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# ESR DATING OF SEA-FLOOR HYDROTHERMAL BARITE: CONTRIBUTION OF [228]Ra TO THE ACCUMULATED DOSE

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**Abstract:** Electron spin resonance (ESR) dating of barite has been recently developed and is now practically applied to barite extracted from sea-floor hydrothermal deposits. The evolution of the accumulated dose to barite is simulated for an actual sample of barite in sea-floor hydrothermal sulfide deposit to find that the contribution of radioactive nuclei of [228]Ra series can be important for the samples younger than 300 years old. Currently, any date over 50 years should be considered a maximum value when the [228]Ra content is not obtained. The method to estimate the contribution from [228]Ra series has to be developed in future for those in which [228]Ra is not detected. The age limit of ESR dating of barite would be 5000 to 6000 years due to the decay of [226]Ra, which is also found by simulation of the accumulated dose.

**Keywords:** ESR, dating, barite, disequilibrium, hydrothermal, radiation.

## 1. INTRODUCTION

Dating of hydrothermal deposits is an important issue in the studies of the evolution of the sea floor hydrothermal fields where geochronological dating methods applied to hydrothermal deposits are the key techniques. Dating methods using radioactive disequilibrium have been employed for hydrothermal sulfide deposits, such as the U-Th method (e.g. You and Bickle, 1998) for sulfide minerals applicable for the age range more than several thousand years, and $^{226}$Ra-$^{210}$Pb and $^{228}$Ra-$^{228}$Th methods (e.g. Noguchi *et al.*, 2011) for barite extracted from sul-

fide deposits for the range less than 150 years. Although the age range of several hundred years is essential to estimate the life time of hydrothermal activities, dating methods for this age range were lacking.

Kasuya *et al.* (1991) investigated the dose responses of the electron spin resonance (ESR) signals observed in natural barite samples and first pointed out that ESR dating of barite is possible. Following Okumura *et al.* (2010), who made the first practical application of ESR dating to a sample of seafloor hydrothermal barite with the signal due to SO$_3^-$, basic studies on ESR dating of barite were performed by Toyoda *et al.* (2011) for the optimum conditions of ESR measurements of the dating signal, by Sato *et al.* (2011) for the thermal stability of the signal, and by Toyoda *et al.* (2012) for the alpha effectiveness value.

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Takamasa *et al.* (2013) examined sulfide deposits in the South Mariana Trough sea-floor hydrothermal field to compare the ESR ages obtained for barite and the U-Th ages for sulfide minerals extracted from the same portions. They showed that the ESR ages are roughly consistent with the U-Th ages. While Toyoda *et al.* (2014) discussed several detailed technical issues such as the dose rate conversion factors, the sample edge effect for gamma ray dose, and the correction for the decay of $^{226}$Ra, Fujiwara *et al.* (2015) made the first practical systematic dating work with ESR on barite of sea-floor hydrothermal sulfide deposits taken at Okinawa Trough on total of 18 samples (60 subsamples) with new formulas which take the radioactive disequilibrium of Ra daughter nuclei into account. The obtained ages range 4 to 16000 years, showing that the ESR method has a wide application age range. Uchida *et al.* (2015) obtained $^{226}$Ra-$^{210}$Pb and $^{228}$Ra-$^{228}$Th ages for the same samples as Fujiwara *et al.* (2015) analyzed and attributed the differences of the ages among these three dating methods to possible multiple formation stages of the sulfide deposits.

## 2. ISSUES IN DETERMINING DOSE RATES TO BARITE EXTRACTED FROM SEA-FLOOR HYDROTHERMAL SULFIDE DEPOSITS

When hydrothermal fluid containing barium ions is mixed with sea water, they react with sulfate ions in the sea water to precipitate barite (barium sulfate, $BaSO_4$). The barite crystals occur in sulfide chimneys and in deposits, incorporating radium ions that are in the hydrothermal fluid. As a radium ion has an ionic radius similar with barium, radium ions easily replace barium in barite to have high concentration up to several tens Bq/g of $^{226}$Ra (Fujiwara *et al.*, 2015).

The source of natural radiation in sulfide deposits containing barite is radium and its daughter nuclei in barite where the doses from the other minerals are negligible (Toyoda *et al.*, 2014). Under these circumstances, the specific issues for the dose rates in calculating the ESR ages are, as summarized by Toyoda *et al.* (2014), the conversion factors, the calculation of internal and external dose rates including the determination of the alpha effectiveness, the water content, the geometric factors such as the grain sizes, and the radioactive disequilibrium. The radioactive disequilibrium is one of the most complex and important issue in calculating the ESR ages.

While Toyoda *et al.* (2014) devised a formula to correct the age due to the decay of $^{226}$Ra assuming radioac-

tive equilibrium, Fujiwara *et al.* (2015) proposed formulas to consider the radioactive disequilibria. The same equation applies both to $^{226}$Ra and $^{228}$Ra series, and the total accumulated natural equivalent dose, $D_E(T)$, which is the summation of the two, is expressed by, where $\lambda_1$, $\lambda_2$, $\lambda_3$, and $\lambda_4$ are the decay constants of $^{226}$Ra, $^{210}$Pb, $^{228}$Ra, and $^{228}$Th, respectively, $Q_1$, $Q_2$, $Q_3$, and $Q_4$ are the conversion factors of $^{226}$Ra to $^{214}$Po, $^{210}$Pb to $^{206}$Pb, $^{228}$Ra and $^{228}$Ac, and $^{228}$Th to $^{208}$Pb, respectively, referring to Guérin *et al.* (2011). $\lambda_1 N_{1p}$ and $\lambda_3 N_{3p}$ are the present activity of $^{226}$Ra and $^{228}$Ra, respectively, and T is the age. When the experimentally obtained equivalent dose is $D_{exp}$, the equation is,

$$D_E(T) = D_{exp} \tag{2.2}$$

In order to solve this equation, a function, f(T) is defined as,

$$f(T) = D_E(T) - D_{exp} \tag{2.3}$$

and the equation to be solved is deduced to

$$f(T) = 0 \tag{2.4}$$

This non-linear equation can be numerically solved by the Newton method, which is

$$T_{n+1} = T_n - \frac{f(T_n)}{f'(T_n)} \tag{2.5}$$

*repeat until* $f(T) = 0$

It should be noted that $^{210}$Pb has the longest half-life of 22.3 y in the decay series after $^{226}$Ra with a half-life of 1600 y (**Fig. 1a**), and that $^{228}$Th has the longest half-life of 1.91 y in the decay series after $^{228}$Ra with a half-life of 5.75 y (**Fig. 1b**), therefore, other radioactive disequilibrium can be neglected.

For the samples, in which $^{228}$Ra is observed, the contributions to the natural accumulated dose from the $^{228}$Ra series as well as that from $^{226}$Ra series can be calculated by **Eq. 2.1** where the age, T, is obtained as the solution of **Eq. 2.4**, as these procedures are actually adopted in obtaining the ESR ages of hydrothermal barite in Okinawa Trough (Fujiwara *et al.*, 2015). As time passes, $^{228}$Ra with a half-life of 5.75 y will decay out so that $^{228}$Ra and its daughter nuclei will not contribute doses any more. Therefore, if the sample is old enough, the contribution of $^{228}$Ra and its daughter nuclei to the natural accumulated dose of barite would be negligible. However, the fact that $^{228}$Ra and its daughter nuclei are not observed would not

$$D_E(T) = \lambda_1 N_{1p} e^{\lambda_1 T} \left\{ \frac{1}{\lambda_1} (Q_1 + Q_2 \frac{\lambda_2}{\lambda_2 - \lambda_1})(1 - e^{-\lambda_1 T}) - \frac{Q_2}{\lambda_2 - \lambda_1}(1 - e^{-\lambda_2 T}) \right\}$$
$$+ \lambda_3 N_{3p} e^{\lambda_1 T} \left\{ \frac{1}{\lambda_3} (Q_3 + Q_4 \frac{\lambda_4}{\lambda_4 - \lambda_3})(1 - e^{-\lambda_3 T}) - \frac{Q_4}{\lambda_4 - \lambda_3}(1 - e^{-\lambda_4 T}) \right\} \tag{2.1}$$
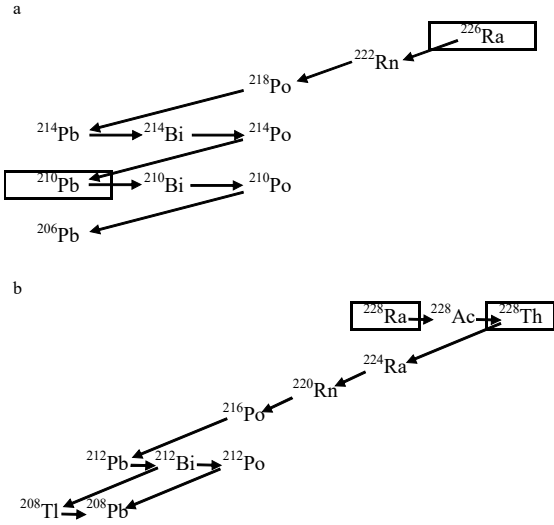
**Fig. 1.** *Radioactive decay chains from (a) $^{226}$Ra and (b) $^{228}$Ra.*

necessarily guarantee that their contribution is negligible. In the present paper, the evolution of the contribution of each nucleus to the accumulated barite dose is simulated by numerical calculation to find that there is an age range in which the contribution from non-observable $^{228}$Ra and its daughter nuclei cannot be neglected.

## 3. THE ANALYSIS FOR THE TEST SAMPLE

The simulation of the contribution from $^{228}$Ra and its daughter nuclei to the accumulated dose is made for an actual test sample, HPD1621R03, taken at a sea-floor hydrothermal area at depth of 1495 m of Hatoma Knoll, Okinawa Trough by the research cruise, KY14-02, operated by Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The sample is a portion of sulfide deposit including barite crystals.

The analysis was made according to the procedures described in Fujiwara *et al.* (2015) and in Uchida *et al.* (2015). A piece of a block cut out of the deposit was soaked in water for 3 days and its mass was measured. After drying in an oven at 60°C for several days until the weight did not change, the water mass was estimated from the difference in the masses as the ratio of the mass of water to the dry mass to be 30.3%. The sample was then crushed and the bulk concentrations of $^{226}$Ra and $^{228}$Ra were obtained by low background gamma ray spectrometry with a pure Ge detector from the gamma ray peaks due to $^{214}$Bi and $^{214}$Pb, and $^{228}$Ac to be 16.9 Bq/g and 1.02 Bq/g, respectively.

The barite crystals were extracted from the crushed bulk sample by using $HNO_3$ and HF. An XRF measurement was made to confirm that the extracted crystals are pure barite. The mass of barite crystals is 70.0% of the total dry mass before the chemical treatment. The barite

grains were separated into 10 aliquots for gamma ray irradiation for the additive dose method. An ESR signal due to $SO_3^-$ was observed in the samples. From the response of the intensity of the signal to the gamma ray dose, the equivalent dose was obtained to be $20.8^{+1.6}_{-1.5}$ Gy by extrapolating the dose response fitted to a saturating exponential curve to the zero ordinate. Using the **Eqs. 2.1** to **2.4** with the corrections for the water content and for the grain size which is typically 20 μm in thickness (Fujiwara *et al.*, 2015), with the alpha effectiveness value of 0.043 (Toyoda *et al.*, 2012), and with the consideration for the external and internal β doses, the ESR age for this present sample was estimated to be 33 ± 1 ka as shown in **Table 1**.

**Table 1.** *Experimental results for HPD1621R03 to be used for the simulation of the contribution of $^{228}$Ra and daughter nuclei to the accumulated doses in barite.*

| | |
|---|---|
| $D_E$ (Gy) | $20.8^{+1.6}_{-1.5}$ |
| Barite content (%) | 70.0 |
| Water content (%) | 30.3 |
| Bulk $^{226}$Ra concentration (Bq/g) | 16.9 |
| Bulk $^{228}$Ra concentration (Bq/g) | 1.02 |
| ESR age (a) | 33±1 |
| Initial bulk $^{226}$Ra concentration (Bq/g) | 17.0 |
| Initial bulk $^{228}$Ra concentration (Bq/g) | 59.4 |
| Initial $^{228}$Ra/$^{226}$Ra activity ratio | 3.47 |

## 4. SIMULATION FOR THE CONTRIBUTION OF THE DOSE FROM $^{228}$Ra AND DAUGHTER NUCLEI

The contribution of the radiation doses from $^{228}$Ra and its daughter nuclei to the accumulated dose to barite in this test sample, HPD1621R03, is simulated as a function of time as in the following. Based on the ESR age obtained as above, the initial (when the age of the sample is zero) bulk concentrations of $^{226}$Ra and $^{228}$Ra are calculated to be 17.0 Bq/g and 59.4 Bq/g, respectively.

The accumulation of the doses to barite given by the nuclei, $^{226}$Ra to $^{214}$Po, $^{210}$Pb to $^{206}$Pb, $^{228}$Ra and $^{228}$Ac, and $^{228}$Th to $^{208}$Pb are respectively calculated from the following formulas, which are deduced from **Eq. 2.1**,

$$D_{E1}(t) = N_{10} Q_1 (1 - e^{-\lambda_1 t})$$

$$D_{E2}(t) = \frac{N_{10} Q_2}{\lambda_2 - \lambda_1} \left\{ \lambda_2 (1 - e^{-\lambda_1 t}) - \lambda_1 (1 - e^{-\lambda_2 t}) \right\}$$

$$D_{E3}(t) = N_{30} Q_3 (1 - e^{-\lambda_3 t})$$

$$D_{E4}(t) = \frac{N_{30} Q_4}{\lambda_3 - \lambda_4} \left\{ \lambda_4 (1 - e^{-\lambda_3 t}) - \lambda_3 (1 - e^{-\lambda_4 t}) \right\}$$

(4.1)

where $D_{E1}$, $D_{E2}$, $D_{E3}$, and $D_{E4}$ are the doses from $^{226}$Ra to $^{214}$Po, $^{210}$Pb to $^{206}$Pb, $^{228}$Ra and $^{228}$Ac, and $^{228}$Th to $^{208}$Pb, respectively, and $N_{10}$ and $N_{30}$ are the initial concentrations of $^{226}$Ra and $^{228}$Ra, respectively.

The values of $D_{E1}$, $D_{E2}$, $D_{E3}$, and $D_{E4}$ are calculated as a function of time for barite crystals in the sample as shown in **Fig. 2**. The accumulated dose from $^{226}$Ra to $^{214}$Po (indicated by $^{226}$Ra in the figure) linearly increases with time as the half-life of $^{226}$Ra, 1600 y, is much larger than the time scale shown in the figure. The one from $^{210}$Pb to $^{206}$Pb (indicated by $^{210}$Pb) slowly increase and then turns linear increase after equilibrated with $^{226}$Ra. The one from $^{228}$Ra and $^{228}$Ac (indicated by $^{228}$Ra) saturates rapidly meaning that those nuclei decay out rapidly where the half-life of $^{228}$Ra is 5.75 y. It is noted that the dose from $^{228}$Th to $^{208}$Pb (indicated by $^{228}$Th) gives a significant contribution when the sample is young. When their parent, $^{228}$Ra, decays out, these nuclei also decay out to give no contribution anymore.

From the values shown in **Fig. 2**, the contributions of the accumulated doses are calculated as a function of time and shown in % (**Fig. 3**) from $^{226}$Ra to $^{214}$Po, $^{210}$Pb to $^{206}$Pb, $^{228}$Ra and $^{228}$Ac, and $^{228}$Th to $^{208}$Pb, indicated by $^{26}$Ra, $^{210}$Pb, $^{228}$Ra, and $^{228}$Th, respectively. The contribution from $^{228}$Th to $^{208}$Pb reaches 60% at its maximum and remains still 30% at 100 years when the nuclei have already decayed out.
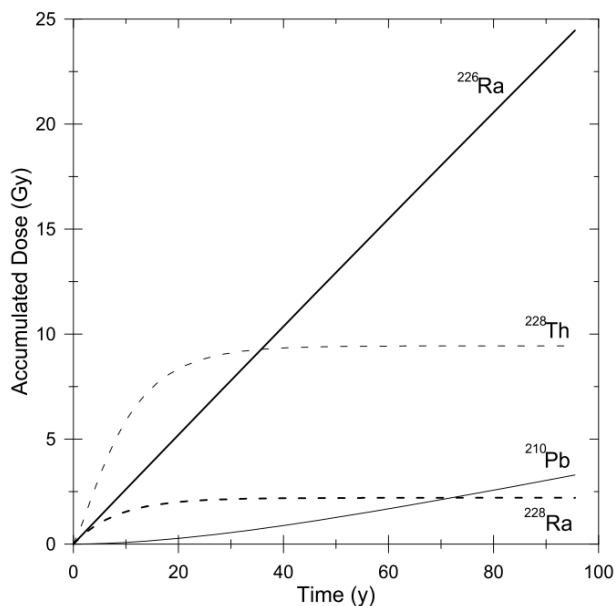
For a longer time scale, the contribution to the accumulated dose from $^{228}$Ra series ($^{228}$Ra to $^{208}$Pb) is calculated as shown in **Fig. 4**, which is in logarithmic time scale. As shown in the figure, even after 300 years, the contribution from $^{228}$Ra series is still 10%. It is obvious that the ESR ages calculated without contribution of $^{228}$Ra series to the accumulated dose will be overestimates. For the present test sample, a simulation indicates that the age will be estimated to be 90 years at age of 50 years when the contribution is not taken into account, while it will still be 360 years, 20% overestimates, at age of 300 year, where the overestimate is comparable as the typical variation, 20%, of the ESR ages from a same portion (Fujiwara *et al.*, 2015) including the measurement error. The overestimate becomes 5% at age of 500 years.

As the half-life of $^{228}$Ra is 5.75 year, although depending on the sample, the nucleus can be detected for young samples. For such young samples, the contribution of the dose from $^{228}$Ra series can be taken into account and the ESR age can be appropriately estimated. For the current test sample, the $^{228}$Ra concentration will become $7 \times 10^{-5}$ Bq/g comparable as the detection limit after 50 years. After this age, the contribution cannot be estimated, because $^{228}$Ra series nuclei have decayed out, but still necessary to be considered according to the above discussion. In summary, the ages of the samples for which the ESR ages have been estimated to be less than 300 years without considering the doses from $^{228}$Ra series, would have probably been overestimated and this would most typically happen for the samples older than 50 years because $^{228}$Ra cannot be detected. Currently, any date
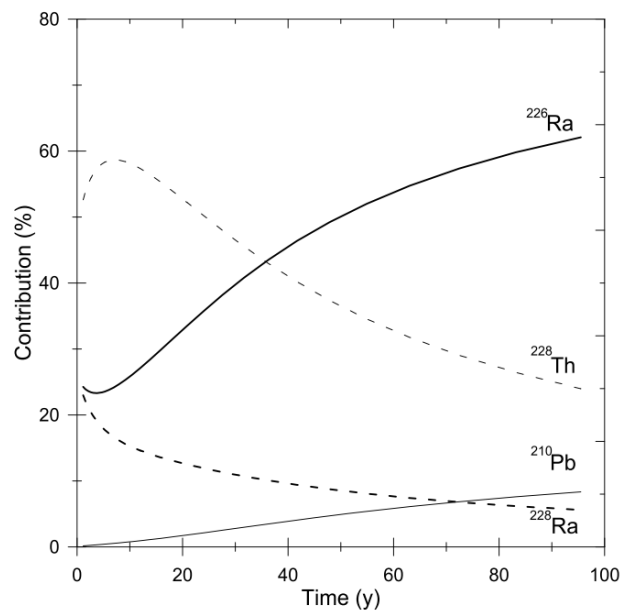


**Fig. 2.** *The results of simulation as a function of time of the accumulated doses given by radioactive nuclei $^{226}$Ra to $^{214}$Po (indicated by $^{226}$Ra), $^{210}$Pb to $^{206}$Pb (indicated by $^{210}$Pb), $^{228}$Ra and $^{228}$Ac (indicated by $^{228}$Ra), and $^{228}$Th to $^{208}$Pb (indicated by $^{228}$Th). The values are calculated for HPD1621R03, taken at a sea-floor hydrothermal area at depth of 1495 m of Hatoma Knoll, Okinawa Trough, the ESR age of which was estimated to be 33 years while the bulk concentrations of $^{226}$Ra and $^{228}$Ra are estimated to be 17.0 Bq/g and 59.4 Bq/g, respectively.*



**Fig. 3.** *The contributions to the accumulated dose as a function of time of the nuclei, $^{226}$Ra to $^{214}$Po (indicated by $^{226}$Ra), $^{210}$Pb to $^{206}$Pb (indicated by $^{210}$Pb), $^{228}$Ra and $^{228}$Ac (indicated by $^{228}$Ra), and $^{228}$Th to $^{208}$Pb (indicated by $^{228}$Th) in %, calculated from the values in Fig. 1.*

over 50 years should be considered a maximum value when the $^{228}$Ra content is not obtained.

How to correct this contribution would be an important but difficult issue. The initial $^{228}$Ra concentration needs to be estimated. For this particular sample examined in the present study, the initial $^{228}$Ra/$^{226}$Ra activity ratio is estimated to be 3.49 from the present $^{226}$Ra and $^{228}$Ra concentrations and the ESR age, which is equivalent to virtually equilibrated Th/U ratio (in ppm) of 10.7. This ratio would be a little high but in the reasonable range as material in the crust. One way would be to investigate and accumulate data on the initial $^{228}$Ra/$^{226}$Ra activity ratio in young or preferably zero age barite samples or in the hydrothermal fluid.

The upper age limit of ESR dating has not been discussed except for the thermal stability, which was estimated to be at least several thousand years (Sato *et al.*, 2011), while the oldest age was reported to be 16000 years (Fujiwara *et al.*, 2015). According to the present simulation of the accumulated dose for further longer time scale, it is found that the dose will be close to saturation after about 5000 years as shown in **Fig. 5**, in which the sum of the accumulated doses from all $^{226}$Ra and $^{228}$Ra series nuclei is calculated as a function of time. This is clearly less than ten times the half-life of $^{226}$Ra, which is 1600 years. As $^{226}$Ra decays, the dose rate gets lower and the accumulated dose increases only slightly. Considering the errors in estimating $D_E$, the age would not correctly be estimated for those more than 5000 or 6000 years old. High precision methods may become available in the future. Until then, when the ESR age appears to be older than 6000 years, it should be considered just to be older than 6000 years.

## 5. CONCLUSIONS

As results of simulation of the doses from the radioactive nuclei of $^{226}$Ra and $^{228}$Ra series, the contribution from $^{228}$Ra series can be significant for samples younger than 300 years. As for the present test sample, the contribution from $^{228}$Th to $^{208}$Pb was calculated to reach 60% at its maximum and to remain still 10% at 300 years. Currently, the ages for these samples without considering doses from $^{228}$Ra series would be overestimates. It is necessary to estimate the initial $^{228}$Ra concentration in barite in order to obtain the correct ages, and therefore, this is the further issue to be investigated especially for the samples older than 50 years old, in which $^{228}$Ra is not detected. Systematic investigations on the $^{228}$Ra/$^{226}$Ra activity ratio in young or zero age samples would help estimate this value. The age limit of ESR dating of barite would be about 5000 to 6000 years due to decay of $^{226}$Ra, rather than the thermal stability of the signal.
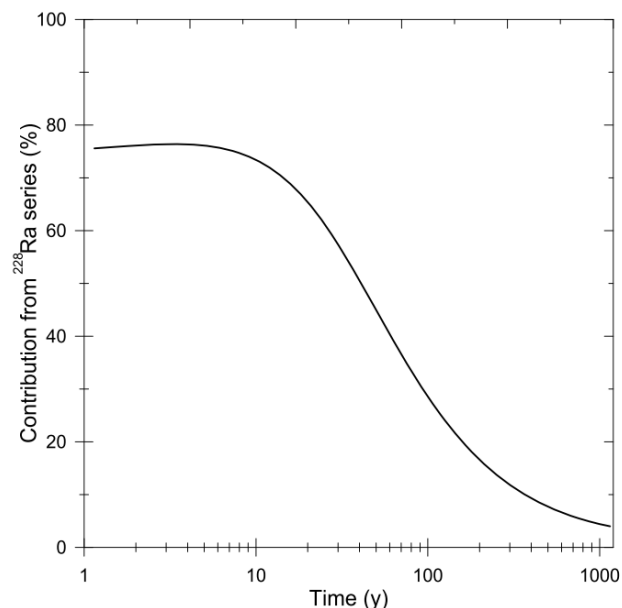
**Fig. 4.** *The contribution to the accumulated dose from $^{228}$Ra series as a function of time in logarithmic scale.*
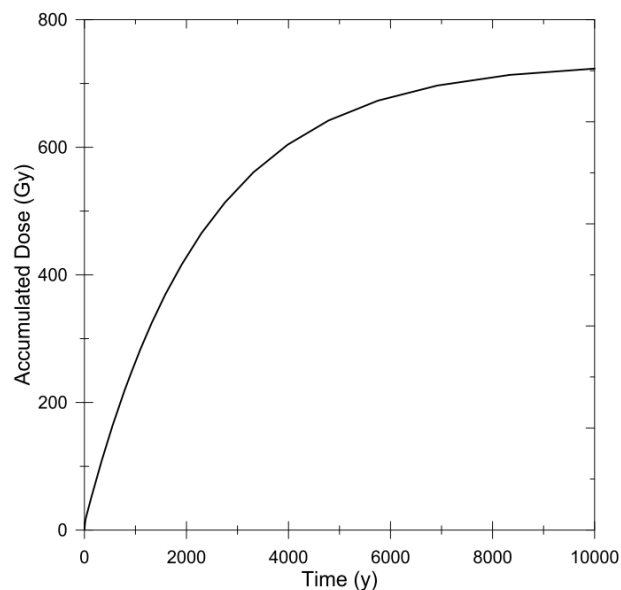


**Fig. 5.** *The total of the accumulated dose as a function of time up to 10 ka. The accumulated dose saturates due to decay of $^{226}$Ra.*

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