TESTING THE POSSIBILITY OF PALAEONTOLOGY DATING VIA GAMMA-RAY SPECTROMETRY

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DOI: 10.5281/zenodo.17939222

Abstract. Fossil age determination is essential for understanding the evolutionary chronicle of life. Relative dating by ordering fossils in accordance to rock layers sometimes needs support from absolute techniques based on radioactivity. Among the latter, well-established procedures help our understanding of how species changed in time intervals of thousands (radiocarbon) to millions (uranium-lead) of years. The uranium-thorium technique suits better the intermediary range, and is typically used by means of alpha spectrometry, but we intend to test the non-destructive gamma-ray protocol in order to date, or at least authenticate such samples. After carrying out the measurements with a HPGe detection system in low background, our first results indicate the method can be successfully applied on the condition the background is reduced even more; still, the possibility of authentication was evidenced from the first test. We also present a potential solution for future method development by thermal neutron irradiation.

Key words: Palaeontology dating, natural radioactivity, gamma spectrometry

1. INTRODUCTION

In palaeontology studies, gamma spectroscopy is generally used to support luminescence age determination by providing dose rates for Uranium, Thorium, and Potassium from the sample environment. Thermoluminescence (TL) and Optically stimulated luminescence (OSL) are meant to determine the energy trapped in luminescence centres (defects within the material which emit light following external stimulation). The number of electrons trapped in those luminescence centres increases over time, scaling with the radiation dose to which the material is exposed during the accumulation period, or since the last heating/light exposure (for TL/OSL). Luminescence measurements provide information on the paleodose, or the amount of trapped charge, while gamma spectrometry provides the dose rate for the spot the samples are collected from. Then, dividing the paleodose by the dose rate provides the age of the sample, provided the proper correction factors are applied - but this is beyond the purpose of the present paper.

Uranium dating consists of a group of methods meant to serve age estimation, generally involving alpha spectrometry and/or mass spectrometry, for a plethora of materials and different time ranges, following the particular radioisotopes used (Rosholt *et al.,* 1966; Hansen and Stout, 1968; Osmond and Cowart, 1974; Gascoyne, 1992; Osmond and Cowart, 1992; Rokop *et al.,* 1996; Fujikawa *et al.,* 1998; Taylor *et al.,* 1998). Particularly, the Uranium - Thorium (^{230}Th - ^{234}U) method, named after the daughter and parent nuclei, was developed for dating carbonates, phosphates and organic matter in the 1 - 400 kiloyear range, the upper limit being dictated mainly by the half-life ($T_{1/2}$) of ^{230}Th and the uncertainty related to the decay curve. In order to determine the age of a sample, this method also requires calculation of the ^{234}U/^{238}U ratio. Typical use cases for this method are the study of limestones, stalactites, or travertines (Bard *et al.,* 1990 and 1990; Augustinus *et al.,* 1997). It is possible to extend the sample range to shells or bones, but the associated uncertainties are much higher. The latter are in the best-case scenarios within the 5-10% range for alpha spectrometry (Schwarcz, 1989) and 1-2% for

mass spectrometry. It is unclear what the actual uncertainty of a gamma-ray evaluation procedure would be, because the method was not used for this purpose, and most of all for the reasons behind this: (i) the emission yields of the concerned nuclei are very low, and (ii) the energies of interest are situated in a typically high background region of the spectrum.

The purpose of this paper is to expose a possible gamma alternative (Simpson and Rainer, 1998) (or at least complementary approach) to the well-established alpha spectrometry for the Uranium - Thorium age determinations, and to try to integrate dose rate estimations for luminescent dating within the same measurement procedure, thus providing a dual approach in a single measurement for palaeontology studies. When it comes to spectrum analysis, the TL/OSL support component is straightforward for most of the low background measurement setups, but for the U-Th alpha surrogate measurement detection and decision limits are technically challenging and physically complicated, as explained in the next section.

2. MATERIALS AND METHODS

Common radiometric techniques measure the accumulation of a stable decay product, *e.g.* Uranium-Lead or Rubidium-Strontium. The difference for the Uranium-Thorium technique is that age estimation is based on the degree of secular equilibrium restoration between the parent ^{234}U and daughter ^{230}Th. Still, one thing is clear: while thorium is not soluble in water given the conditions at the Earth's surface, uranium is, which means any material grown in such a medium contains at least a few ppb of uranium, which subsequently decays to thorium. As the latter is also radioactive, it approaches a secular equilibrium with its parent. Age determination by this method is performed via equation solving algorithms, because it does not have a closed-form expression. Figure 1 presents the calculated curves as functions of the $^{230}TH/^{234}U$ and $^{234}U/^{238}U$ ratios.

Generally, the main characteristic of the $^{234}U/^{238}U$ activity ratio is its considerable variation in groundwater. The reason for variation is isotopic fractionation at the rock–water interface.

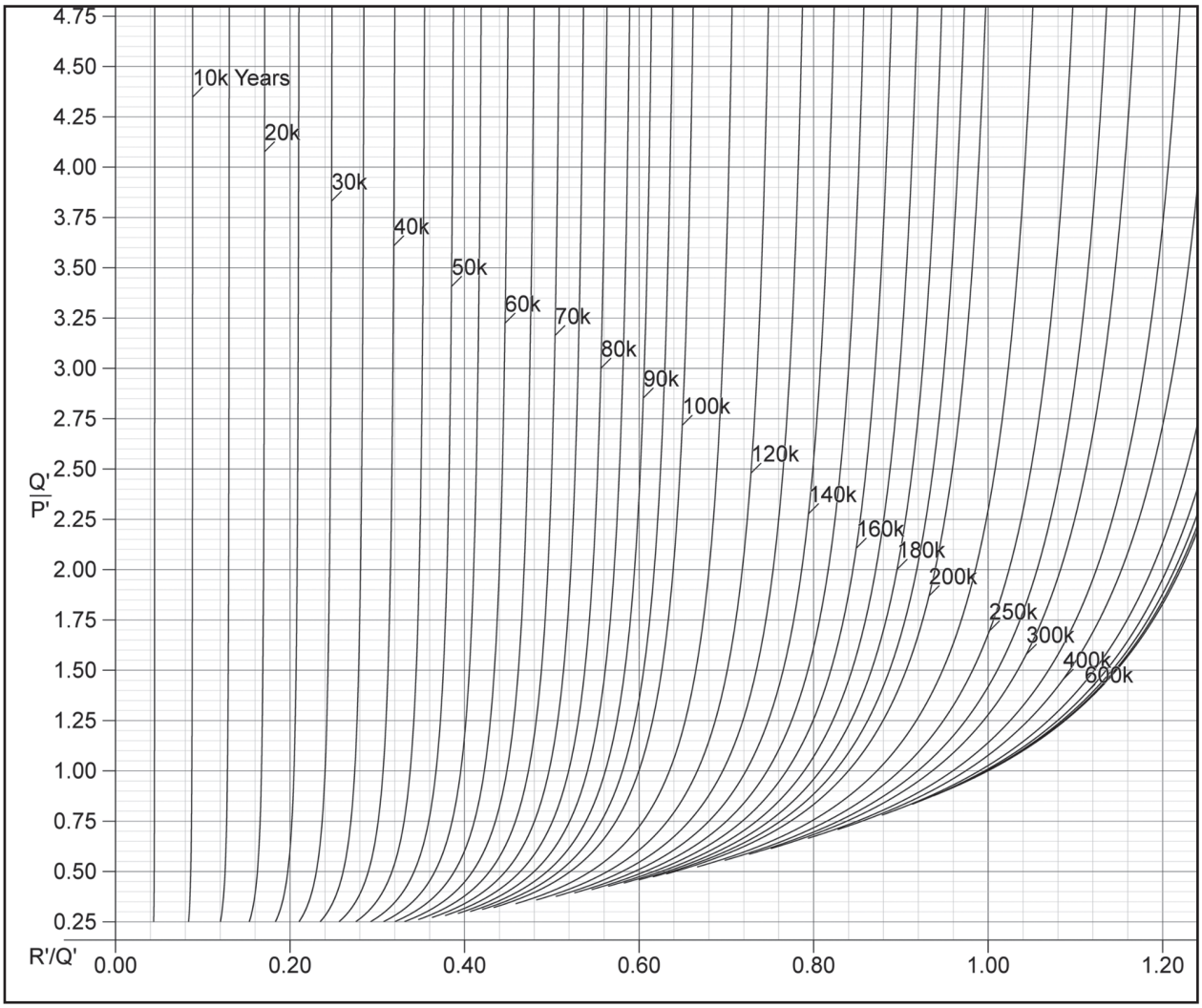

Fig. 1. Age from two activity ratios, assuming that thorium is initially absent. The horizontal axis is $R'/Q' = {}^{230}Th/^{234}U$, while the vertical axis is $Q'/P' = {}^{234}U/^{238}U$. Each curve is a linear fractional hyperbola; there is no closed form expression for the age as a function of the ratios (Courtesy of Paul Sheer).

However, the reason why the activity ratio varies in groundwater is not well known (Suksi *et al.,* 2006). As in most cases one expects to find a 1:1 ratio of ^{238}U to ^{234}U activity, we consider this valid for the purpose of the present work. This is mostly the case of sediments and rocks, and generally the departures from this value given by the secular equilibrium between ^{238}U of $T_{1/2}$ 4.5 Gy and ^{234}U of $T_{1/2}$ 245 ky are observed in water (ground or sea ~), for ^{234}U is more soluble. Notably, leaching of ^{234}U is higher compared to ^{238}U, because of radiation induced damage of the crystal lattice when ^{238}U undergoes α decay and oxidation of ^{234}U initially tetravalent insoluble) to a hexavalent, soluble form during decay (Carvalho *et al.,* 2023). Still, there are several potential reasons for departure from the secular equilibrium, from the above cited to anthropogenic discharge.

From the available spectroscopic range of our measurement system, the ^{230}Th of $T_{1/2}$ 75.4 ky has a gamma emission of E_γ 67.67 keV and I_γ 0.377% which unfortunately may interfere with the ^{231}Th emission of E_γ 68.48 keV and I_γ 0.0057%. However, as the yield of the latter is low and the parent ^{235}U abundance and activity ratios are approximately 1:140, respectively 1:22 to ^{238}U which decays successively to ^{234}Th, ^{234m}Pa, ^{234}U and ^{230}Th, we can a priori assume this does not lead to a significant deviation in the count rate for that region of the spectrum. Additionally, the FWHM of the peak should be influenced by the convolution if there is a significant effect. The ^{234}U nucleus, of $T_{1/2}$ 245.5 ky, has a gamma line of E_γ 53.2 keV and I_γ 0.123% which has a priori no close peaks for such a measurement. The 53 and 67 keV lines are the ones used for the analysis, as both nuclides have emissions around 13 keV, which lead to a convolution hard to interpret, as there are other contributions to the latter from the natural series in first place. All nuclear data was retrieved from the Brookhaven National Laboratory repository (National Nuclear Data Center).

The spectroscopic chain consisted of a n-type HPGe detector, an ORTEC 600 HV source, a Canverra 2062 amplifier, an ORTEC 671 multi-channel analyser, with the associated lead shielding in which we recirculated the evaporated nitrogen from the cooling system in order to lower the contribution of the radon descendants and implicitly the overall background, which are shown in figure 2. The detection and decision limits were calculated according to the ISO 11929-1:2019. Energy and efficiency calibration were performed with ^{133}Ba and ^{152}Eu standardised volume sources. All Monte Carlo computations for calibration completion, efficiency adapting to measurement geometry, self-attenuation coefficients, real coincidence summing effects and subsequent corrections were performed with GESPECOR 5.0 (Gurau *et al.,* 2023). Measurements were carried out for more than 48 h, for blank sample, dummy sample and the sample of interest, in order to have a reasonable balance between statistics and spectrum acquisition time.

The purpose of this work being a test for evaluating the feasibility and limitations of gamma ray analysis for this dating purpose, we analysed a blank sample for background subtraction, a dummy sample which contained recent material, and a real paleontological sample of which we intended to determine the age, without knowing what is inside each box.

3. RESULTS AND DISCUSSION

Spectrum analysis lead to the results summarised in table 1. The ^{230}Th and ^{234}U values are meant to support the idea of testing gamma spectrometry as an alternative to alpha determinations, while other natural series and non-chain element results are given as examples for support of TL/OSL dose estimation for luminescent dating procedures, which use the age equation for this purpose (Galbraith and Roberts, 2012).

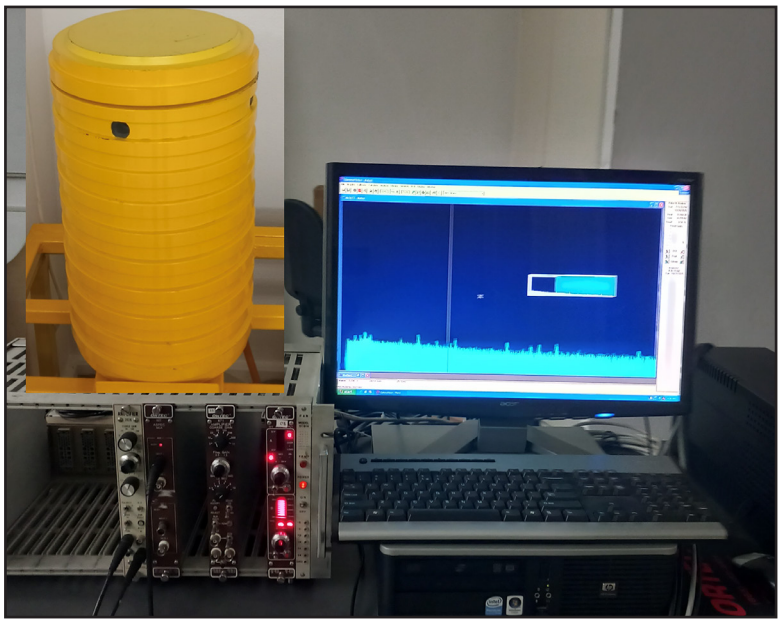

Fig. 2. The spectroscopic chain which follows the HPGe preamplifier. The HPGe detector is located in the lead shield pictured in the upper left detail.

Table 1. Experimental results for blank, dummy and actual sample. All SA (specific activities) in Bq/kg, except for blank (in counts per second). Ld denotes results lower than the detection limits. The ^{226}Ra SA is estimated as contributing by 58% to the 186 keV peak, the rest being attributed to ^{235}U.

Nuclide	U-234		Th-230		Th-234		Ra-226/ U-235	Ra-226	Cs-137		K-40		M (g)	T (s)
Peak [kVe]	53	SA 53	67	SA 67	93	SA 93	186	SA Ra 186	662	SA 662	1461	SA 1461	-	-
Yield (%)	0.12		0.38		4.25		58%+42%	3.64	85.10		10.66		-	-
Efficiency	5.8		7.6		11.3		9.9		3.5		1.9		-	-
Blank	Ld	0.00	Ld	0.00	3732	0.0192	1995	0.0103	Ld	0.00	6214	0.0345	n/a	194403
Sample	145	16.19	192	5.30	8391	76.99	4141	26.92	Ld	0.00	12786	236.69	64.29	195288
Dummy	110	17.62	Ld	0.00	5202	45.89	2618	15.69	Ld	0.00	9325	193.13	51.33	170505

The ^{234}U and ^{238}U descendent (^{226}Ra) results are not inconsistent with the 1:1 activity ratio hypothesis for ^{234}U and ^{238}U, for secular equilibrium between ^{238}U and its progenies is not necessarily valid in this case. Additionally, the high uncertainties which apply to both values lead us to the idea that the most reasonable scenario is this hypothesis is actually valid, but we have a certain departure from the point of view of counting statistics which was expectable. Consequently, we used the Q'/P'=1 ratio for the curves shown in figure 1. This leads to a 0.327 R'/Q' ratio, or 42 kiloyear estimation for one sample, and impossibility of dating for the two others (which turned out to be the blank and the dummy sample after associating sample codes to the inventory).

However, the 60% uncertainty refers strictly to the counting statistics, so the overall uncertainty on the result is close to 70%. This means under the given conditions it is possible to authenticate such samples (i.e. differentiating between paleo and recent samples), but the current precision is not enough for a real dating procedure (i.e. distinguishing between 30 and 60 kiloyear samples with an uncertainty smaller than half their age difference for example). However, lowering the overall background and adding extra multi-metal interior shielding strata (such as Cd-Cu-Al) in order to cut the characteristic X-rays from the Pb material and their Compton scattered radiation will certainly reduce the current limitations. Another method we are looking forward to test is the neutron irradiation of such a sample, after measuring its natural spectrum: the natural spectrum will serve as blank for the irradiated one while searching peaks for ^{231}Th and ^{235}U, which are obtained by slow neutron capture, as both ^{230}Th and ^{234}U have high cross sections for thermal neutrons.

The common results for the natural series (U, Th) and non-chain ^{40}K provide low-uncertainty values, useful for other dating methods, such as thermoluminescence or optical stimulated luminescence (TL/OSL), which can be reasonably obtained within the same measurement sequence, even with a lower spectrum acquisition time.

4. CONCLUSIONS

The present study was meant to evidence the possibility of using gamma-ray detection as an alternative to the alpha spectrometric technique for paleontological sample dating, by using test and dummy samples with no a priori information. The results show the dating procedure cannot be applied as such in the present background. Still, authentication is possible, as it is clear the dummy had no accumulation of thorium, while the actual sample was evaluated to a few tens of thousands of years, which is in the real range. The spectra also provide useful information for supporting TL/OSL dating.

Looking forward to develop this non-destructive approach, we believe lowering the background and providing larger sample quantities will enhance the possibilities for authentication, or even dating with a precision of some 20-30%, while irradiating the samples with neutrons will enable more precise dating by analysing the resulting ^{231}Th and^{235}U nuclei, which have gamma emission yields two orders of magnitude higher.

ACKNOWLEDGEMENTS

The financial support was provided by the Project PN 23 30 04 01 (Core Programme GEOMARDIGITAL of INCD GeoEcoMar) of the Ministry of Education and Research.

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