SECULAR EQUILIBRIUM IN ORES

FROM THE PNC EXPLORATION SITE

REPORT TO PNC EXPLORATION PTY LTD

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SUMMARY

The uranium ores obtained from the PNC exploration site are highly unusual as they exhibit marked disequilibrium between uranium-238 and its daughters and have very high radon emanation coefficients. The high emanation coefficients of the peat samples suggest that radium is not present in the mineral lattice but as an adsorbed species on the surface of a highly porous material.

1. INTRODUCTION

Samples of ores and sediments from the PNC exploration site were analysed for the degree of secular equilibrium in the uranium-238 chain, the activities of individual radionuclides and emanation coefficients. This information was required for the calibration of the gamma-logging probe used in the exploration bore holes.

2. BACKGROUND

Secular Equilibrium

Disequilibrium develops in decay chains when they are present in chemically open systems and when the different physical and chemical properties of each nuclide permit their fractionation. The uranium-238 system is particularly susceptible to the development of disequilibrium because it contains several chemically distinct nuclides with long half-lives. Several studies have shown that these nuclides may be separated during weathering and other alteration processes.

A number of different forms of disequilibrium have been categorised; the two most applicable to this study are daughter product excess and deficiency. Daughter product excess is usually found in oxidising environments and is produced by leaching of the parent uranium-238. On the other hand, daughter product deficiency can be due to the very recent introduction of the parent or to chemical leaching of the daughters. The latter process is considered to be the more important and usually radium-226 is the most easily leached daughter.

Emanation Coefficient

The radon emanation coefficient is usually defined as the fraction of radon generated which escapes the particle in which it is formed and is free to diffuse through the bulk medium. It is generally accepted that radon escape from a grain is as a result of its recoil when its parent, radium-226, decays. If the recoil terminates outside the particle or in an open pore, the radon is able to migrate to a free surface. However, as the recoil range in solids is small (4×10^{-5} mm), most of the recoiling atoms are contained within the mineral grain. Movement of the atom is then controlled by diffusion through the mineral grain. This process does not significantly contribute to radon release because of the very small radon diffusion coefficient through minerals, 10^{-25} to 10^{-27} $m^2{}_s{}^{-1}$.

Measured values of the emanation coefficient vary from almost 0 to I, however, for uranium ores they generally lie between 0.1 and 0.3. The emanation coefficient depends on uranium and host rock mineralogy, particle size and moisture content.

3. ANALYSIS TECHNIQUES

The uranium levels measured by Sheen Laboratories were used in this study with the exception of some special cases discussed in Section 4.

Gamma-spectrometry was used to measure the activity of the members of the uranium and thorium decay series in the samples. Solid samples were analysed by:

- packing about 40 g of the material into a tared plastic container [1],
- noting the loading time and sample weight,
- sealing the beaker lid onto the container (with Silastic, a Dow-Corning sealant),
- counting the sample on a gamma detector within 4 hours of loading, and
- recounting the sample after secular equilibrium had been established between radon and its daughters.

A gammax detector (EG&G Ortec) was used for these analyses. The peak areas from the gamma spectra were converted to activities by comparing them with those obtained from reference ores packed in the same geometry as the samples. The activity of the standards used was 125 Bq g^{-1} for uranium-238 decay chain and 64 Bq g^{-1} for the thorium-232 decay chain. Activities in the samples were calculated from;

Equation 1:

$$a_s = \frac{\left[\frac{C_s}{t_s\, w_s}\right]}{\left[\frac{C_{std}}{t_{std} w_{std}}\right]}\, a_{std}$$

where a = activity (Bq g^{-1})

c = counts

t = counting time (s)

w = weight (g)

and subscripts s and std refer to sample and standard, respectively.

[1] A re-entrant container commonly referred to as a Marinelli beaker, was used. It had the following dimensions: external height 36 mm, external diameter 87 mm, recess diameter 77 mm and recess height 30 mm.

The degree of secular equilibrium (S_{eq}) in the uranium-238 chain was calculated by;

$$S_{eq} = \frac{^{238}U}{^{226}Ra}$$

where ^{238}U = uranium -238 activity [2] (Bq g^{-1})

^{226}Ra = radium -226 activity (Bq g^{-1})

Radium-226 activity was determined by the averaging the activity of its daughters lead-214 and bismuth-214. The activity of the daughters was measured after secular equilibrium had been established between radon-222 and radium-226.

The emanation coefficients in this report have been measured by the 'sealed-can' method. In this method, the build-up of radon activity in a sealed container is determined by measuring the increase in gamma activity of the radon daughters with time. After the samples have been packed in the container for four hours the gamma activity associated with the 0.609 MeV peak of bismuth-214 and the 0.351 MeV peak of lead-214 are determined as a measure of residual radon trapped in the crystalline matrix. Thirty days after sealing the sample, radon is in equilibrium with radium-226 and a second measurement of gamma activity is made. The increase in gamma activity is a measure of the radon that is normally emanated from the solid. The emanation coefficient is calculated from;

Equation 2:

$$E = 1 - \frac{a_0}{a_\infty}$$

where a_0 = initial activity in the sample and

a_∞ = activity in the sealed sample at secular equilibrium

For this study, the emanation coefficient is quoted as the average of the values calculated from Equation 2 for the increase in activity measured by the 0.351 MeV peak of 1ead-214 and the 0.609 MeV peak of bismuth-214.

4. RESULTS

Eighty-nine samples of uranium ore and sediments were received from PNC Exploration between the period 27-10-1988 and 23-12-1988. Results of the measurements of the degree of secular equilibrium and the radon emanation coefficients are reported in Appendix A. Levels of the thorium decay chain and potassium-40 were low in all cases and should not significantly affect the interpretation of gamma logs.

[2] One ppm of uranium is equivalent to 0.0123 Bq g^{-1}. The Becquerel (Bq) is the SI unit of activity and is the amount of activity that results in one disintegration per second. An alternative unit, the curie, is still in common use. It is defined as the activity of one gram of radium-226 (3.7×10^{10} disintegrations per second). One becquerel is equivalent to 27 pCi.

Uranium

A few of the analyses for uranium provided by the Sheen Laboratories appeared to be in disagreement with the expected trend in the boreholes and the gamma analysis of the samples. The delayed neutron activation analysis (DNA) technique was used to check the uranium levels in these samples (Table 1 gives the results of these measurements).

Table 1: Uranium concentrations in selected PNC samples

Sample	Uranium (ppm)	
	Sheen	DNA
1587 - 14846	6	116
1587 - 14861	70	310
1575 - 14883	7200 *	2370
1575 - 14885	570	590
1572 - 15191	1500	1210

* This figure was partly illegible in the fax transmission and may not be correct.

For the calculation of the degree of secular equilibrium, the discrepancy between the uranium values was resolved in the following manner, viz.;

- When the uranium levels determined by Sheen and gamma analysis agreed, that value was used in the calculation
- If the value measured by DNA and Sheen disagreed, then the DNA value was used
- For samples containing <1 ppm U, the gamma analysis value was used.

Only a small number of samples were affected by changes to the uranium levels measured by Sheen as above. The values used for these samples were;

1587 - 14843 -	4	ppm
1587 - 14846 -	116	ppm (see Table 1)
1587 - 14861 -	310	ppm
1575 - 14879 -	3170	ppm (not measured by Sheen)
1575 - 14883 -	2370	ppm
1572 - 15191 -	1210	ppm
1572 - 15209 -	9	ppm
1572 - 15212 -	8	ppm
1582 - 14675 -	35	ppm
1582 - 14676 -	2	ppm

Inspection of the ratio of analytically determined uranium levels to daughter activities obtained using this approach showed that fairly smooth data trends were observed for each borehole.

Secular Equilibrium

Appendix A gives the measured degree of secular equilibrium in the ore and sediment samples. Included also is a description of the samples. This description is only qualitative as sediment and peat could only be differentiated between on the basis of colour and to a limited extent texture. The measurement errors for secular equilibrium were calculated from the counting errors and the error in uranium measurement (taken to be ±1 ppm U or 0.0123 Bq uranium-238 g^{-1}). The majority of samples had errors in the degree of secular equilibrium ranging from 1 and 5 %, however some low level samples had higher errors, these errors are noted as footnotes in Appendix A.

The calculated uranium activities are compared to the radium activities measured in this study for each borehole in Figures 1, 2, 3 and 4. Similarly, Figures 5, 6, 7 and 8 show the activity of thorium [3], calculated from the analytical measurements made by Sheen Laboratories, in the boreholes. Thorium and uranium show very similar distributions. As discussed in Section 2 above, the secular disequilibrium may be caused by the peat layers containing 'young' uranium or the uranium and radium having different mobilities in the peat layers. Figures 1, 2, 3 and 4 show that radium activities are generally highest in the layers immediately below the maximum uranium activities, suggesting that radium is being eluted from the uranium-rich layers and redeposited. Previous studies have found that uranium and radium are not in equilibrium in stream waters because the uranium is preferentially absorbed by organic matter. It is not possible with the data measured in this study to differentiate between these two mechanisms for disturbances to secular equilibrium.

Emanation Coefficients

The emanation coefficients for the samples are reported in Appendix A. Our previous measurements of emanation coefficients for Australian uranium ores and tailings and soils, have been in the range of 0 to 0.30 for low moisture content samples. This range of values is consistent with radium being distributed through the mineral matrix. The emanation coefficients in the sediments are similar to these values and tend to suggest that the radium is distributed through the matrix and that it is likely that uranium has been leached from these materials. The peat has very high emanation coefficients which are consistent with uranium and radium being sorbed on the surface of a highly porous material.

[3] One ppm of thorium is equivalent to 0.00407 Bq g^{-1}.

Figure 1: **Radium and Uranium Distribution in Hole 1572**

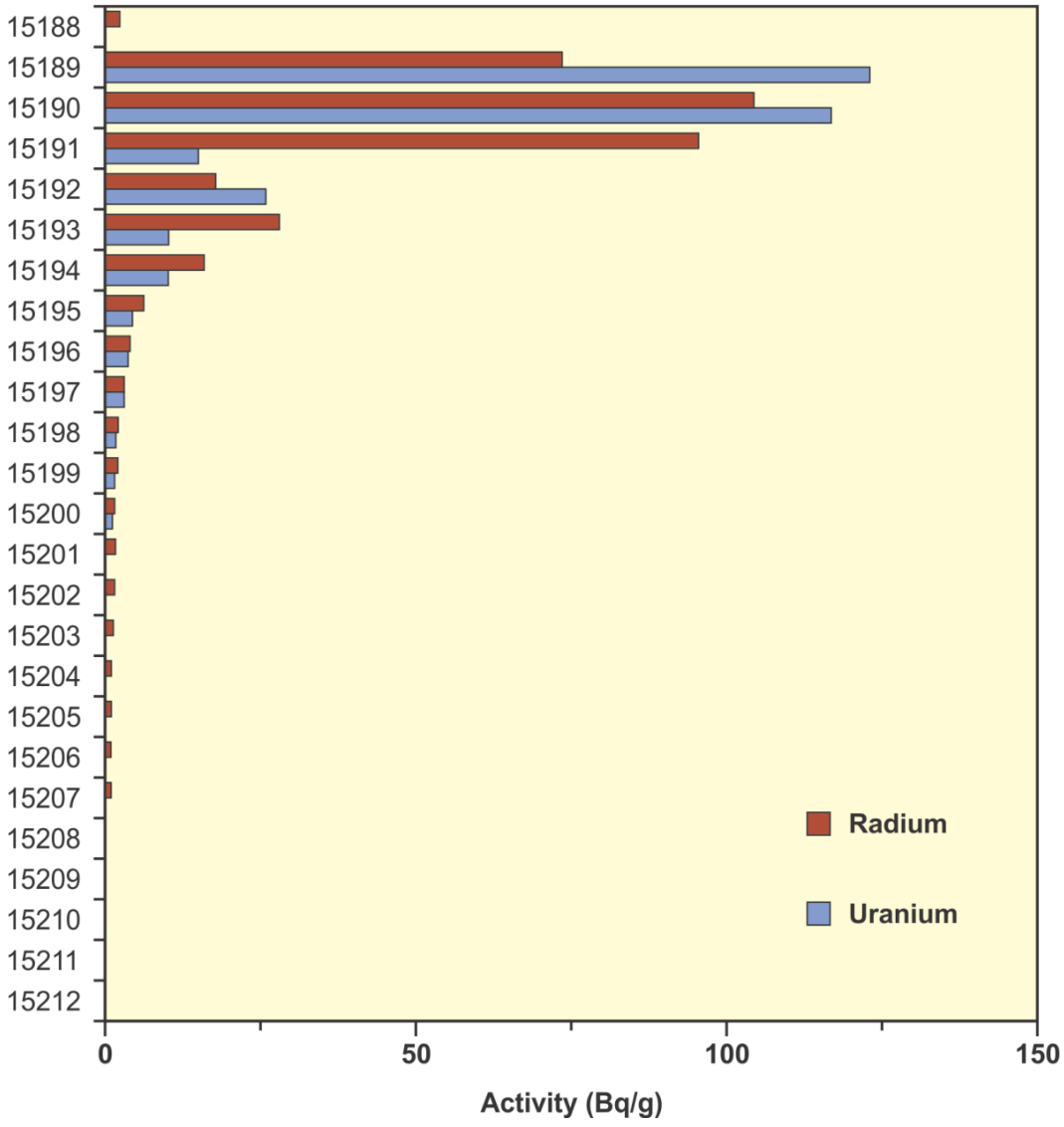


Figure 2: Uranium and Radium Distribution in Hole 1575

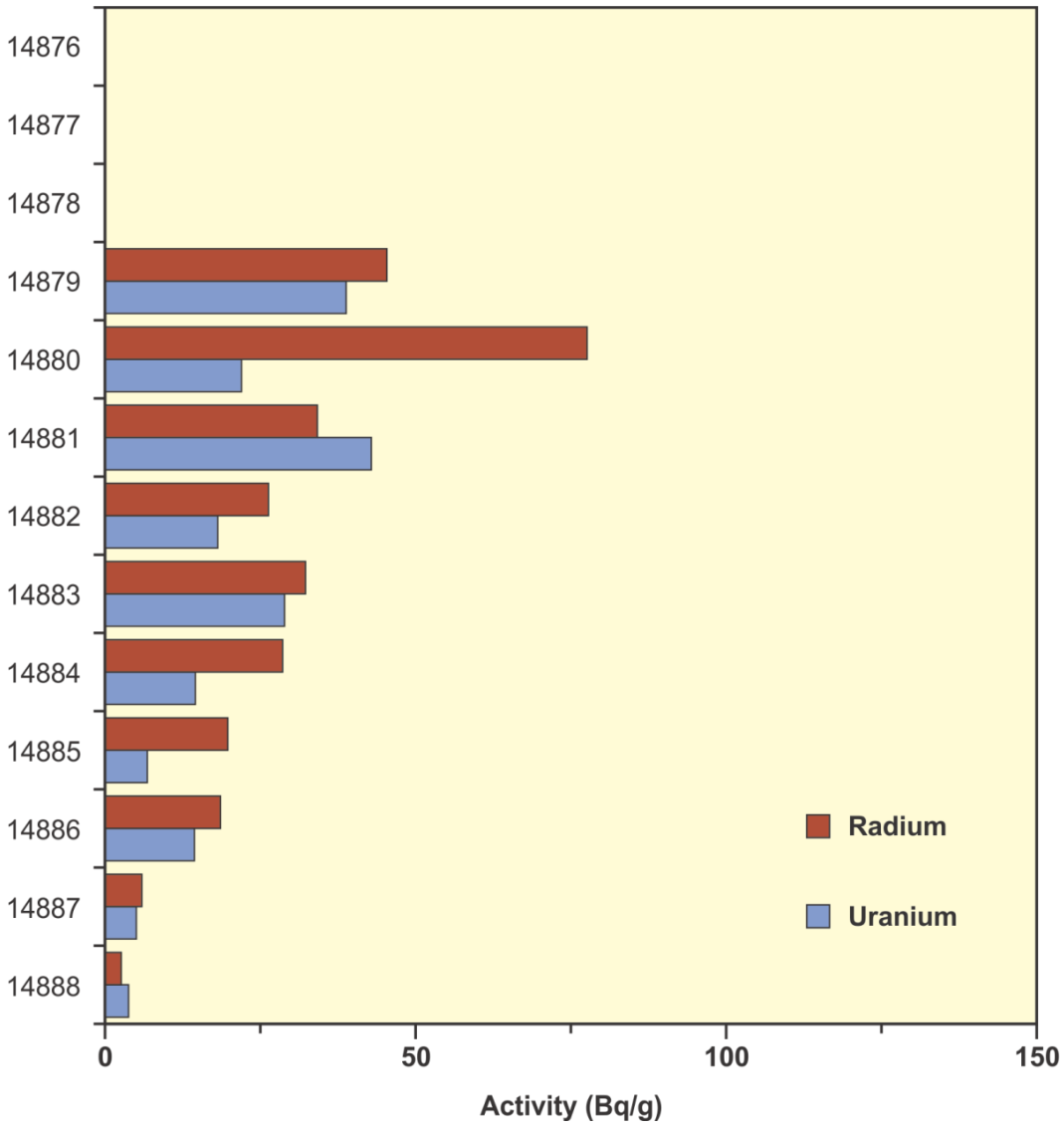


Figure 3: Uranium and Radium Distribution in Hole 1581

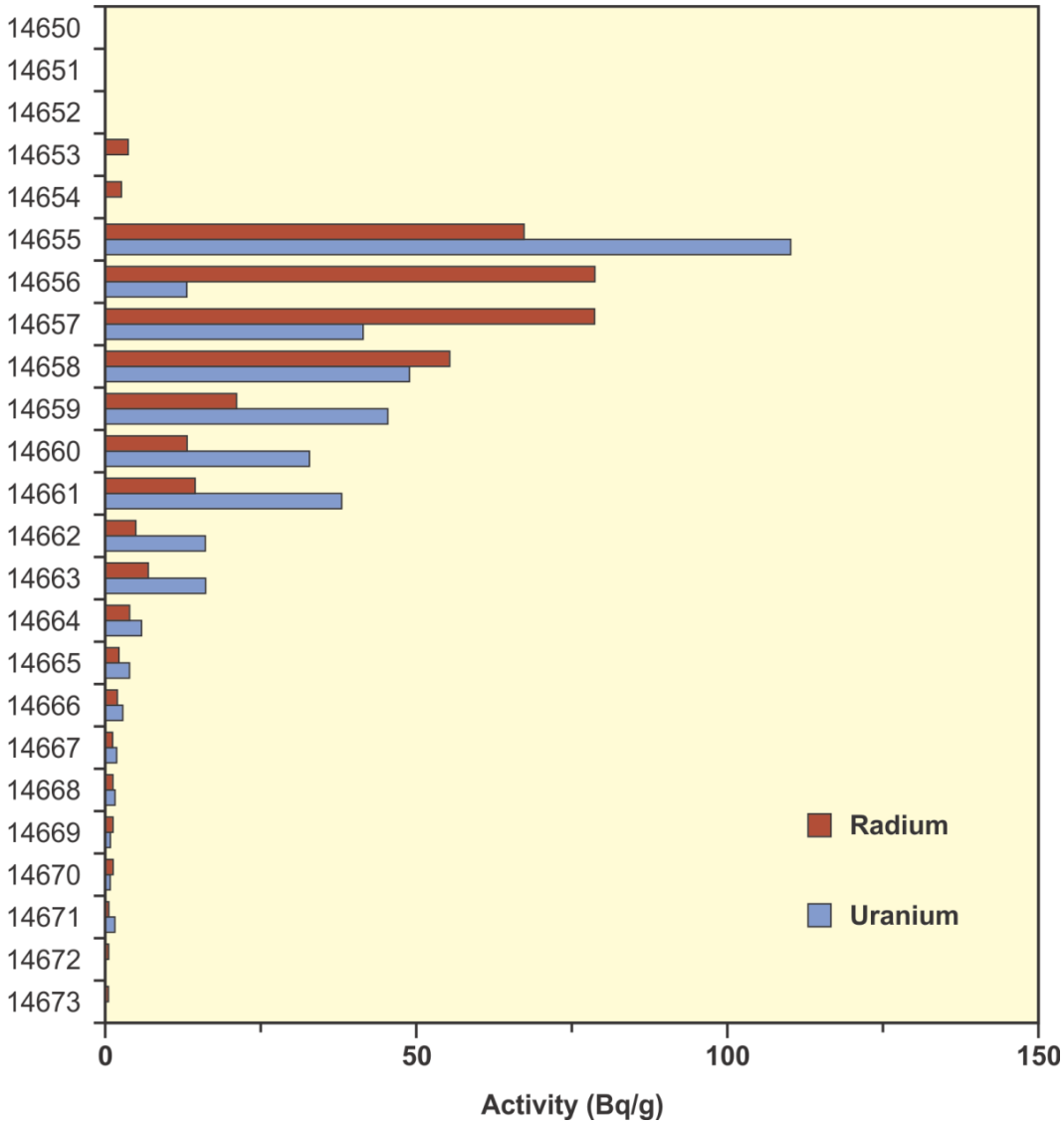


Figure 4: Uranium and Radium Distribution in Hole 1587

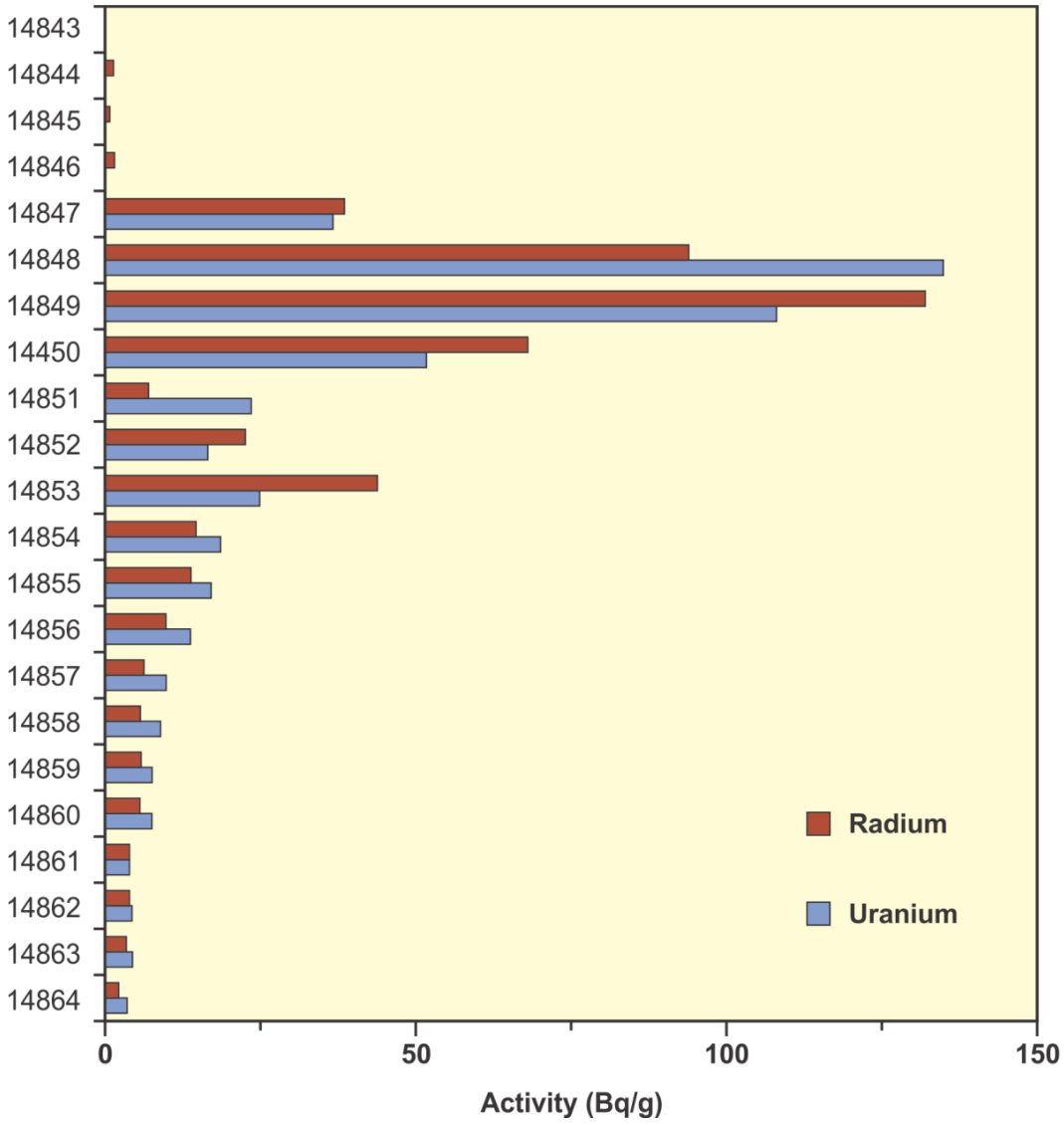


Figure 5: Thorium Distribution in Hole 1572

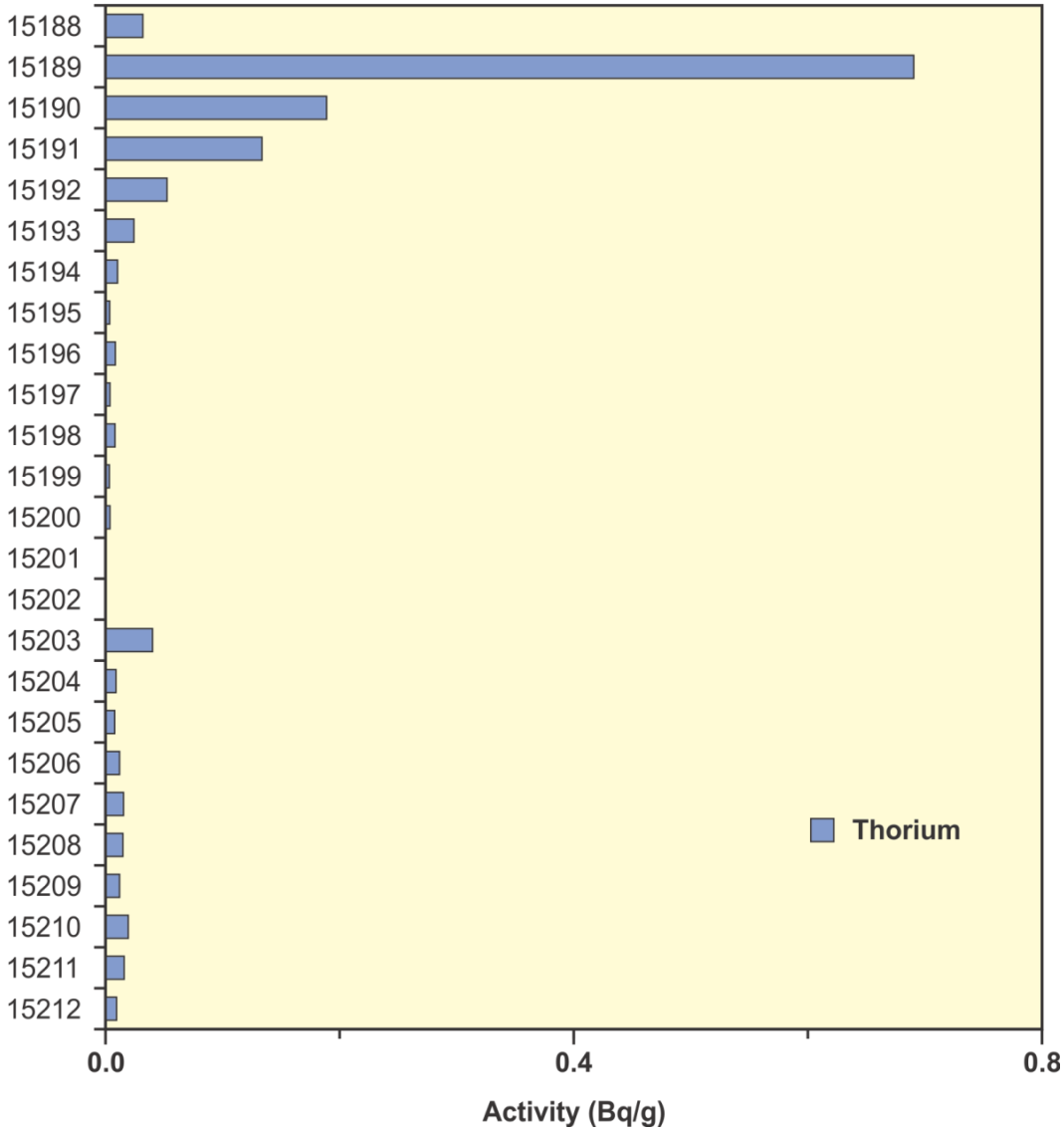


Figure 6: Thorium Distribution in Hole 1575

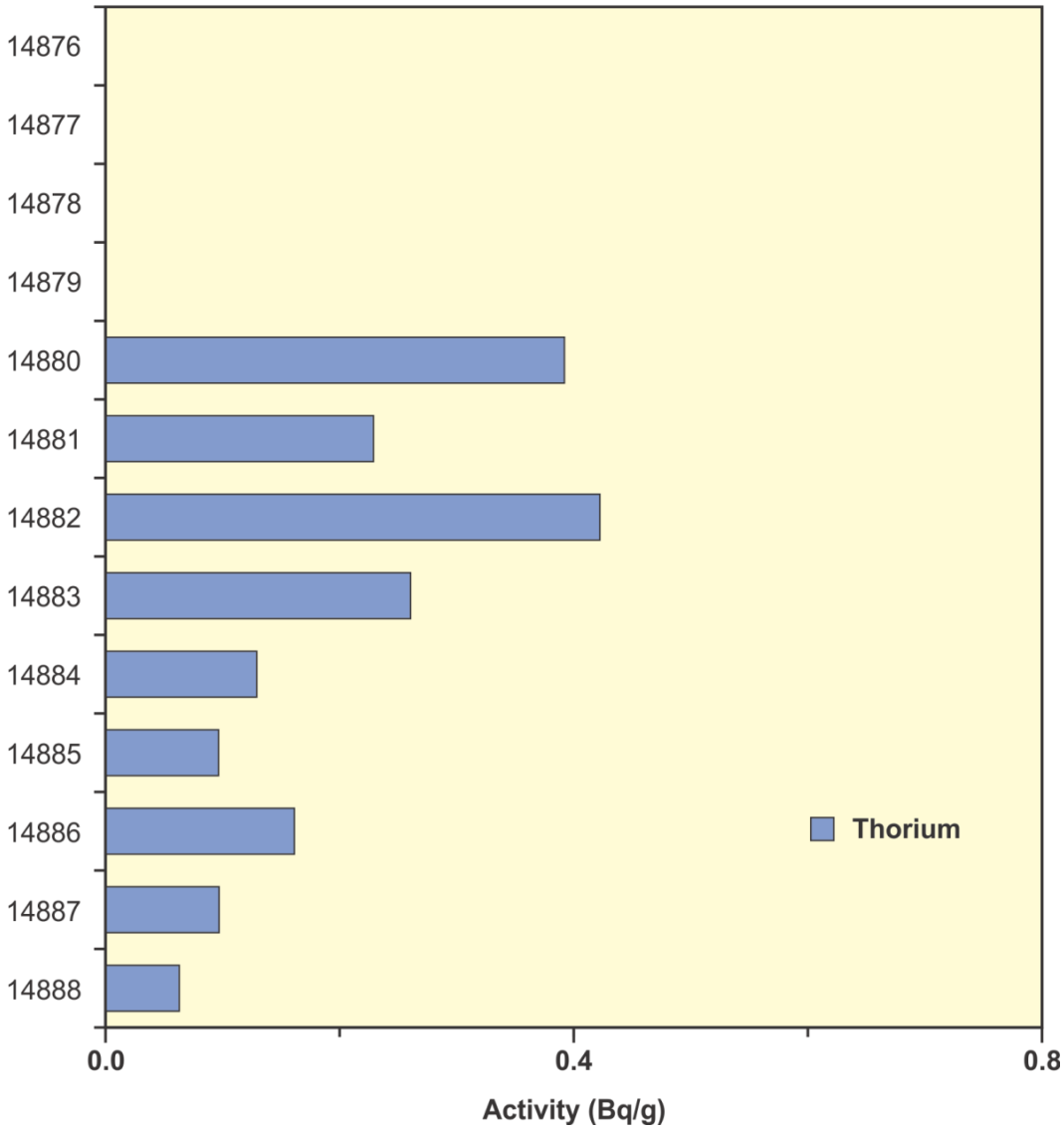


Figure 7: Thorium Distribution in Hole 1581

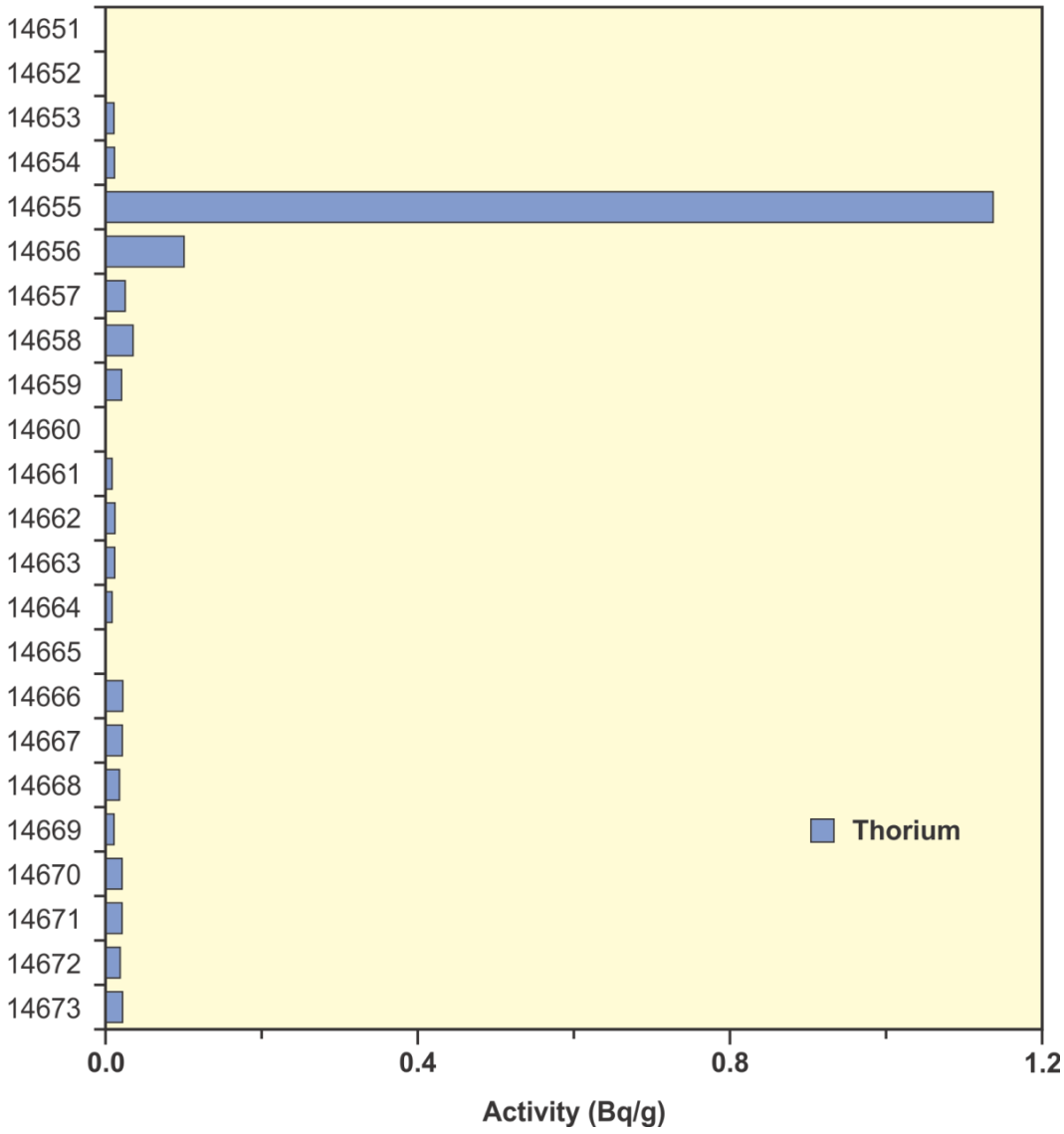
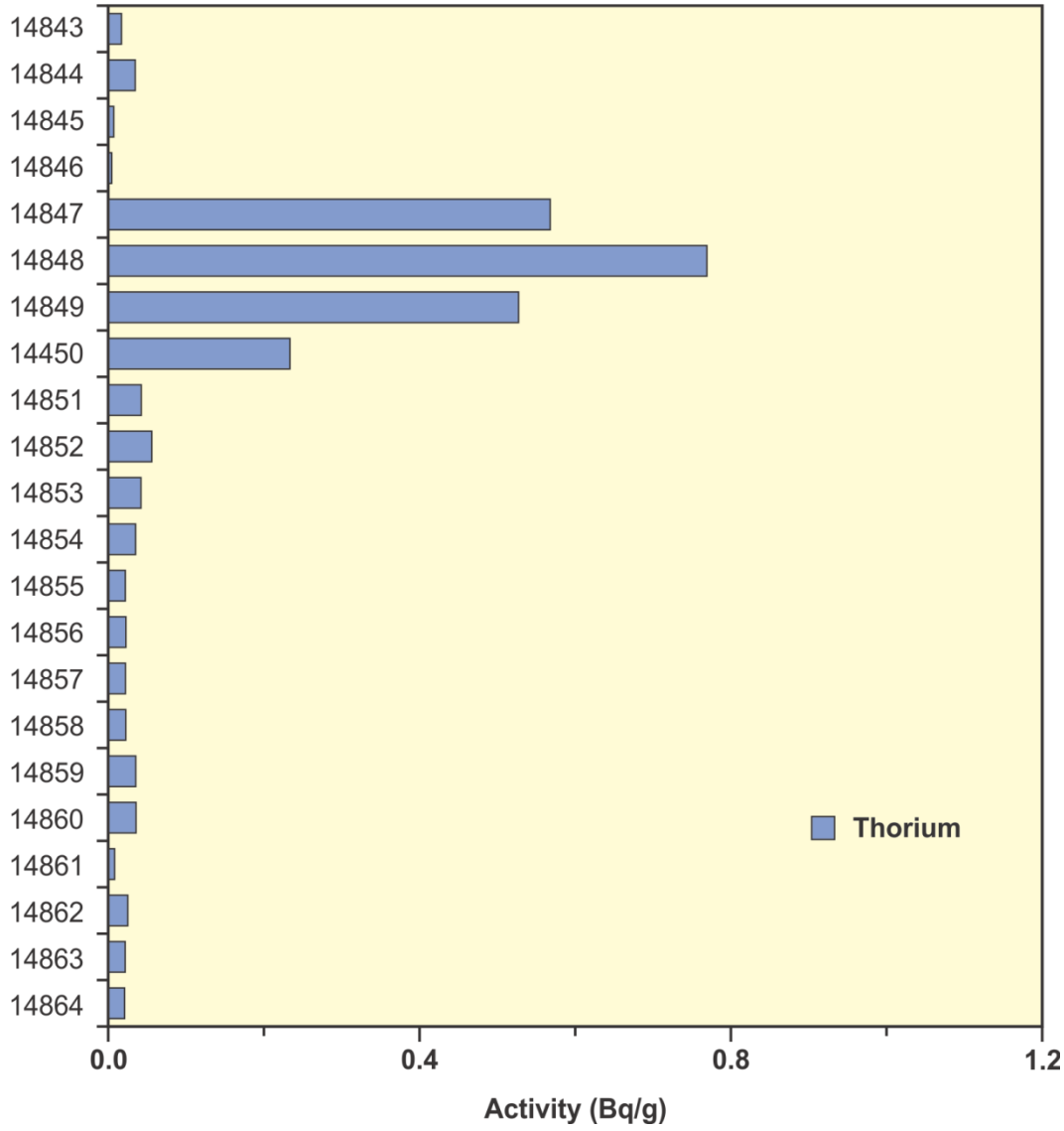


Figure 8: Thorium Distribution in Hole 1587



5. RECOMMENDATIONS

Gamma-probe logging of the boreholes in this site is complicated by the lack of secular equilibrium between uranium and its daughters. The major radionuclides measured by gamma probe logging are radium-226, lead-2l4 and bismuth-214. These radionuclides are only indicators of uranium activity if secular equilibrium has been established. As the disequilibrium in this deposit is highly dependent on the type of strata and their relative location to the reducing zone, it seems unlikely that definitive uranium reserves can be obtained purely from the gamma logging of the boreholes.

APPENDIX A – EXPERIMENTAL MEASUREMENTS

HOLE 1587

Sample	Secular Equilibrium	Emanation Coefficient	Sample Description
1587-14843	0.58	0.17	cream sediment
1587-14844	0.04	0.34	cream / brown sediment
1587-14845	0.48	0.21	grey / white sediment
1587-14846	1.29	0.22	grey / white sediment
1587-14847	2.72	0.36	dark / grey sediment
1587-14848	1.44	0.31	dark / grey sediment
1587-14849	0.82	0.26	dark / grey sediment
1587-14850	0.76	0.36	dark / grey sediment
1587-14851	3.38	0.74	dark brown peat
1587-14852	0.72	0.53	dark brown peat
1587-14853	0.56	0.44	dark brown peat
1587-14854	1.30	0.61	dark brown peat
1587-14855	1.27	0.63	dark brown peat
1587-14856	1.43	0.68	dark brown peat
1587-14857	1.50	0.60	dark brown peat
1587-14858	1.51	0.76	dark brown peat
1587-14859	1.34	0.63	dark brown peat
1587-14860	1.31	0.72	dark brown peat
1587-14861	1.38	0.61	dark brown peat
1587-14862	1.08	0.57	dark brown peat
1587-14863	1.23	0.68	dark brown peat
1587-14864	1.66	0.77	dark brown peat

HOLE 1575

Sample	Secular Equilibrium	Emanation Coefficient	Sample Description
1575-14876	0.14	0.16	white sediment
1575-14877	0.98	0.19	white sediment
1575-14878	0.71	0.23	yellow / cream sediment
1575-14879	0.85	0.39	dark grey sediment
1575-14880	0.29	0.25	grey sediment
1575-14881	1.26	0.29	dark grey brown peat
1575-14882	0.70	0.43	dark brown peat
1575-14883	0.89	0.40	dark brown peat
1575-14884	0.51	0.49	dark brown peat
1575-14885	0.36	0.37	dark brown peat
1575-14886	0.77	0.35	dark brown peat
1575-14887	0.85	0.56	dark brown peat
1575-14888	1.41	0.66	dark brown peat

HOLE 1572

Sample	Secular Equilibrium	Emanation Coefficient	Sample Description
1572-15188	0.08	0.16	grey / white sediment
1572-15189	1.68	0.21	grey / brown sediment
1572-15190	1.12	0.33	dark grey sediment
1572-15191	0.16	0.32	dark sediment
1572-15192	1.50	0.53	grey / brown peat
1572-15193	0.35	0.65	dark grey / brown peat
1572-15194	0.63	0.57	dark grey / brown peat
1572-15195	0.75	0.69	dark brown peat
1572-15196	0.99	0.48	dark brown peat
1572-15197	1.09	0.59	dark brown peat
1572-15198	0.82	0.72	dark brown peat
1572-15199	0.67	0.77	dark brown peat
1572-15200	0.71	0.58	grey / brown peat
1572-15201	0.39	0.65	dark brown peat
1572-15202	0.14	0.38	dark brown peat
1572-15203	0.10	0.35	dark brown peat
1572-15204	0.15	0.36	dark brown peat
1572-15205	0.19	0.59	dark brown peat
1572-15206	0.28	0.59	dark brown peat
1572-15207	0.65	0.45	dark brown peat
1572-15208	0.29	0.57	dark brown peat
1572-15209	0.91	0.77	dark brown peat
1572-15210	0.83	0.43	dark brown peat
1572-15211	1.36	0.68	dark brown peat
1572-15212	1.97	0.77	dark brown peat

HOLE 1581

Sample	Secular Equilibrium	Emanation Coefficient	Sample Description
1581-14650	0.14	0.30	cream / white sediment
1581-14651	0.17	0.28	cream sediment
1581-14652	0.09	0.31	grey sediment
1581-14653	0.05	0.19	white sediment
1581-14654	0.13	0.17	white / grey sediment
1581-14655	1.65	0.56	grey / brown sediment
1581-14656	0.17	0.44	grey / brown sediment
1581-14657	0.53	0.49	dark grey sediment
1581-14658	0.89	0.28	dark grey peat
1581-14659	2.15	0.65	grey / brown peat
1581-14660	2.49	0.54	grey / brown peat
1581-14661	2.61	0.66	brown peat
1581-14662	3.15	0.64	light brown peat
1581-14663	2.31	0.76	dark brown peat
1581-14664	1.53	0.70	dark brown peat
1581-14665	1.66	0.67	brown peat
1581-14666	1.46	0.75	brown peat
1581-14667	1.41	0.65	brown peat
1581-14668	1.20	0.71	brown peat
1581-14669	0.74	0.77	brown peat
1581-14670	0.63	0.72	light brown peat
1581-14671	0.60	0.66	light brown peat
1581-14672	0.38	0.69	dark brown peat
1581-14674	0.42	0.65	dark brown peat

HOLE 1582

Sample	Secular Equilibrium	Emanation Coefficient	Sample Description
1582-14675	0.17	0.31	white silica
1582-14676	0.01	0.27	white sediment
1582-14677	0.50	0.16	white / grey sediment
1582-14678	0.58	0.34	dark grey sediment
1582-14679	0.50	0.26	dark grey brown peat