since these isotopes were expected to behave the same chemically. Cherdyntsev (1955) reported an activity ratio $^{234}\text{U}/^{238}\text{U}$ of 3.7 in the secondary uranium mineral Schroeckingerite and excess ^{234}U in leach solutions of minerals. The $^{234}\text{U}/^{238}\text{U}$ ratio was found to be less than 1 in some very weathered residual uranium minerals and greater than 1 in some secondary minerals (Chalov, 1959). Weathered granites may show a deficiency of ^{234}U from preferential leaching and uranium-enriched areas in oxidized sandstone have excess ^{234}U which indicates recent accumulation of transported uranium (Rosholt *et al.*, 1964). The relation $^{234}\text{U} \geqq {}^{238}\text{U} \geqq {}^{230}\text{Th} \geqq {}^{226}\text{Ra}$ indicates an epigenetic character of uranium accumulation and a young age. $^{234}\text{U} \geqq {}^{230}\text{Th} \simeq {}^{226}\text{Ra} \geqq {}^{238}\text{U}$ also shows accumulation but an older age. $^{230}\text{Th} \geqq {}^{226}\text{Ra} \geqq {}^{238}\text{U} \geqq {}^{234}\text{U}$ shows a recent partial leaching of old uranium accumulation and $^{230}\text{Th} > {}^{226}\text{Ra} >> {}^{234}\text{U} > {}^{238}\text{U}$ shows old accumulation of U and strong leaching in present time (Syromyatnikov *et al.*, 1967).

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^{230}Th, ^{231}Pa, ^{226}Ra

Disequilibrium of ^{230}Th, ^{231}Pa, and ^{226}Ra has been described by Rosholt (1959). He classified disequilibrium according to the ratios of these daughters into 6 types, which are briefly summarized below.

1. (^{238}U > ^{231}Pa > ^{230}Th > ^{226}Ra)

Type 1 indicates that leaching of daughter products has taken place or uranium may have migrated to its present location in a time less than that required by its daughter products to reach approximate equilibrium; that is less than 300 000 years ago. The former explanation is more probable in carnotite and other types of deposits where uranium fixative agents such as vanadium or phosphate are present.

2. (^{238}U >> ^{231}Pa > ^{230}Th > ^{226}Ra)

Type 2 shows considerable daughter product deficiency. The most probable explanation is a recent accumulation of U.

3. (^{238}U < ^{231}Pa > ^{230}Th < ^{226}Ra)

Type 3 disequilibrium is believed to be the result of rather recent deposition of uranium contaminated with significant amounts of daughter products other than ^{230}Th.

4. (^{238}U << ^{231}Pa > ^{230}Th > ^{226}Ra)

Disequilibrium of type 4 is found in samples taken from an oxidized environment, and is the result of leaching of uranium. The high ^{231}Pa content and near equilibrium abundances of U, ^{230}Th and ^{226}Ra is very significant for many uranium anomalies.

5. (^{238}U < ^{231}Pa > ^{230}Th << ^{226}Ra)

Type 5 disequilibrium occurs in pyritic ores or ore dumps and is the result of differential leaching of all components.

6. (^{238}U = 0; ^{231}Pa = 0; ^{228}Ra < ^{226}Ra)

Type 6 disequilibrium is commonly associated with oil- and gas-field brines. Radioactive hot-spring deposits also show this type of disequilibrium.

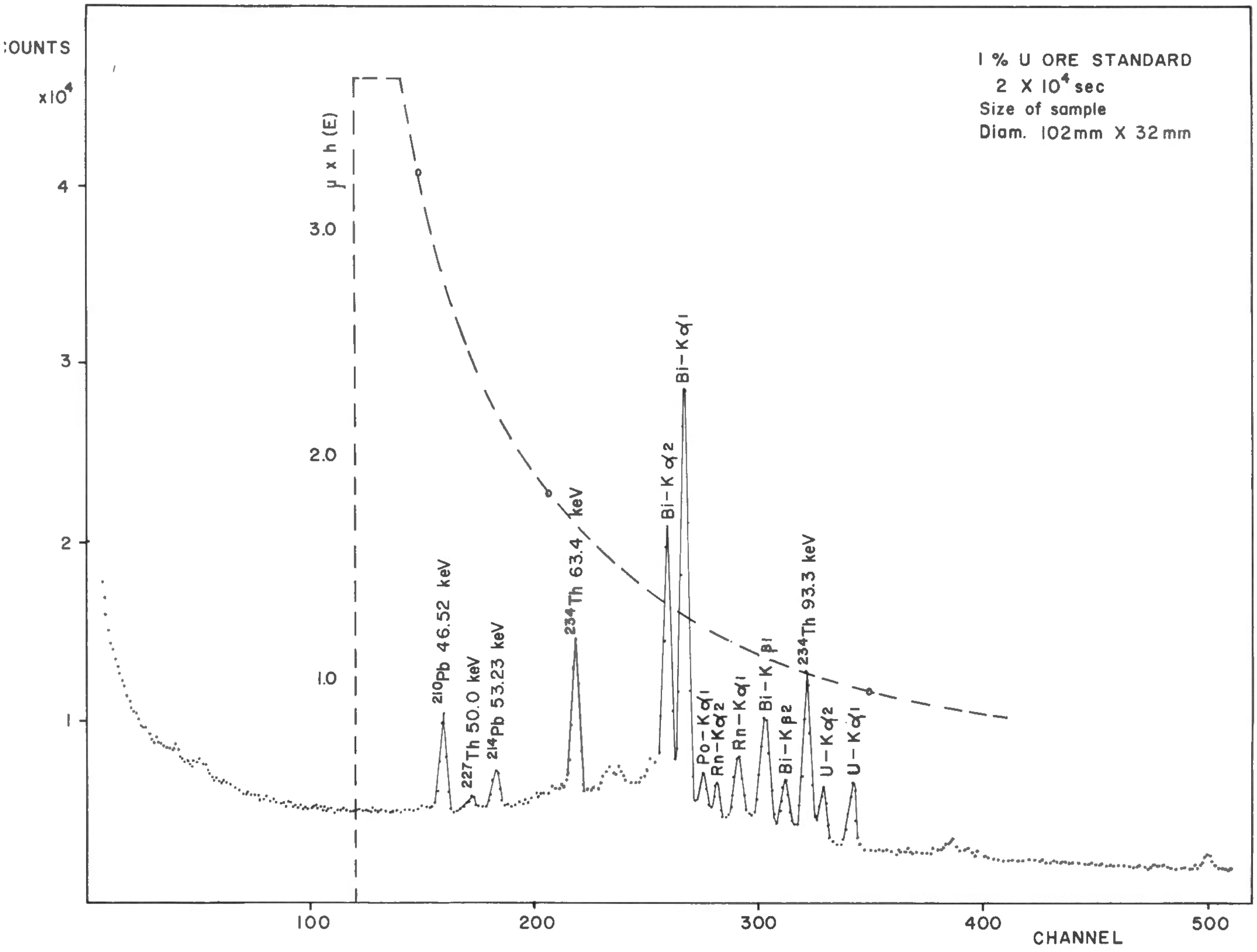

Figure 2. 1. Spectrum of the uranium ore standard.

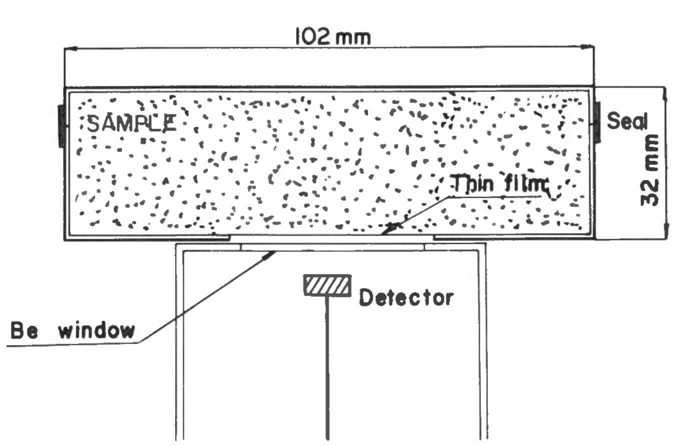

Figure 2. 2. The arrangement of detector and sample.

Determination of radioactive equilibrium in uranium ore samples by gamma-ray spectrometry

The low energy gamma-ray spectrum of uranium ore (energy range from 40 KeV to 200 KeV) has a number of gamma or X-ray conversion lines which can be used for determination of radioactive equilibrium in the uranium decay series. Figure 2. 1 shows the spectrum obtained from the 1% U ore standard used in this work. The intensities (number of counts in peak) of the spectral lines of a given isotope for standard and sample cannot be compared directly. The absorption effect plays an important role in this low energy region and the sample and standard may have different linear absorption coefficients. For that reason the following formula has been derived to take into account the linear absorption coefficients (*see* Appendix 1).

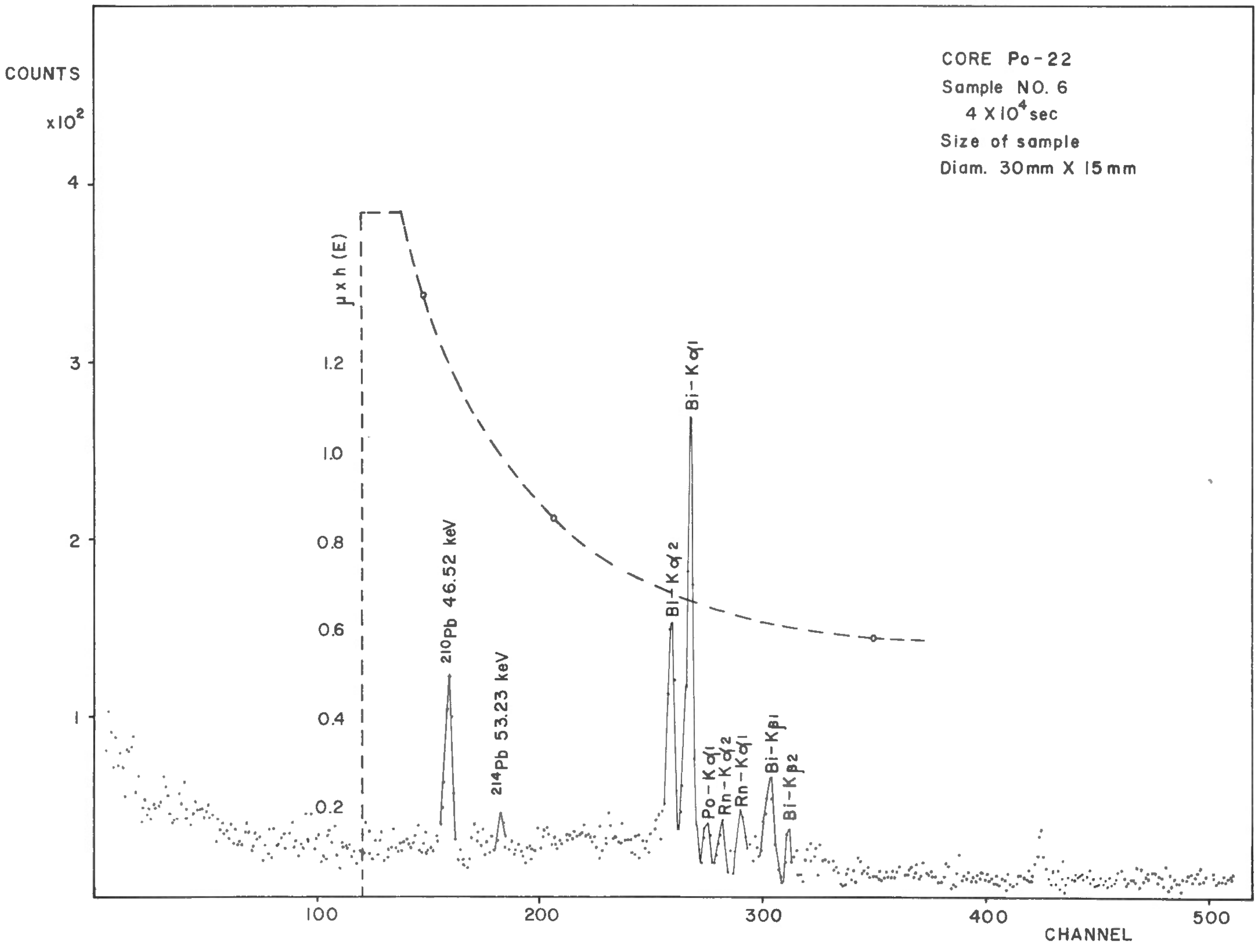

Figure 2. 3. Example spectrum showing ^{238}U deficiency.

$$\text{Eqn. 1} \ldots \; Q_{sa} = Q_{st} \; \frac{P_{sa} g_{st} \mu_{sa} \; [1 - \phi\,(\mu_{st} h) - \cos\psi}{P_{st} g_{sa} \mu_{st} \; [1 - \phi\,(\mu_{sa} h) - \cos\psi} \; \frac{[1 - \phi\,(\mu_{st} h \sec\psi)\,]\,]}{[1 - \phi\,(\mu_{sa} h \sec\psi)\,]\,]}$$

where

Q_{sa} is concentration of given isotope in sample
Q_{st} is concentration of this isotope in standard
P_{sa} and P_{st} are number of counts in peaks for sample and standard
g_{sa} and g_{st} are weights of sample and standard
μ_{sa} and μ_{st} are linear absorption coefficients
h is the thickness of sample and standard
2 ψ is the visible angle of sample. Supposing that h and ψ are the same for standard and sample.

ϕ is King's function [which can be found in tables (e.g. Gorshkov, 1967)]. The linear absorption coefficient for the energy of a given peak is measured experimentally using the equation $J = J_o e^{-\mu h}$ detecting radiation J passing through the sample. The method of measurement of absorption coefficient is described in Appendix 2. The calculated value from equation 1 is not the absolute concentration of radioactive isotope in the sample but the ratio of radioactivity of the isotope in the sample to the radioactivity of the isotope in the uranium ore standard which is considered to be in equilibrium with its daughter products (for 1% U standard the activity of each isotope = 1). This value is called equivalent content of uranium. The same applies for thorium isotopes and thorium standard.

Instrumentation and method of measurement

Measurements were performed using an Ortec Inc. semi-conductor gamma-ray spectrometric system. A Ge(Li) detector with diameter of 10 mm and sensitive depth of 5 mm and Be window was used. The resolution is better than 400 eV for 14.4 KeV gamma-rays. The spectrometric system was connected to a Nuclear Data 1024 channel analyzer. Two types of samples were measured.

1) Small sample diameter 3.0 cm and thickness 1.5 cm for drill cores (weight about 25 gr).
2) Large sample diameter 10.2 cm (4 inches) and thickness 3.2 cm for samples of low activity collected from the surface of outcrops (weight about 400 gr).

The large samples were ground to pass a 60-mesh standard sieve and loaded into shallow cylindrical steel cans (as used for packing tobacco), with a diameter of 4 inches. The bottom of the can had an opening covered by a thin film for the measurement of X-rays and soft gamma-rays (Fig. 2.2). The detector and the sample were shielded by lead of 2-inch thicknesses. The sensitivities for small samples were:

^{210}Pb	0.197 counts/ppm/hour
^{234}Th	0.227 counts/ppm/hour
^{223}Ra	0.086 counts/ppm/hour

The sensitivities for large samples were:

^{210}Pb	0.312 counts/ppm/hour
^{234}Th	0.455 counts/ppm/hour
^{223}Ra	0.209 counts/ppm/hour

Small samples with a concentration of equivalent U over 300 ppm were counted for 6 hours. Up to 24 hours counting time was used for lower concentration levels. Concentration levels down to 20 ppm equivalent U were measured in 5 hours using the large samples.

The ore samples were measured in a substantially shorter time. One per cent uranium and one per cent thorium ore samples from U.S. Atomic Energy Commission New Brunswick Laboratory were used as standards. The same standards were used for gamma-ray spectrometry at higher energies. In order to measure spectra, a straight line or curve was drawn by using the compton continuum points in the vicinity of the peak. The area (number of counts) of a peak above this straight line or curve was the value used to determine the concentration. This value was corrected as described above (using equation (1) for calculation of concentrations knowing the linear absorption coefficient μ for the energy of the peak).

The three spectral lines chosen for measurement

1. ^{210}Pb line 46 KeV

As a longer-lived ($T\frac{1}{2}$ = 22 years) decay product of radon, ^{210}Pb is a convenient isotope for comparison of intensities with short-lived decay products of radon measured by field instruments. Because in certain cases its equilibrium with ^{226}Ra is rather uncertain due to the possibility of radon loss the ^{214}Bi content has been measured using scintillation detection of the 1.76 MeV peak. In sealed boxes ^{214}Bi is in equilibrium with ^{226}Ra after 30 days. Thus the ^{214}Bi measurement yields information about radon loss, and the content of radium, and the ^{210}Pb measurement is another radium determination. Both are in units of equivalent uranium as mentioned earlier.

2. ^{234}Th line 63 keV

^{234}Th is the first decay product of ^{238}U and is always in radioactive equilibrium with it. The ^{234}Th measurement (in equivalent uranium units) thus indicates the amount of ^{238}U actually present in the sample.

3. $K_{\alpha}1$ - Rn conversion X-ray line of ^{223}Ra 83.3 keV

This isotope is assumed to be in radioactive equilibrium with ^{231}Pa which has a long half-life, and therefore should be a good indication of the amount of uranium present before the rock was subjected to weathering. The line of ^{227}Th can also be used but it is very weak in low activity samples. The K_α-Rn lines are overlapped with K_α-lines of ^{226}Ra, and also with ^{231}Th (short lived product of ^{235}U) and ^{228}Th from the thorium series. The following formula for the concentration of $Q_{223_{Ra}}$ has been determined:

Eqn. 2.
$$Q_{223_{Ra}} = Q_{Peak} - 0.142\, Q_{226_{Ra}} - 0.146\, Q_{231_{Th}} - 0.408\, Q_{228_{Th}}$$

Q_{Peak} is concentration calculated from equation (1) using $K_{\alpha 1}$ - Rn peak (83.3 KeV)

$Q_{226_{Ra}}$ is concentration from ^{214}Bi measured in 1.76 MeV peak using NaI(Tl) crystal

$Q_{231_{Th}}$ is concentration from ^{234}Th which is in a constant ratio with ^{231}Th

$Q_{228_{Th}}$ is concentration from ^{208}Tl measured in 2.62 MeV peak using NaI(Tl) crystal

Disequilibrium gamma-ray spectra of samples from Elliot Lake area

Three types of radioactive disequilibrium have been found in the samples from the Elliot Lake area:

1. ^{238}U deficiency (Fig. 2.3)

The sample spectrum illustrated in Figure 2.3 represents an extreme case of uranium deficiency. The only lines present are those of radium and its decay products. Comparing this spectrum with the uranium ore standard (Fig. 2.1) we can identify the following spectral lines:

^{210}Pb - 46.52 KeV, ^{214}Pb - 53.2 keV, Bi - K X-ray lines which relate to ^{214}Pb in the U series and ^{212}Pb in the thorium series, Po-K_α X-ray lines

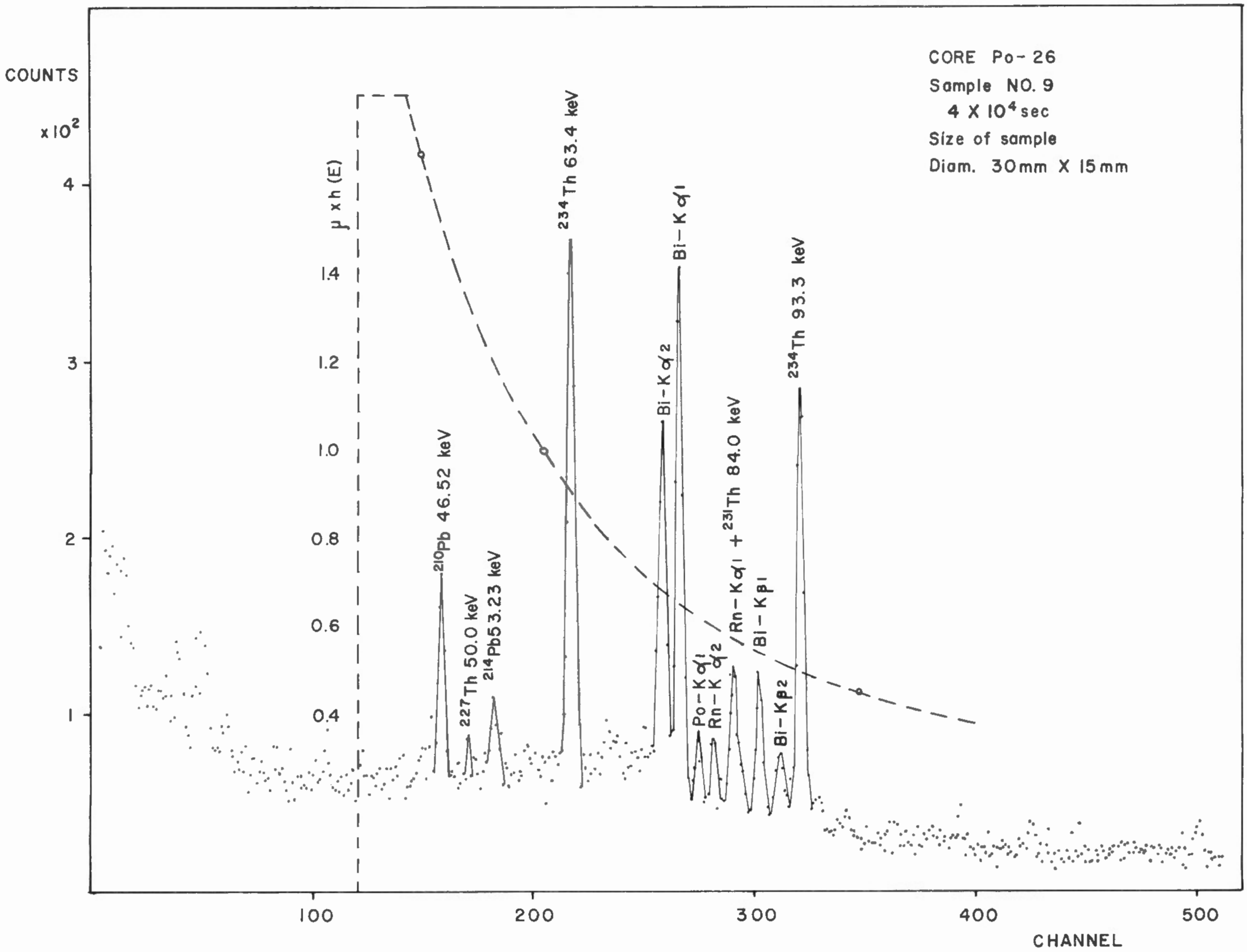

Figure 2.4. Example spectrum showing ^{238}U excess.

which relate to ^{214}Bi, and Rn-K X-ray lines which relate to both ^{223}Ra and ^{226}Ra.

It is presumed that uranium has been removed from the sample by leaching.

2. ^{238}U excess (Fig. 2.4)

In addition to the radium series lines found in the previous example there are in this spectrum strong lines of ^{234}Th (63 and 93 keV). ^{234}Th is the first decay product of ^{238}U and is always in radioactive equilibrium with it.

This example shows fresh deposition of uranium in rock. The decay products did not reach equilibrium which requires a time of about 300 000 years after deposition.

3. ^{231}Pa excess (Fig. 2.5)

Strong lines of ^{231}Pa decay products are present in this spectrum. There are: ^{227}Th 50 keV and Rn-Kα X-ray lines relating to ^{223}Ra.

This type of disequilibrium can be explained as differential leaching of all components except ^{231}Pa which has eminent resistance against leaching. Such type can be found in very weathered rock samples or in soils.

Results of measurement of radioactive disequilibrium of samples from Elliot Lake area

The purpose of measurement was to estimate the effect of radioactive disequilibrium on the results from field radiometric instruments; most of which determine uranium by measuring the ^{214}Bi line at 1.76 MeV, assuming that daughter to be in radioactive equilibrium with uranium. The penetrating depth of this radiation is about 1 foot for a rock density of 2.5 g/cm^3. 90% of the radiation comes from the top layer 5 inches thick. This surface layer was the subject of the present investigation. Six short holes have been core-drilled on the outcrop of the Pronto Mine uranium deposit (*see* location in Fig. 2.6). One hole has been core-drilled on the outcrop of the Buckles Mine uranium deposit.

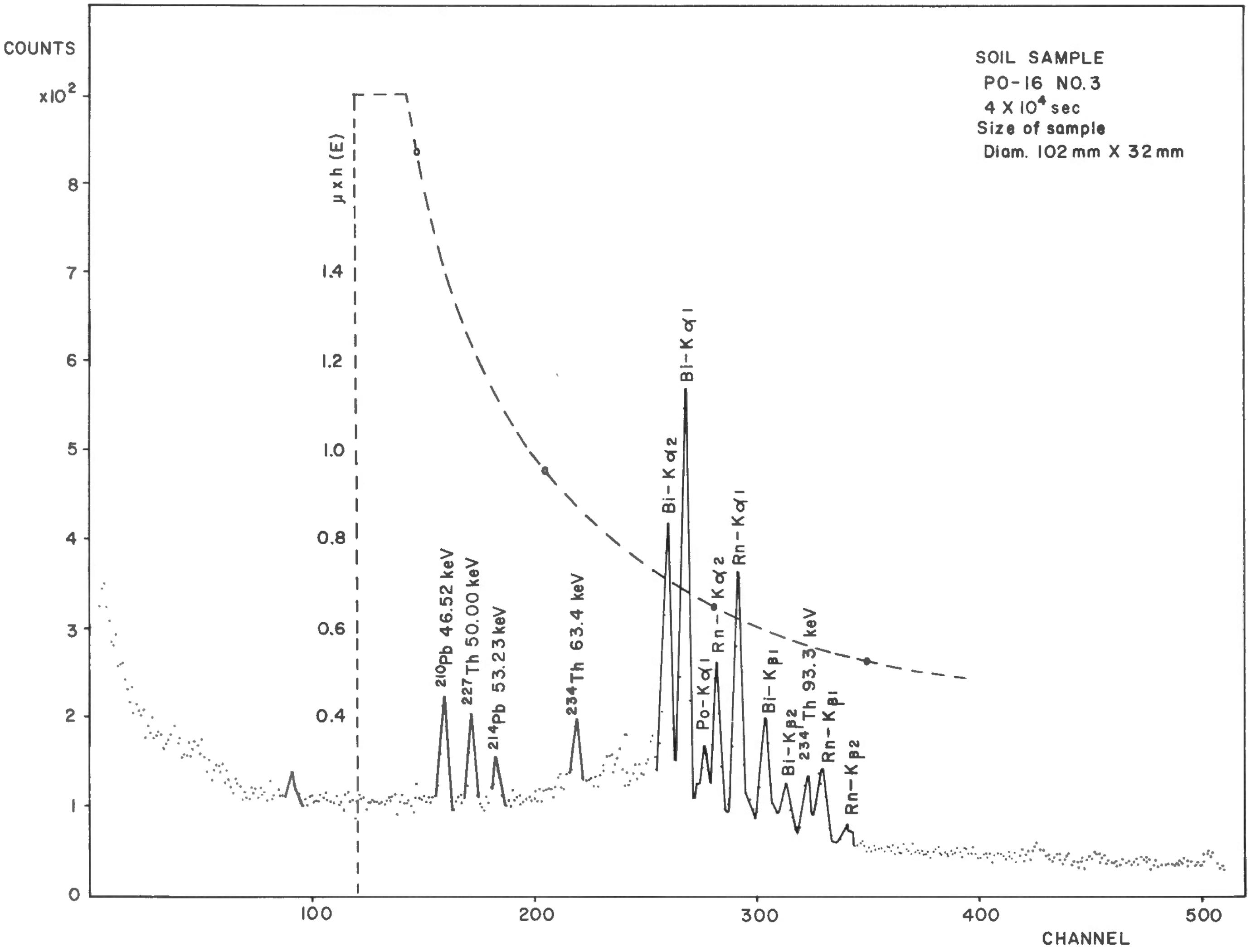

Figure 2.5. Example spectrum showing ^{231}Pa excess.

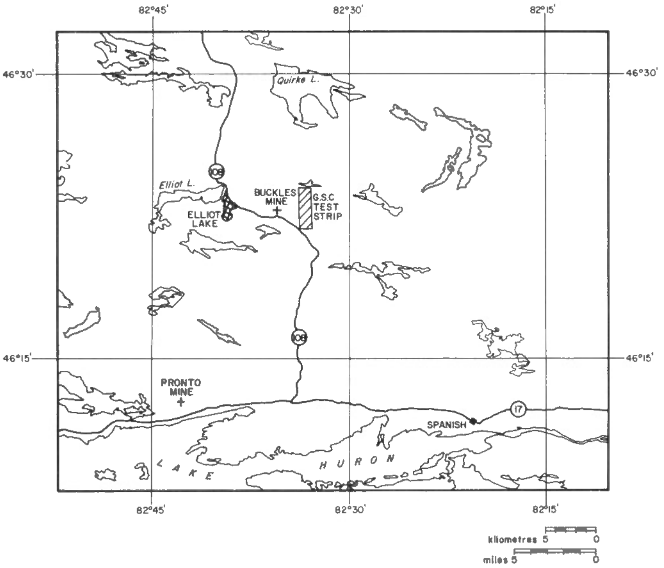

Figure 2. 6. Map showing location where samples were collected.

Several surface samples have been collected from a test strip used for earlier airborne radiometric measurements 2 miles east of Elliot Lake and also from the outcrop near the Pronto Mine. Some soil samples from the area of the Pronto Mine and Elliot Lake test strip were also collected. The average length of the cores was approximately 16 inches.

Cores from the outcrop on Pronto Mine

Core Po-3

Core Po-3 was taken from compact unweathered pyritic radioactive quartz pebble conglomerate. Fresh unweathered pyrite was found under a very thin (1 mm) weathered crust. Some uranium deficiency is apparent ($^{223}Ra/^{224}Th > 1$) along the length of core. This deficiency is the highest above a joint in the core at 15 inches depth and not close to the surface as expected (*see* Fig. 2. 7). In the vicinity of the joint a high ^{223}Ra equivalent uranium content indicates there was a higher original uranium content. Sample 23 at 18 inches depth gives the highest Ra (^{210}Pb) and U(^{234}Th) content measured in this core and thus there is apparent downward movement of uranium. Uranium almost reaches equilibrium at sample 25 (19 inches depth). The $^{223}Ra/^{234}Th$ ratio is slightly less than 1 in this place which also means that some fresh uranium is present. The two extremely high values of $^{223}Ra/^{234}Th$ ratio shown in Figure 2. 7 are found in quartz pebbles where the extremely low U content (i. e. low ^{234}Th) along with significant amounts of ^{223}Ra cause the ratio to blow up. It should be noted that the ^{231}Pa needs nearly 300 000 years before it reaches equilibrium with ^{235}U. Therefore both the ratios $^{223}Ra/^{234}Th$ and $^{231}Pa/^{235}U$ are always less than 1 for uranium accumulated less than 300 000 years ago.

Core Po-14

This core was obtained in the same type of rock as the previous sample about 15 feet south of core Po-3. The $^{234}Th/^{210}Pb$ ratio shows radioactive equilibrium between Uranium-238 and Radium-226 almost along the whole core (Fig. 2. 8). Equilibrium is reached at a depth of 17 inches, although this equilibrium may be only locally created by the high equivalent uranium (^{234}Th) content 2 inches above. The original U distribution with depth was probably similar to the variation of ^{223}Ra content, with a maximum at 16 inches. There are 2 accumulations of new U located at minima on the $^{223}Ra/^{234}Th$ ratio graph which are less than the equilibrium value of 1. The first one is above the original maximum concentration, the second one below it. The uranium is also leached in the vicinity of the joint at 10-11 inches depth where there is also a high ^{231}Pa (^{223}Ra) content. The $^{223}Ra/^{234}Th$ ratio again reaches extreme values in pebble.

Core Po-19

Core Po-19 was drilled in a very weathered part of the conglomerate about 20 feet south of Po-3. The core could not be taken from the first eight inches because it crumbled. The core has small cavities and rusty spots due to weathered pyrite. This visible leaching is confirmed by the extremely high ^{223}Ra (in equilibrium with ^{231}Pa) content and extreme $^{223}Ra/^{234}Th$ (equivalent to $^{231}Pa/^{238}U$) ratio which shows that the original uranium content in the upper part of the core must have been as much as 30 times higher than at present, regardless of ^{231}Pa decay (Fig. 2. 9). It is interesting that amounts of uranium and radium are almost the same as in previous cores with fresh pyrite. The uranium (^{234}Th) maximum with fresh pyrite at a depth of 20 inches has some accumulation of fresh uranium beneath it, indicated by the $^{223}Ra/^{234}Th$ ratio of less than 1.

Core Po-26

Core Po-26 is a short core drilled in a small island of conglomerate in saprolite which is stratigraphically below the uranium orebody, about 30 feet west of Po-3. The conglomerate has small cavities where pyrite is weathered out. The graphs (Fig. 2. 10) show transportation of uranium from conglomerate into originally low radioactivity basement saprolite. The upper part of the core shows deeply leached uranium and the lower part shows a U excess of 2. 5 times with respect to radium. The original concentration of U in the upper part must have been up to 25 times higher as indicated by the $^{223}Ra/^{234}Th$ ratio. The concentration of newly produced ^{231}Pa (in equilibrium with ^{223}Ra) is about 20% higher than the concentration of ^{210}Pb (in equilibrium with ^{230}Th) because ^{231}Pa has a shorter half-life (3.48×10^4 years) than ^{230}Th (7.52×10^4 years) and is therefore produced quicker.

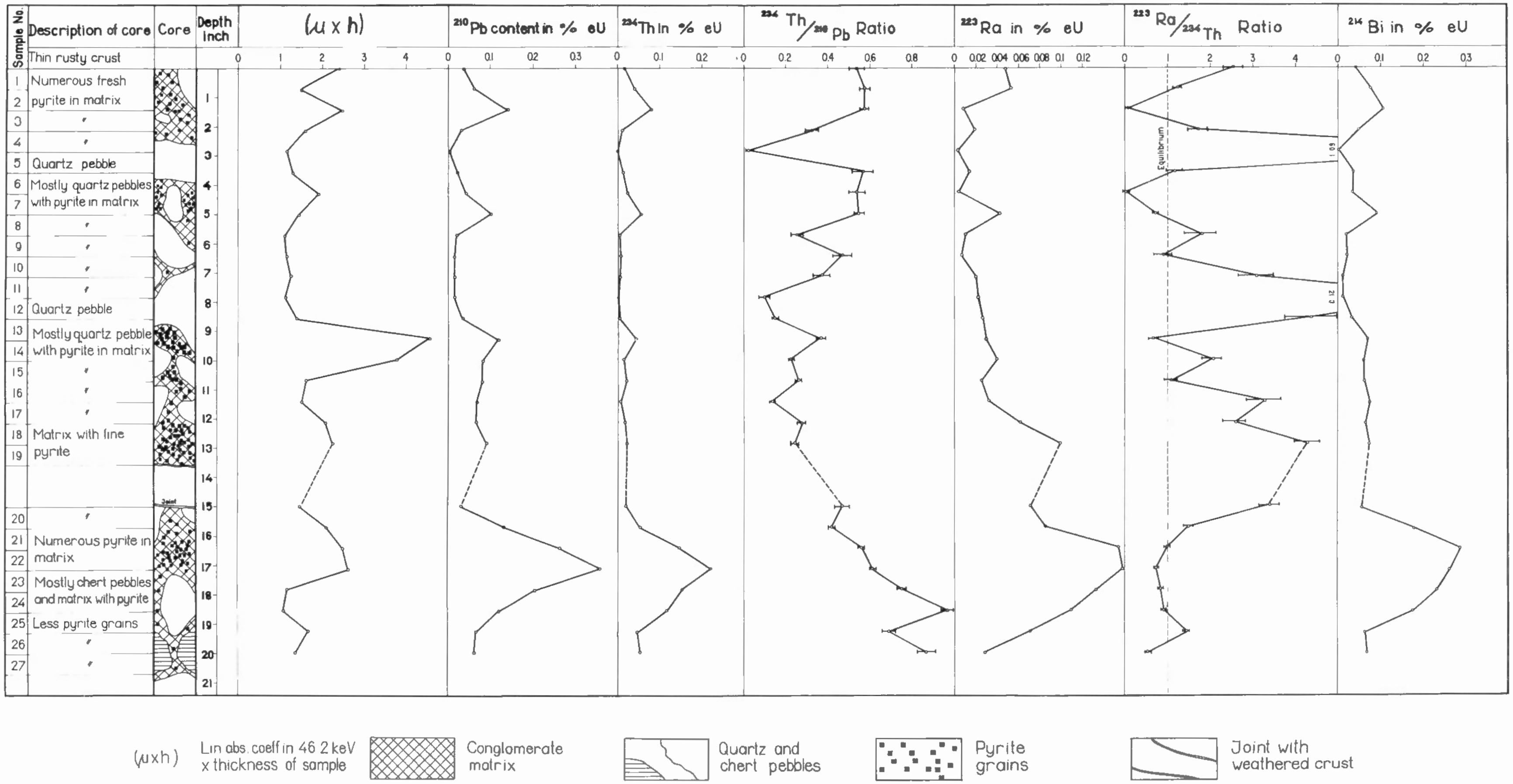

Figure 2. 7. Variations of the isotope concentrations and their ratios measured along drill core Po-3.

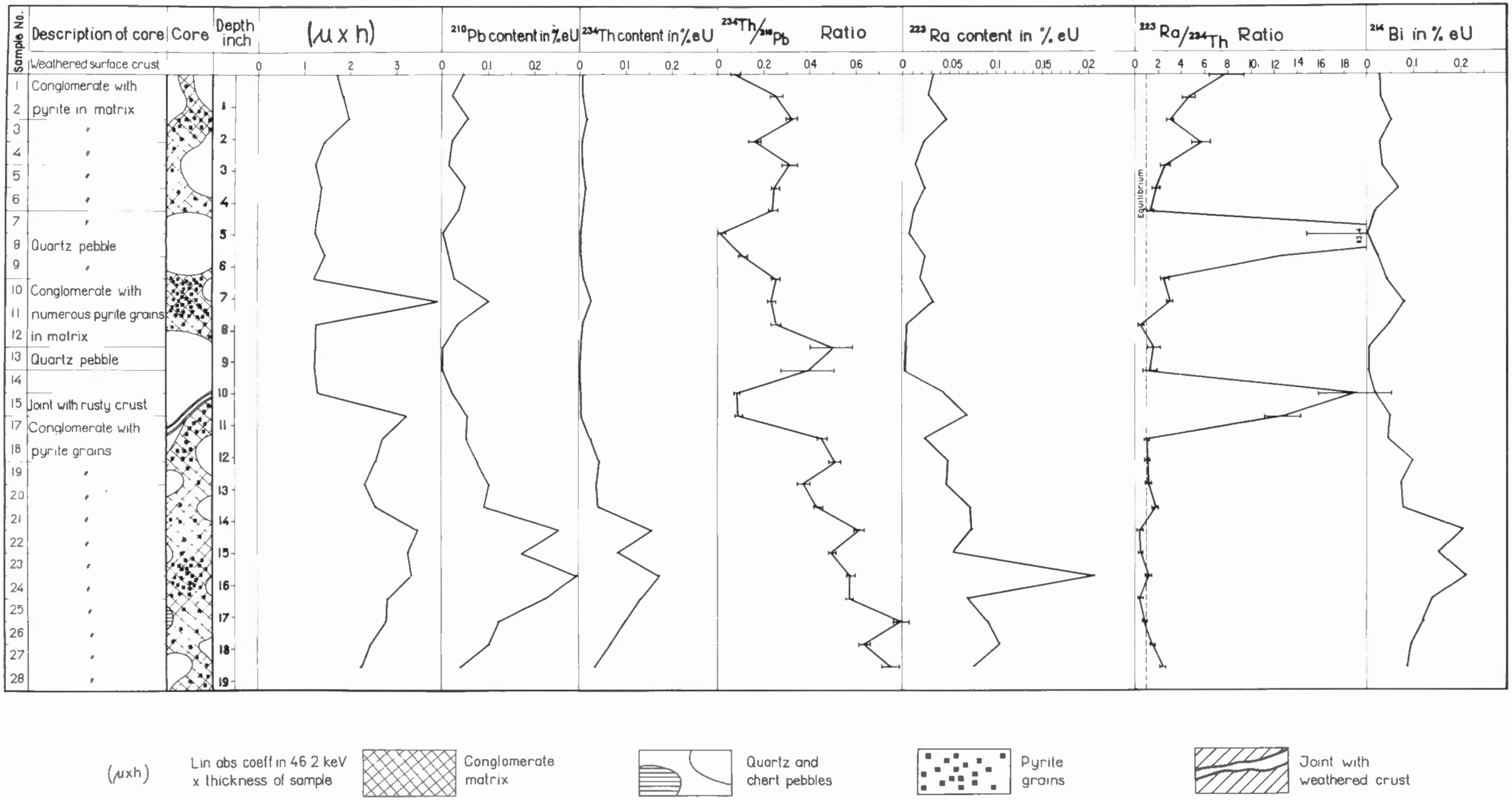

Figure 2. 8. Variations of the isotope concentrations and their ratios measured along drill core Po-14.

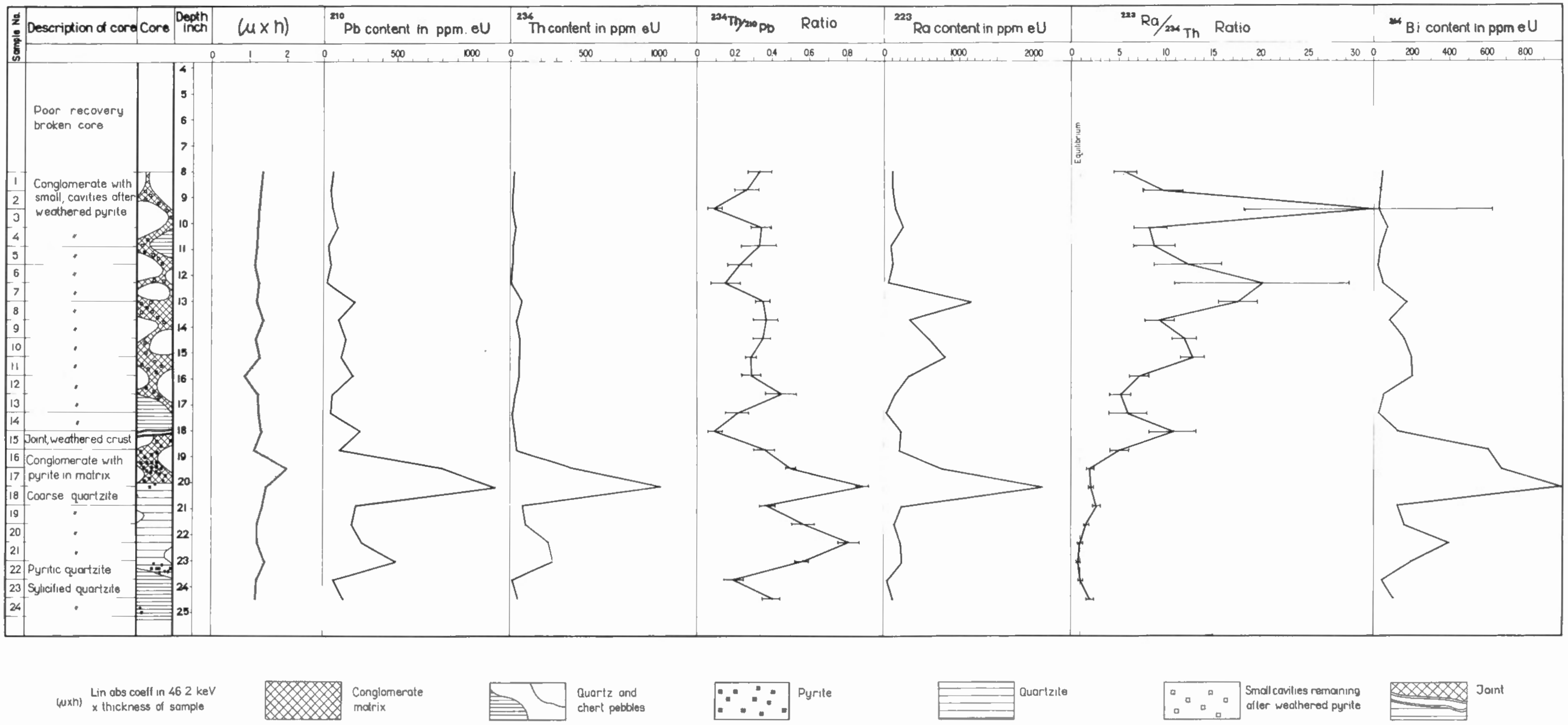

Figure 2. 9. Variations of the isotope concentrations and their ratios measured along drill core Po-19.

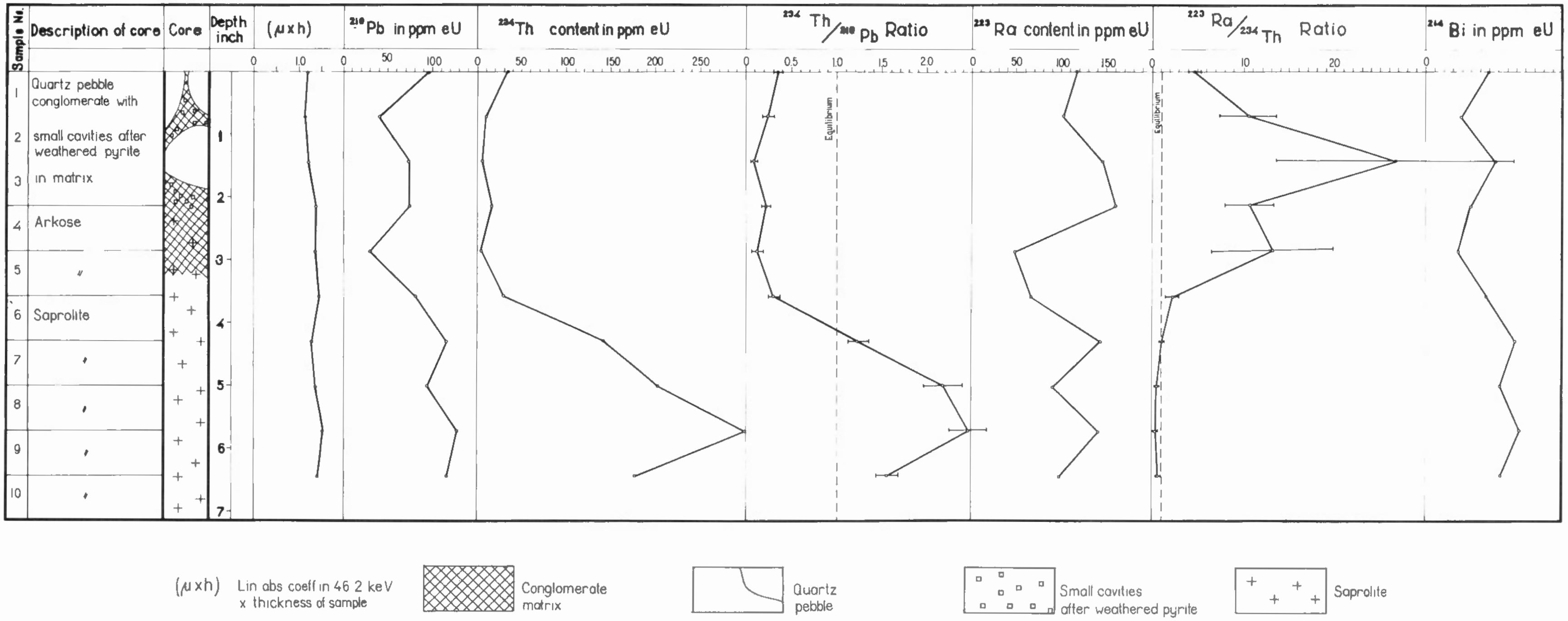

Figure 2. 10. Variations of the isotope concentrations and their ratios measured along drill core Po-26.

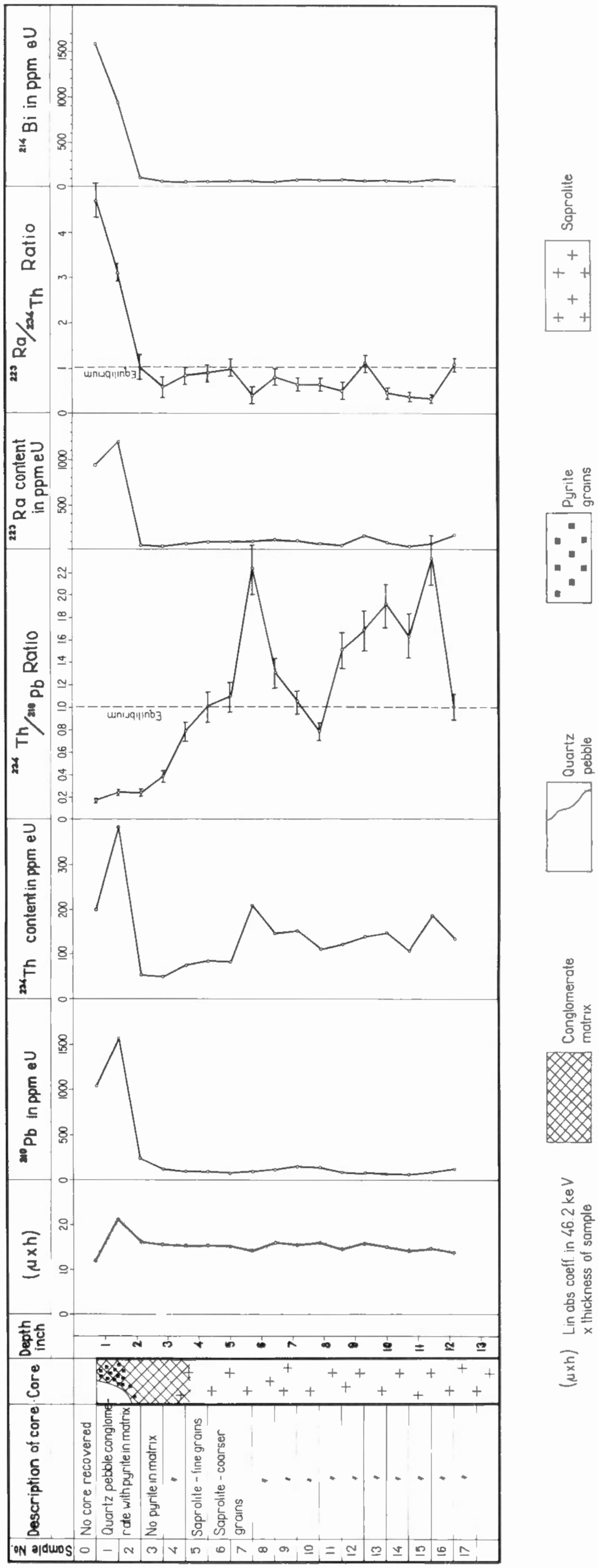

Figure 2. 11. Variations of the isotope concentrations and their ratios measured along drill core Po-21.

TABLE 2.1

Average values of radioactivity of samples taken from surface on Pronto Mine outcrop

SAMPLE NO.	DESCRIPTION OF SAMPLE	^{210}Pb ppm e.U	^{234}Th ppm e.U	^{234}Th / ^{210}Pb	^{223}Ra ppm e.U	^{223}Ra / ^{234}Th	^{214}Bi ppm e.U
Po-13	Weathered uraniferous conglomerate	115.8 ±6.42%	33.1 ±10.31%	0.286 ±12.13%	328.4 ±5.23%	9.92 ±11.55%	110.7 ±1.5%
Po-14	Uraniferous conglomerate with fresh pyrite	705.4 ±2.72%	97.6 ±5.75%	0.138 6.36%	384.6 ±5.12%	3.94 ±7.69%	670.9 ±0.5%

TABLE 2.2

Radioactivity of soil samples and rock covered by soil. (Pronto Mine outcrop)

SAMPLE NO.	DESCRIPTION OF SAMPLE	DEPTH (INCHES)	^{210}Pb ppm e.U	^{234}Th ppm e.U	^{234}Th / ^{210}Pb	^{223}Ra ppm e.U	^{223}Ra / ^{234}Th	^{214}Bi ppm e.U
1	Black soil with plant remains	2	103.8 ±6.98%	30.1 ±4.4%	0.289 ±13.36%	326.9 ±5.62%	10.86 ±12.7%	113.6 ±1.5%
2	Red coloured soil from FeS	4	88.3 ±8.11%	43.1 ±9.70%	0.488 ±12.64%	427.0 ±5.01%	9.90 ±10.91%	109.3 ±1.5%
3	Red coloured soil above solid rock	6	97.6 ±7.53%	47.3 ±8.31%	0.484 ±10.64%	339.7 ±5.0%	7.18 ±9.69%	92.2 ±1.5%
4	Rock crust	6.1	943.8 3.3%	216.1 ±6.7%	0.228 ±7.46%	1099.2 ±5.9%	5.09 ±8.91%	921.1 ±1.3%
5	Uraniferous conglomerate with pyrite	8.1	901.2 ±2.9%	415.0 ±4.0%	0.460 4.93%	479.8 7.74%	1.15 8.71%	895.9 ±0.9%

Core Po-21

Core Po-21 was taken in an area with similar conditions to the previous core. This core has unweathered pyrite in a matrix of conglomerate. The core was drilled about 50 feet NW of Po-3. The transport of uranium from the top 2 inches and its deposition along the lower part of the core is apparent (Fig. 2.11).

Core Po-22

Core Po-22 was drilled about 30 feet NW of Po-3. This core passes through about 3 inches of radioactive conglomerate, then through quartzite. The partial deposition of uranium is apparent in the lower part of the conglomerate but beneath it is a layer showing extreme uranium leaching (high ^{223}Ra/^{234}Th ratio) (sample 6 — *see* Fig. 2.12). It is possible that uranium from this layer was leached and deposited in the lower part of the conglomerate mentioned above (sample 5).

The lower part of the core has very low activity and a definitive measurement would require longer counting.

Samples collected from surface and soil samples

Table 2.1 gives the average results for 20 additional radioactive samples taken from the Pronto Mine outcrop. These samples were collected by hand or chipped by hammer. The samples were divided into 2 groups:

1. Weathered uraniferous conglomerate.
2. Uraniferous conglomerate with fresh pyrite.

The outcrop samples show a high ^{223}Ra content similar to some core samples. An interesting observation is that fresh looking samples with unweathered pyrite show more than double the uranium leaching with respect to radium than shown by weathered samples (from ^{234}Th/^{210}Pb ratio). Weathered samples show leaching of both

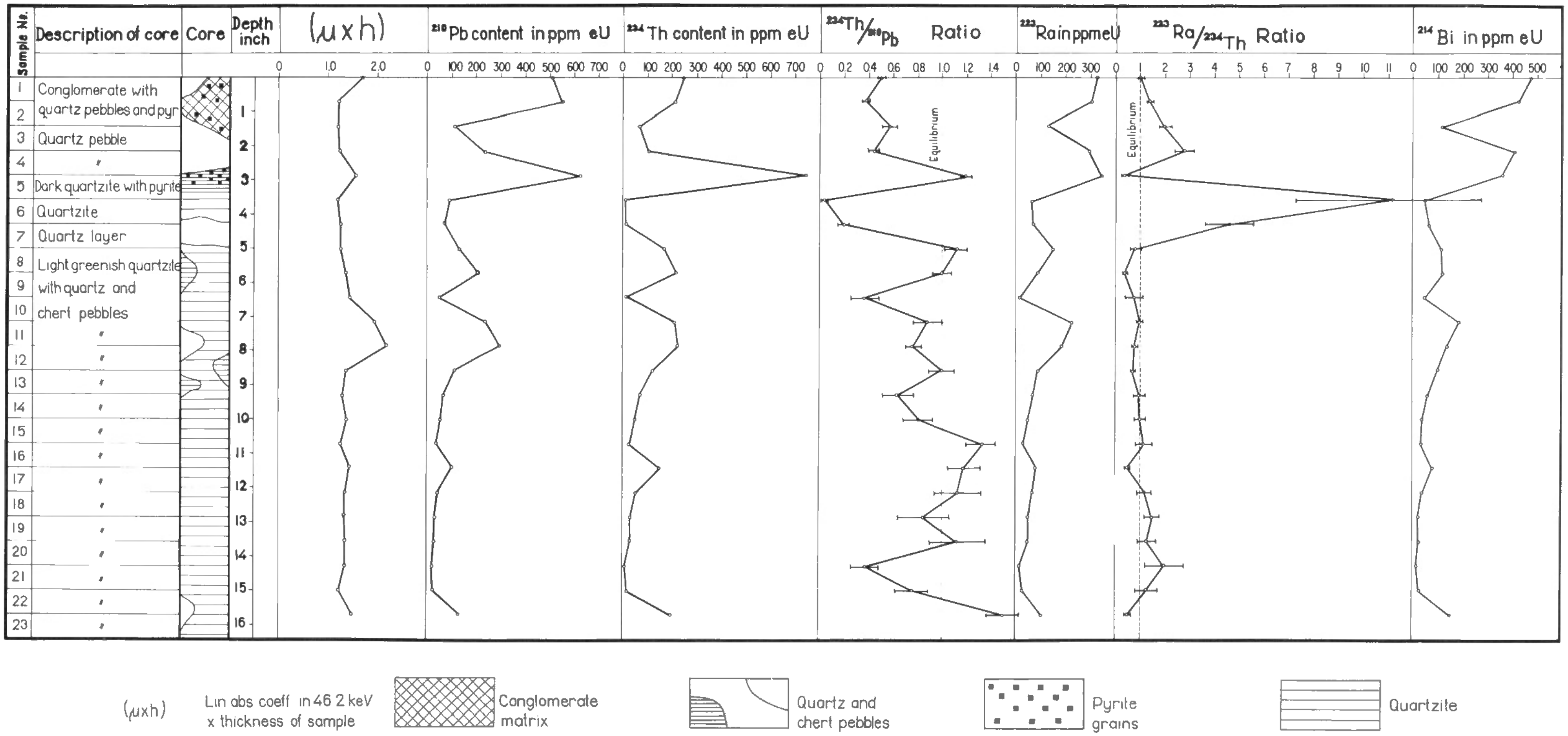

Figure 2. 12. Variations of the isotope concentrations and their ratios measured along drill core Po-22.

TABLE 2. 3

Radioactivity of rock samples collected from surface. (test strip)

SAMPLE	DESCRIPTION OF SAMPLE	^{210}Pb ppm e. U	^{234}Th ppm e. U	^{234}Th / ^{210}Pb	^{223}Ra ppm e. U	^{223}Ra / ^{234}Th	^{214}Bi ppm e. U
X-2	Quartzite	422. 2 ±3. 28	82. 3 ±6. 44%	0. 19 ±7. 22%	362. 6 5. 43%	4. 40 ±8. 41%	390. 6 ±0. 8%
X-20	"	28. 6 ±11. 36	15. 5 ±13. 32%	0. 53 ±17. 60%	18. 3 28. 73%	1. 18 31. 66%	29. 8 ±1. 8%
X-38	"	45. 3 ±9. 69%	18. 3 ±13. 30%	0. 40 ±16. 45%	24. 0 28. 67%	1. 31 ±31. 60%	38. 1 ±2. 4%
X-39	"	70. 6 ±7. 77%	10. 2 ±17. 9%	0. 14 ±19. 51%	54. 7 18. 56%	5. 36 ±25. 78%	65. 8 ±1. 9%
X-40	"	178. 6 ±5. 40	18. 0 ±14. 91%	0. 10 ±15. 85%	133. 8 11. 18%	7. 43 ±18. 62%	146. 2 1. 4%
X-42	"	9. 2 ±23. 57%	5. 2 ±28. 40%	0. 56 ±34. 65%	13. 7 29. 2%	2. 63 ±38. 7%	5. 3 ±4. 2%

TABLE 2. 4

Results from underground samples. (Denison Mines)

SAMPLE NO.	DESCRIPTION OF SAMPLE	^{210}Pb ppm e. U	^{234}Th ppm e. U	^{234}Th / ^{210}Pb	^{223}Ra ppm e. U	^{223}Ra / ^{234}Th	^{214}Bi ppm e. U
Den-4	Uraniferous conglomerate	7075 ±1. 1%	9436 ±0. 9%	1. 33 1. 42%	8375 2. 59%	0. 887 ±2. 74%	11457 ±0. 2%
Den-3	Uraniferous pyritic conglomerate	793 ±2. 8%	1037 ±2. 4%	1. 31 ±3. 68%	703 6. 08%	0. 679 ±6. 53%	969 ±1. 1%

uranium (^{234}Th) and radium (^{210}Pb) while unweathered samples indicate only uranium is leached.

Soil samples (Table 2. 2) show lower concentration of ^{223}Ra (in equilibrium with ^{231}Pa) than the rock samples. It is interesting that soil samples still have a certain amount of uranium (^{234}Th) and the disequilibrium between uranium and radium (^{234}Th/^{210}Pb) is not as high as in many rock samples.

Core from the outcrop at the Buckles Mine

The core Bu-17 was drilled about 150 yards east of Highway 108 on the highest point of the Buckles Mine outcrop south of the town of Elliot Lake. The core passes through quartzite which has four radioactive layers (Fig. 2. 13). The uranium appears to be leached from the upper part of layers and deposited about 1 inch below. The ^{223}Ra/^{234}Th ratio is greater than 1 above the layers which indicates uranium leaching and the ratio is less than 1 under the layers which indicates accumulation of fresh uranium.

Measurement of samples from the test strip

Several samples have been collected from a test strip 2 miles east of Elliot Lake (Fig. 2. 6). These samples have been collected from the surface or chipped from the rock by hammer. The information about disequilibrium obtained from these samples concerns only the surface two inches of rock not deeper. Results are given in Table 2. 3. Samples with high radioactivity show a similar type of disequilibrium as samples from the previously discussed outcrops. Low activity samples (X-20, X-42) show a lesser degree of uranium loss as indicated by the ^{234}Th/^{210}Pb ratio. Because samples with U concentrations of 10 ppm or less require

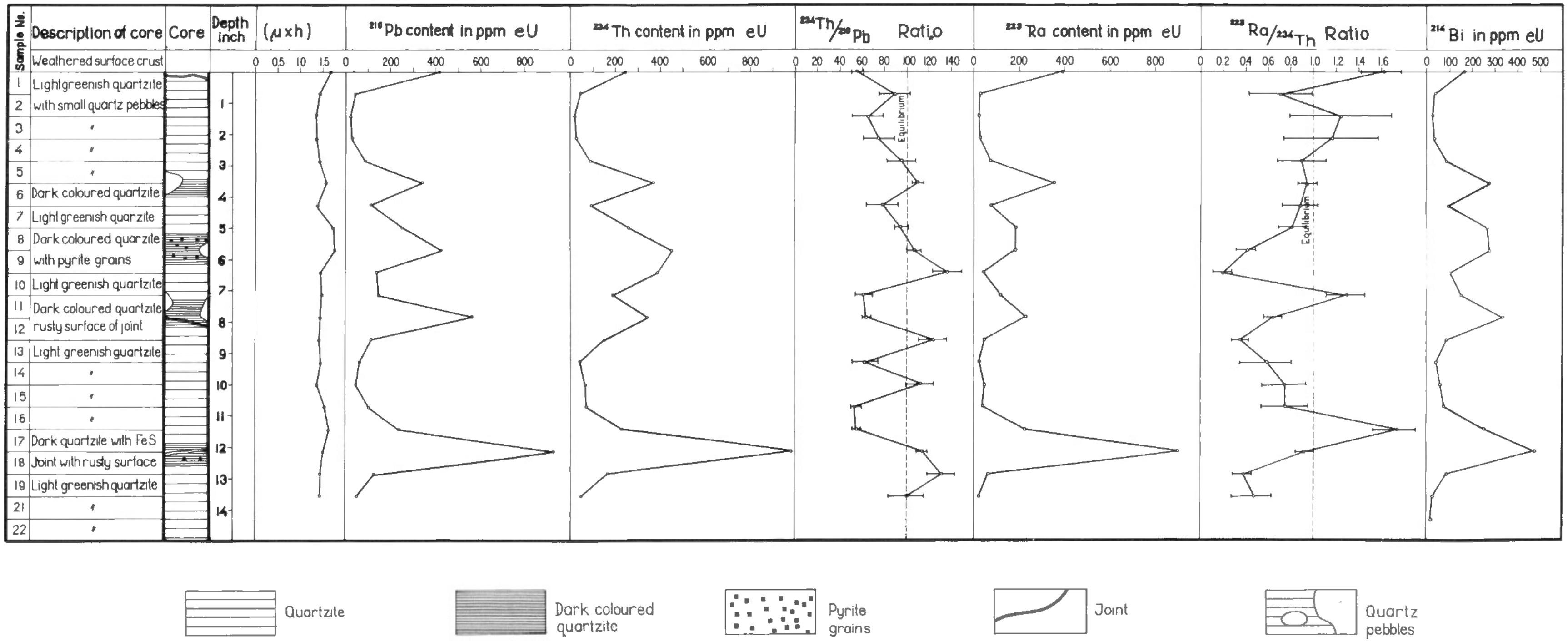

Figure 2. 13. Variations of the isotope concentrations and their ratios measured along drill core Bu-17.

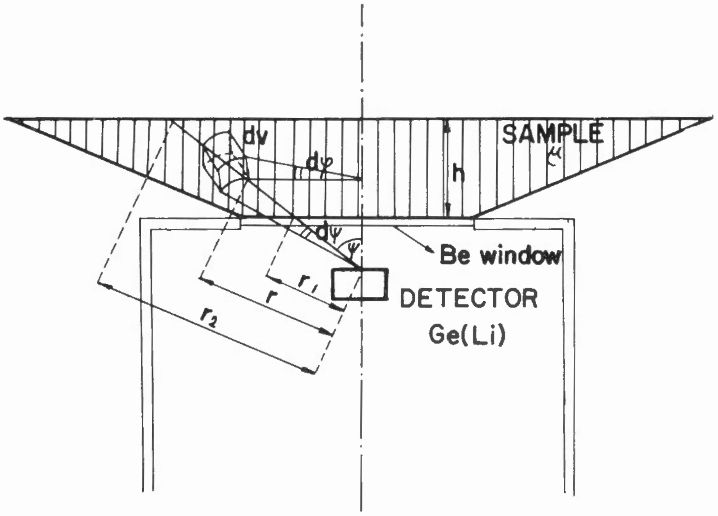

Figure 2. 14. The passage of gamma rays in the sample showing geometry for derivation of equation 1.

counting times of at least 24 hours, it was not possible to analyze all of the test strip samples.

Measurement of deep samples

Two underground samples from the Denison Mine have been measured for comparison with samples from the outcrops. Results are shown in Table 2. 4. The samples show a slight enrichment of uranium (^{234}Th) with respect to radium (^{210}Pb) and a slight deficiency of ^{231}Pa (^{223}Ra). Thus preliminary indications are that there has been some movement of U even at great depth, although this requires further study.

Conclusion

Measurements have been made on 164 samples from three locations in the Elliot Lake uranium mining region, to determine the state of radioactive equilibrium in the ^{238}U decay series, using a Ge(Li) detector to examine the low energy portion of the gamma-ray spectrum.

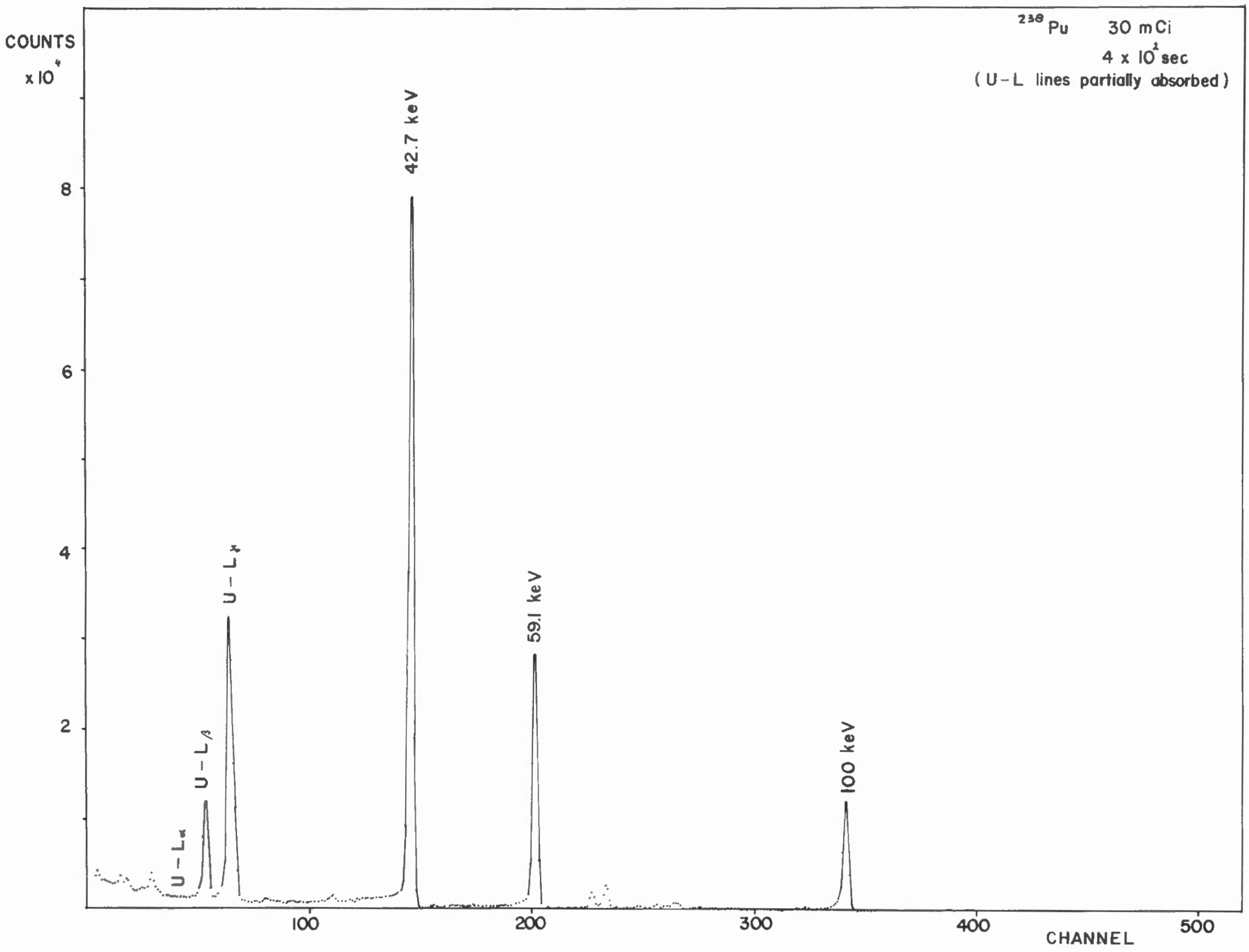

Figure 2. 15. The gamma spectrum of ^{238}Pu.

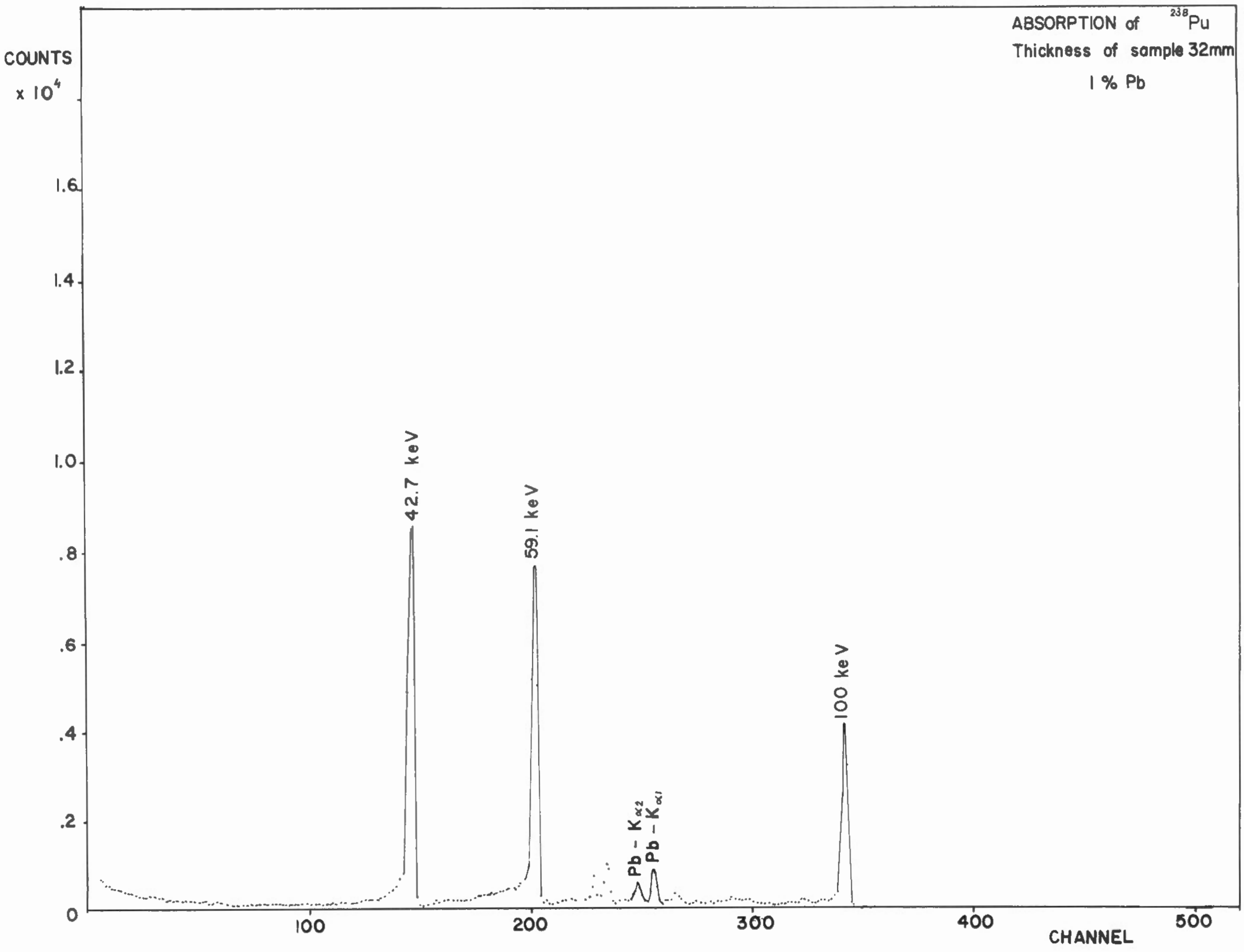

Figure 2.16. The gamma spectrum of ^{238}Pu radiation after passing through the sample.

Most of these (151) were drill core samples from shallow (less than 2 feet) holes. A considerable degree of disequilibrium was observed in most of the core samples. Results indicate a deficiency of uranium with respect to radium near the tops of the cores and some fresh uranium accumulation below where the ^{234}Th/^{210}Pb ratios approach or exceed the equilibrium value of 1.

The greatest uranium deficiency (as high as 90%) occurs in fresh-looking samples containing pyrite, collected from the outcrop surface. The cause of disequilibrium in pyritic uranium ores has been discussed by Phair and Levine (1953). Sulphates formed in those minerals would retain the radium even though it might migrate somewhat, whereas the sulphuric acid formed would leach and remove uranium. Also an excess of ^{231}Pa (by a factor of almost 30) has been found in weathered rock and soils. The excess of ^{231}Pa and ^{223}Ra in some minerals is also known (Kuroda, 1955; Cherdyntsev *et al.*, 1961).

The equivalent uranium concentrations as determined by ^{214}Bi and ^{210}Pb measurements, for the samples listed in Tables 2.1 to 2.4 are generally in quite good agreement. Since gamma-ray spectrometric determinations of uranium are usually based on the measurement of ^{214}Bi activity, then the ^{234}Th/^{210}Pb ratio should be a good indication of how a chemical uranium analysis would compare with a gamma-ray spectrometer analysis. Results in Table 2.4 indicate that spectrometric analyses of the two underground samples would give a slightly low uranium value, and surface spectrometric analyses would yield equivalent uranium values greater than the true uranium concentration.

This investigation has shown that rapid changes in the state of radioactive equilibrium can occur over a very small area and over small changes in depth. The highly leached places may be located very close to places with high uranium accumulation.

In the samples tested, both rocks and soil show some surface disequilibrium, decreasing with depth (i.e. returning to equilibrium). In general the degree of disequilibrium appears also to relate to the levels of uranium concentration as indicated by results given in the tables.

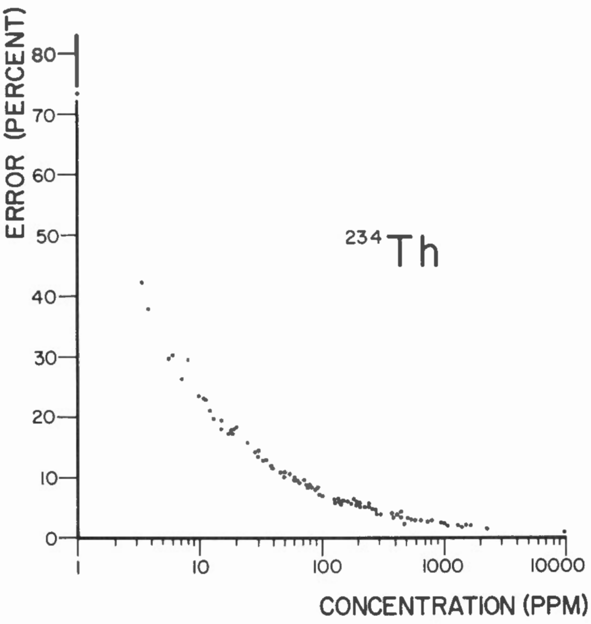

Figure 2.17a. The relative error in concentration of ^{234}Th.

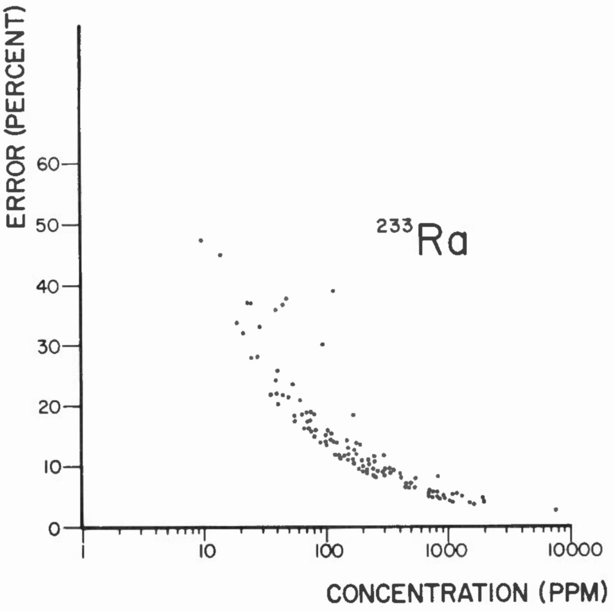

Figure 2.17b. The relative error in concentration of ^{233}Ra.

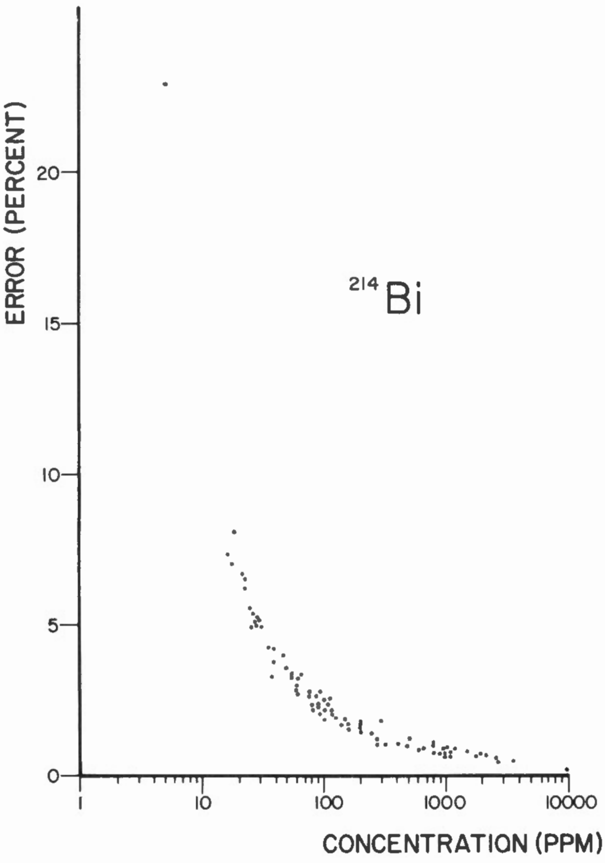

Figure 2.17c. The relative error in concentration of ^{214}Bi.

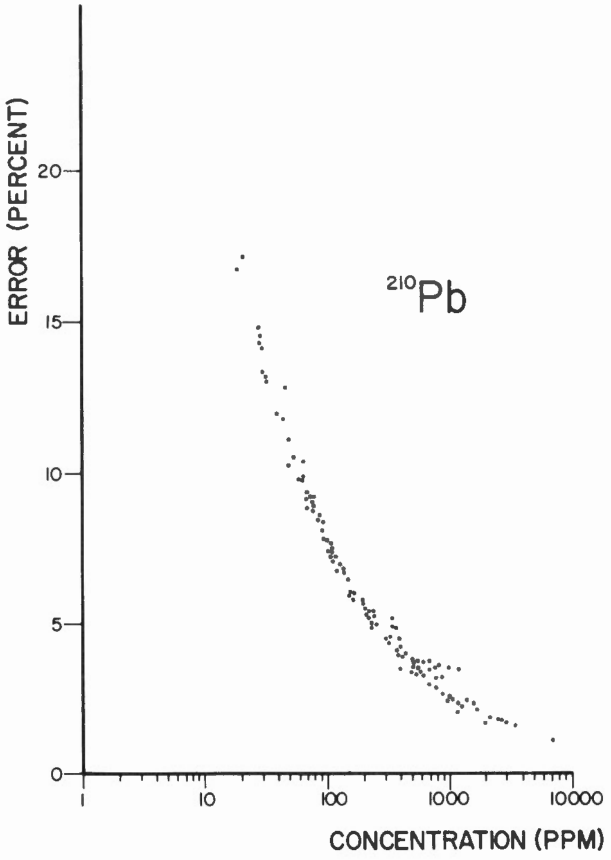

Figure 2.17d. The relative error in concentration of ^{210}Pb.

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APPENDIX 1

Corrections for matrix effect in a sample

The intensity P_γ of gamma-rays from a small volume dv in a measured sample is given by Gorshkov (1967).

$$dP = P_\gamma \frac{q\,dv}{r^2} e^{-\mu(r-r_1)} \qquad \text{....} \quad (3)$$

where P_γ is a constant, q the volume concentration of radioactive substance in a sample, r the distance from a detector and μ the linear coefficient of absorption.

In spherical coordinates this volume is:

$$dv = r^2 \sin\psi \, d\psi \, d\phi dr$$

and the radiation of the whole sample is given by: (*see* Fig. 2.14):

$$P = P_\gamma q \int_o^{2\pi} d\phi \int_o^{\psi_o} \sin\psi \, d\psi \int_{r_1}^{r_2} e^{-\mu(r-r_1)} \, dr =$$

$$= 2\pi P_\gamma q \int_o^{\psi_o} \sin\psi \, d\psi \, (1 - e^{-\mu(r_2 - r_1)}) =$$

$$= \frac{2\pi P_\gamma q}{\mu} \left[(1 - \cos\psi_o) - \int_o^{\psi_o} e^{-\mu h \sec\psi} \sin\psi \, d\psi \right]$$

because $r_2 - r_1 = h \sec\psi$.
where h is the thickness of the sample.
This integral can be solved using King's function ϕ

$$\phi(x) = e^{-x} - x \int_x^{\infty} e^{t} \frac{1}{t} \, dt$$

Then from Gorshkov (1967) we have:

$$\int_o^{\psi_o} e^{-\mu\eta\sec\psi} \sin\psi \, d\psi = \int_o^{\frac{\pi}{2}} e^{-\mu h \sec\psi} \sin\psi \, d\psi - \int_{\psi_o}^{\frac{\pi}{2}} e^{-\mu h \sec\psi} \sin\psi \, d\psi =$$

$$= \phi(\mu h) - \cos\psi_o \; \phi(\mu h \sec\psi_o)$$

Finally, the radiation of a sample is

$$P = \frac{2\pi P_\gamma q}{\mu} \left[(1 - \cos\psi_o) - \phi(\mu h) + \cos\psi_o \; \phi(\mu h \sec\psi_o) \right] \qquad \text{....} \quad (4)$$

P is intensity of radioactive radiation or the number of counts per unit of time. If we consider the number of counts only as the area of a narrow peak of a given spectral line, then we can eliminate the effect of scattered radiation and the above is correct.

The volume concentration q can be found from equation (4)

$$q = \frac{\mu P}{2\pi P_\gamma \left[(1 - \cos\psi_o) - \phi(\mu h) - \cos\psi_o \; \phi(\mu h \sec\psi_o) \right]} \qquad \text{....} \quad (5)$$

Constant P_γ is determined from the standard of known volume concentration q and ϕ is King's function, which is given in tables. The value of μh is measured for each sample by measuring the absorption (*see* Appendix 2). Quantity h is the thickness of the sample. Quantity ψ_o is dependent on the position of the sample and the detector and is constant.

Note:

The value q from the equation (4) is the volume concentration. The weight concentration is $Q = q/\rho$ ..... where ρ is density. Using this relation, with equation (5) for the standard and then for the sample, and taking the ratio of standard and sample we get:

$$Q_{sa} = Q_{st} \frac{P_{sa}\,\rho_{st}\,\mu_{sa}\,[1 - \phi(\mu_{st}h_{st}) - \cos\psi_{st}[1 - \phi(\mu_{st}h_{st}\sec\psi_{st})]]}{P_{st}\,\rho_{sa}\,\mu_{st}\,[1 - \phi(\mu_{sa}h_{sa}) - \cos\psi_{sa}[1 - \phi(\mu_{sa}h_{sa}\sec\psi_{sa})]]} \qquad \ldots.\ (6)$$

where values marked st and sa define the standard and the sample respectively. P_{sa}/P_{st} is the ratio of number of counts in the peaks. ρ_{sa}/ρ_{st} is the correction for densities. μ_{sa}/μ_{st} is the correction for linear absorption coefficients. Expressions in the bracket are the corrections for different geometry (visual angle 2ψ) and thickness h as the samples in higher energies are not saturated by gamma-radiation. (If the standard and the sample have the same volume then the ratio of weights g_{sa}/g_{st} can be substituted for ρ_{sa}/ρ_{st}.)

APPENDIX 2

Determination of the linear absorption coefficient in a sample for a given energy

Equation 6 requires that the linear absorption coefficient (μ) for the energy of the measured spectral line be known. It can be found directly from the equation $I = I_o e^{-\mu h}$ if the transmission of radiation of given energy through the sample is measured. I_o is the intensity of radiation before, and I after, passing through the sample; h is thickness of sample and μ is the linear absorption coefficient.

It has been found very useful to measure the coefficients of absorption by means of a ^{238}Pu source, which has very strong uranium L — lines and 2 prominent gamma lines with energies 42.7 KeV, and 100.0 KeV. In addition the source contains a 59.1 KeV peak from ^{241}Am (Fig. 2.15). The spectrum of radiation after passing through the sample is shown in Figure 2.16. The absorption coefficients for a given energy are obtained by interpolation; setting the curve $\mu = KE^{-n} + 1$ through 3 measured points (3 prominent energies of ^{238}Pu). μ is the linear absorption coefficient, E energy, and k, 1, n are constants. These experimental curves are shown on Figures 1, 3, 4, 5. (μ is then multiplied by thickness h to obtain the value for Equation 6.)

Note:

If the concentration of heavy elements in the sample is high, there are jumps in the absorption curve. The height of the jump for the K — absorption edge is $\delta_K = E_K/E_{LI}$ where E_K and E_{LI} are the critical absorption energies for the K and LI shells respectively. The corresponding change of absorption for an element with concentration Q at its critical energy E_K is

$$\frac{\mu}{\mu_k} = 1 - \frac{1 - \delta_k}{100} Q$$

The absorption jumps can be neglected for concentrations of heavier elements less than 1%.

APPENDIX 3

The estimation of errors

1. Errors for ^{208}Tl and ^{214}Bi measured by scintillation gamma-ray spectrometry

The least squares method (Salmon, 1961) was used for calculation of concentrations and relative errors of these two isotopes.

The basic condition of this method is given by relation

$$N_i = \sum_{j=1}^{m} a_{ij} x_j + Z_i$$

where N_i is the number of counts in the i channel

m is the number of measured nuclides which in this case equals 3, i.e. each rock has contributions from the Th series, U series and K

a_{ij} is the number of counts of the standard j in the channel i

x_j is the ratio of unknown activity to the activity of the standard

Z_i is a random error

The condition of minimum gives in our case three equations for calculation of concentrations of ^{214}Bi, ^{208}Tl and ^{40}K.

The error (standard deviation) is then given as:

$$\sigma(Q_{214_j}) = \sqrt{\sum_{i=1}^{n} \frac{(N_i - a_{iBi} x_{Bi} - a_{iTl} x_{Tl} - a_{iK} x_K)^2 A_{jj}}{n-3}}$$

j = Bi, Tl, K.

where n is the number of channels used.

A_{jj} is the first member of the diagonal on the inverse matrix of the three equations for calculation of concentrations.

The similar equations are for Tl and K. The concentration of K is not presented in paper. The relative errors are plotted against concentrations in Figure 2. 17.

2. Errors for ^{234}Th, ^{210}Pb and ^{223}Ra measured by the solid state detector

In the case of ^{234}Th and ^{210}Pb, the number of counts in each peak above the line connecting minimum points in the vicinity of the peak was counted.

If we consider that all variables of Equation 1 except P_{sa} (number of counts) are measured absolutely correct then the error* is

$$\sigma(Q_{sa}) = k \sqrt{P_{sa} + B} \qquad \ldots\ldots (7a)$$

or the relative error

$$\sigma(Q_{sa})_{rel} = \frac{\sqrt{P_{sa} + B}}{P_{sa}} \; 100 \qquad \ldots\ldots (7b)$$

---

*The error of counting is $\sqrt{N}$ where N is number of counts.

where k covers the part of Equation 1 except P_{sa} and B is background.

We can plot again (*see* Fig. 2.17) the graph of $\sigma(Q_{sa}) = f(Q_{sa})$ where the dispersion of points show the possible error of neglecting other factors.

The error in the determination of ^{223}Ra can be estimated from Equation 2 by applying the general formula for errors

$$\sigma(V) \quad = \quad \sigma f(x, y, z. \dots) \quad = \quad \sqrt{\frac{(\delta f)^2}{(\delta x)} \sigma^2(x) + \frac{(\delta f)^2}{(\delta y)} \sigma(y) + \frac{(\delta f)^2}{(\delta z)} \sigma^2(z)} \qquad \dots (8)$$

where x, y, z, ... are the measured variables.

In this case

$$\sigma(Q_{223_{Ra}}) = \sqrt{\sigma^2(Q_{peak}) + 0.142^2 \sigma^2(Q_{226_{Ra}}) + 0.146^2 \sigma^2(Q_{231_{Th}}) + 0.408^2 \sigma^2(Q_{228_{Th}})}$$

where:

$\sigma(Q_{peak})$ is calculated for the uncorrected ^{223}Ra peak using Equation (7a). $\sigma(Q_{231_{Th}}) = \sigma(Q_{234_{Th}})$ is calculated using Equation (7a). The errors $\sigma(Q_{226_{Ra}}) = \sigma(Q_{214_{Bi}})$ and $\sigma(Q_{228_{Th}}) = \sigma(Q_{208_{Tl}})$ are calculated by the least squares method described above in section 1. Errors of ^{223}Ra are shown on Figure 2.17d. The errors of ratios ^{234}Th/^{210}Pb, ^{223}Ra/^{234}Th and ^{208}Tl/^{214}Bi are simply expressed as

$$\sigma(\text{Ratio})_{rel} = \sqrt{\sigma^2(\text{numerator}_{rel} + \sigma^2(\text{denominator})_{rel}}$$

These errors transferred on the absolute are plotted on the graphs of the cores.

APPENDIX 4

The radioactive decay series for Uranium-238, Thorium-232, Uranium-235

Disintegration Series of Uranium 238

(Principal members only; isotopes constituting less than 0.2 per cent of the decay products are omitted)

Uranium 238 [4.51 × 10^9y]

↓ α

Thorium 234 [24.10d]

↓ β

Protactinium 234 [1.14m]

↓ β

Uranium 234 [2.48 × 10^5y]

↓ α

Thorium 230 [8.0 × 10^4y]

↓ α

Radium 226 [1,622y]

↓ α

Radon 222 [3.825d]

↓ α

Polonium 218 [3.05m]

↓ α

Lead 214 [26.8m]

↓ β

Bismuth 214 [19.7m]

↓ β

Polonium 214 [1.50 × 10^{-4}s]

↓ α

Lead 210 [22y]

↓ β

Bismuth 210 [5.02d]

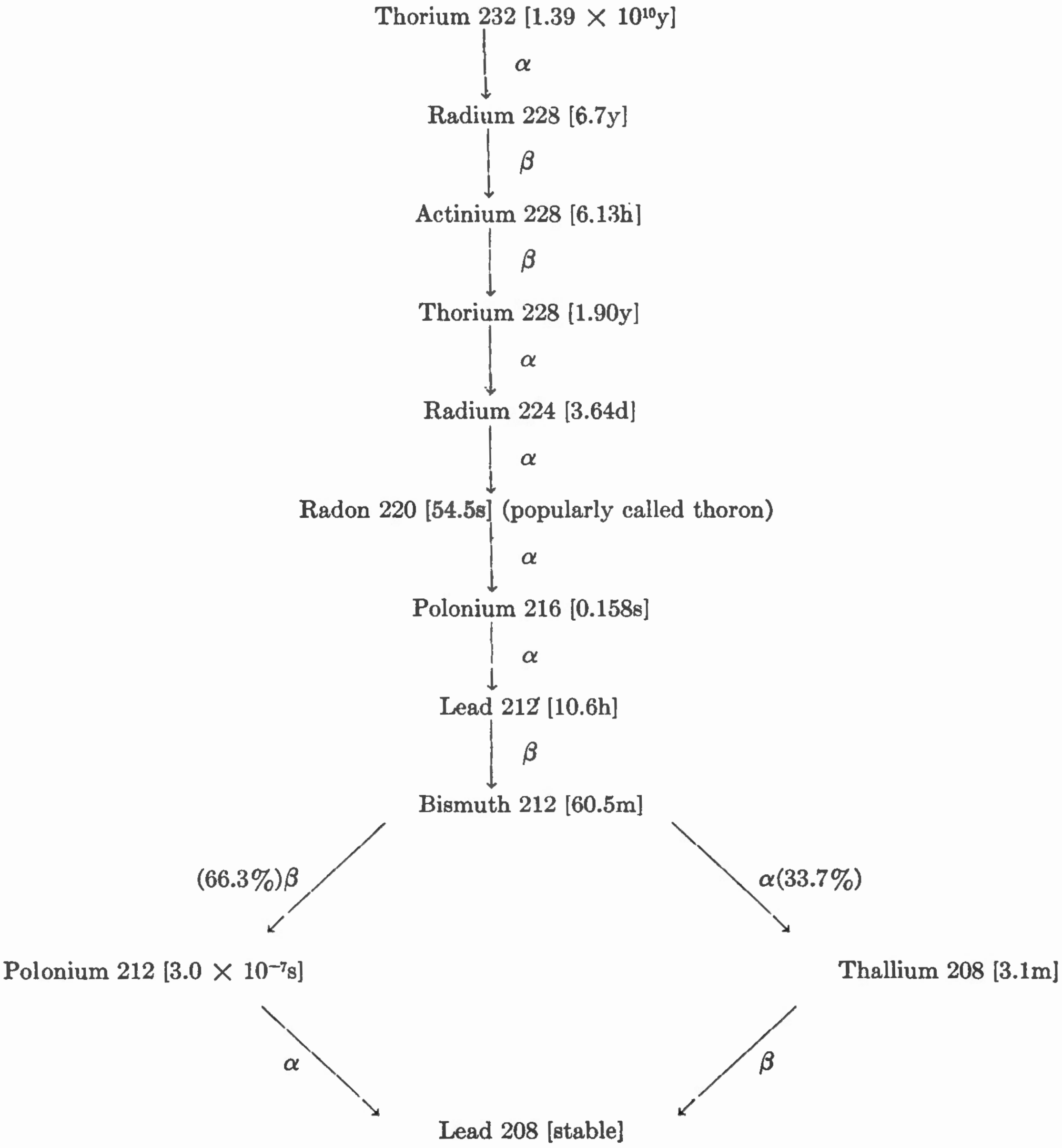
↓ β

Polonium 210 [138d]

↓ α

Lead 206 [stable]

Disintegration Series of Thorium 232



Disintegration Series of Uranium 235