

Radiological Investigation of French Fossils

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Aceratherium, humerus (Montaigu)

Summary

The accurate investigation of uranium-containing fossils in a museum of the City of Basel showed the following crucial points

- Storage of uranium-containing minerals or fossils may lead to elevated radon exposures for the staff. The monitoring of the room air is recommended: Eventual taken measures will reduce the exposure to radon (permanent air ventilation, airtight storage of contaminated objects).
- The handling and preparation of such contaminated objects may lead to significant doses by inhalation of radioactive dust. Such work should not be envisaged without special precautions. These could be wearing protective mask and gloves, working in a clean-bench.
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Introduction

During a visit at a museum in the City of Basel, we got aware of high background dose rates in one of the storerooms. In this room, a special osteological collection from different find spots in France was the source for elevated dose rates near to the store facilities. The question arose, whether the measured dose rates could be problematic. Supposing uranium and other nuclides of this decay chain as the source, one has first to check for radon (^{222}Rn). Emanated radon gas is hazardous for man. Several working places were situated in this storeroom and therefore exposed to radon. Another important question had to be answered about the exposition to radiation when such objects were worked with (inner radiation by inhalation of dust particles).

Legal basis

In annex two of the Swiss Radioprotection Ordinance (SRO) specific activity limits are defined for uranium and thorium¹. For minerals and rocks, these limits must be lower than the exemption limit for NORM (normally occurring radioactive material), lower than 1 Bq/g each. The total mass must be lower than 10g of thorium metal (40 kBq of ²³²Th) and 100g of uranium metal (1.25 MBq of ²³⁸U).

For the calculation of incorporated doses, dose conversion factors for inhalation were taken from SRO.

Materials and Methods

Investigated fossil materials

The museum made available selected bone samples for a detailed investigation. All selected materials showed elevated dose rates. The fossils were collected at different places in Central France and were dated to the early Miocene. It is well known that fossil and subfossil specimens can be radioactive due to depositions of NORM. It is important to know the grade of this contamination of the specimens and to avoid any harmful effects caused by either direct radiation of the objects or incorporation of radioactive particles from such objects^{2,3}.



Figure 1 the nine fossils

¹ Swiss Radioprotection Ordinance (SRO) from April 26th 2017

² Gun-Aazhav et al. Investigation of the radioactivity of dinosaur bones with a high-resolution gamma spectrometer. Atomnaya Energiya 35 (1973): 755-757.

³ Charalambous S and Papastefanou C. On the radioactivity of fossil bones. Nucl. Instrum. & methods 142 (1977): 581-588.

Specie	Bone fragment	Find spot	Sample weight (g)
Rhinoceros	costae	Saucelet	59
Rhinoceros	femur	Montaigu	174
Rhinoceros	femur	Ronville	2,620
Rhinoceros	humerus	Chilleurs-au-Bois	203
Rhinoceros	calcaneus	Artenay-Autroche	250
Aceratherium	radius fragm.	Gannat	1,386
Aceratherium	humerus	Montaigu	1,064
Potamotherium	cranium fragm.	Montaigu	163
Potamotherium	radius dext.	Montaigu	13

Table 1 Weight and origin of the investigated fossils

Dose rate measurements

The dose rate of each fossil was determined at a distance of 10 cm using a dose rate meter from Autotomess.

Gamma ray spectrometry

The fossils had to be investigated in a non-destructive way. Therefore, they were placed on top of a high-resolution germanium detector. Each fossil was counted at least twice with changing positions. The different counting of each object showed that the radionuclides were distributed relatively homogeneous within the bones.

For the quantitative estimation of the radioactivity, a geometry of a petri dish (4 cm height, diameter 6 cm) was applied. All emission lines and emission probabilities were compared with LNHB⁴.

Decay series of ²³⁸U

Only few members of this series are analysable with gamma spectrometry: ²³⁴Th, ^{234m}Pa, ²²⁶Ra, ²¹⁴Pb, ²¹⁴Bi, and ²¹⁰Pb.

The emission line of ²³⁴Th, the first daughter of ²³⁸U, at 63.3 keV, was taken for calculation the activity of ²³⁸U. Both radionuclides were in equilibrium. The presence of ²³⁵U caused problems for the determination of ²²⁶Ra at 186.2 keV (interference with 185.7 keV line from ²³⁵U). Instead, ²²⁶Ra was calculated via its daughter nuclides, ²¹⁴Bi and ²¹⁴Pb, knowing that there was no real equilibrium between ²²⁶Ra and the two beta-daughters. A secular equilibrium can be assumed only from ²³⁸U to ²²⁶Ra. ²¹⁰Pb near the end of the decay chain showed lower activities than ²³⁴Th, the second nuclide of this chain.

⁴ LNHB: Laboratoire National Henri Becquerel. Available from: http://www.nuclide.org/DDEP_WG/DDEPdata.htm [Accessed: November 07, 2019]

^{210}Pb and its daughters ^{210}Bi and ^{210}Po were again in secular equilibrium. Both nuclides are no gamma emitters.

Decay series of ^{228}Th

Only six members of this series are detectable with gamma spectrometry: ^{232}Th , ^{228}Ac , ^{224}Ra , ^{212}Pb , ^{212}Bi , and ^{208}Tl . One can expect that the whole decay series is in secular equilibrium. Losses by volatilization of the ^{220}Rn are negligible due to the short half-life of 56s. ^{232}Th was analysed by its emission line at 63.8 keV, even though one has to consider interferences with the ^{234}Th line at 63.3 keV. However, the activities showed to be nearly the same as its daughter ^{228}Th . ^{228}Ra , a beta-emitter, was determined via its daughter ^{228}Ac , which is in secular equilibrium with ^{228}Ra and ^{228}Th .

Decay series of ^{235}U

All members of this decay series are in secular equilibrium, from ^{235}U to ^{211}Po . Losses of the volatile ^{219}Rn are negligible due to its short half-life of 4s. Only a few members of this decay series show reasonable intensive gamma emission lines suitable for a gamma spectrometry. ^{235}U , ^{231}Pa , ^{227}Th , ^{223}Ra , ^{219}Rn , and ^{211}Pb . Other members of this series show only weak lines.

Global fallout

Radionuclides of global fallout and of the fallout from the fire at the nuclear power plant (NPP) of Chernobyl in 1986 were also analysed for. For the determination of the most important fallout parameter, radiostrontium (^{90}Sr), a destruction of the objects would be unavoidable. Therefore, we had to resign analysing for ^{90}Sr , the objects were too precious. The focus was laid on the radiocesium nuclides ^{134}Cs and ^{137}Cs .

Radon in air

The radon activity (^{222}Rn) of the storeroom was monitored in real time near two working places. Radon monitors, radon scouts from Sarad, were used for registration of the radon activity during two months.

Results

Radon exposure

Without any doubt, the highest contribution of an exposure comes from radon, which is emanated from the fossils and diffuses to the room air. Some working places are situated in the storeroom for the fossil collections. People working permanently in this room will get a dose from radon exposure, even when the room is ventilated permanently. Radon in air was measured at two working places. Radon activities were 421 ± 5 resp. 427 ± 5 Bq/m³. This is below the Swiss limit of annual mean activities

for radon exposed working places⁵ (1000 Bq/m³). According to Darby et al.⁶, a mean annual activity of 300 Bq/m³ in the room air leads to an annual dose of about 10mSv. This is the limit value for permanently inhabited zones. For working places, there is a threshold level of 1000 Bq/m³ ⁷.

Radiation analyses of the fossils

External dose estimation

We measured dose rates of 0.01 up to 0.7 µSv/h at a distance of 5 cm from the fossil objects.

This is about seven to ten fold the ambient dose rate in Basel-City. When working with such fossils at a distance of 5 cm eight hours a day, on would receive a dose of about 1.2 mSv/year. However, such a long exposure at 5 cm distance is not realistic. Therefore, we suppose that the risk for external radiation is not relevant.

Fossil species	Dose rate (µSv/h)*	¹³⁴Cs (Bq/kg d.w.)**	¹³⁷Cs (Bq/kg d.w.)**
Fossil, Aceratherium – Humerus	0.03	<1	<1
Fossil, Aceratherium – Humerus	0.01	<3	<3
Fossil, Aceratherium - Radius fragm.	0.69	<1	4.8 ± 1.1
Fossil, Potamotherium - Cranium fragm.	0.04	<1	<1
Fossil, Potamotherium - Radius dext.	0.01	2.3 ± 0.8	<2
Fossil, Rhinoceros – Femur	0.06	<2	<2
Fossil, Rhinoceros – Femur	0.49	<1	<1
Fossil, Rhinoceros – Calcaneus	0.07	<2	<4
Fossil, Rhinoceros -Costae fragm.	0.03	16 ± 1.2	3.2 ± 1.2
Fossil, Aceratherium – Humerus	0.03	<1	<1

Table 2 Dose rate and measured activity concentrations of the fallout-nuclides radiocesium

⁵ Limit for working places of the SRO from January 1, 2018 (article 156.2)

⁶ Darby S. et al. (2006). Residential radon and lung cancer: detailed results of a collaborative analysis of individual data on 7148 subjects with lung cancer and 14208 subjects without lung cancer from 13 epidemiologic studies in Europe.

Scand J Work Environ Health, 32 Suppl1:1-83.

⁷ SRO: Art. 155

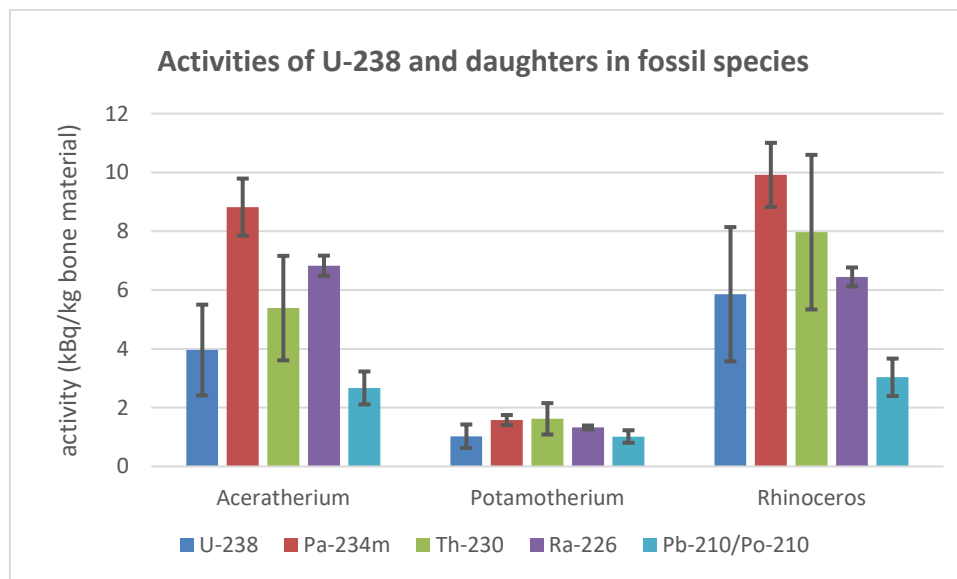
Artificial radionuclides

In two samples, radiocesium could be detected (see Tabel 1). The sum of the found activities was between 2 and 18 Bq/kg. The detection of ^{134}Cs seems not to be plausible. The half-life of ^{134}Cs is two years. Therefore, any contamination with this nuclide should be disintegrated totally within 20 years after the collection of the fossil samples.

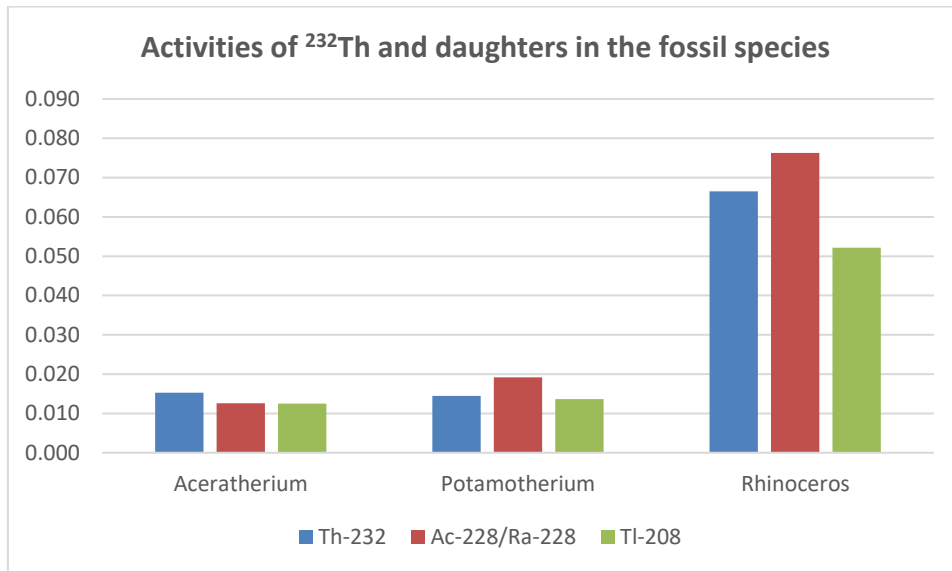
Natural radionuclides of the decay series

The analysis of the measured activity concentrations in the bones showed no correlation with the found spots. E.g., the four fossil samples from Montaigu showed very variable activity concentrations. Therefore, we built mean activity concentrations of each radionuclide for the three animal species Aceratherium, Rhinoceros and Potamotherium.

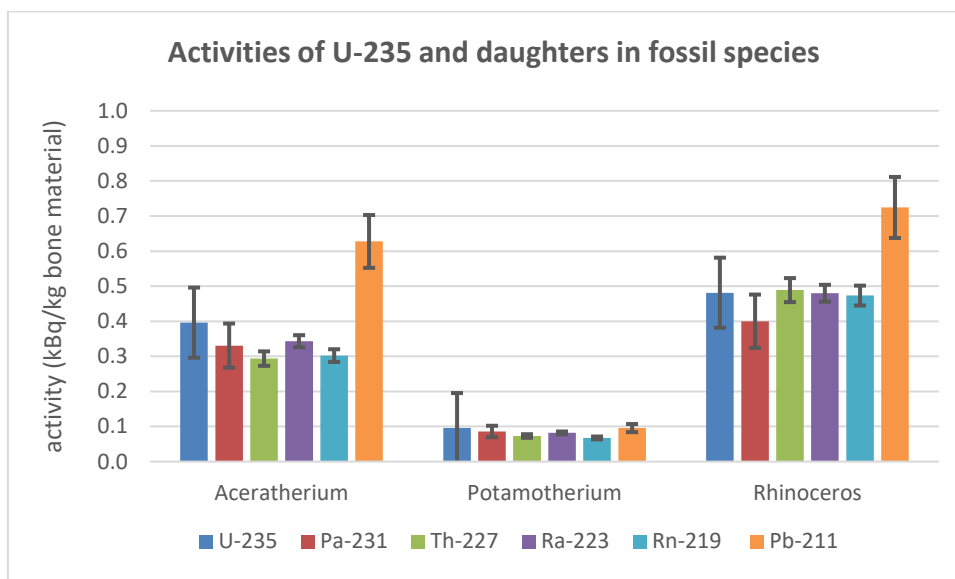
We found ^{238}U at its daughters to be the most prominent radionuclides, whereas there seemed to be no real equilibrium in the decay chain. These inconsistencies can be probably explained with different solubility behaviour of the radionuclides and the loss of ^{222}Rn by emanation. ^{238}U (via its daughter ^{234}Th) showed activities between 1 and 10 kBq/kg of bone material. The bone material of the Potamotherium species showed a significantly lower contamination degree.



The fossils contained ^{232}Th and its daughters in activity concentrations less than 10% of the ^{238}U series. Here, secular equilibrium seems to be reached: The activities of ^{232}Th are nearly the same as for ^{208}Tl at the end of the decay chain. The loss of the volatile ^{220}Rn is negligible due to its short half-life of 56s). Therefore, equilibrium is maintained until the end of the decay chain. The Rhinoceros species were most contaminated.



Besides some higher activities of ^{211}Pb , a radionuclide near to the end of the decay chain of ^{235}U , the radionuclides seemed to be in secular equilibrium, also the volatile species ^{219}Rn (it has a very short half-life of 4s). As expected, the activity concentrations are lower than those of the other decay series. Potamotherium species were least contaminated.



In an undisturbed environment, the quotient of the activity concentrations of ^{238}U and ^{235}U is expected to be 21.7 due to the isotopically pattern of natural uranium. In the fossils, this factor is 11.3 ± 2.0 ; therefore, considerably lower. The ^{235}U in the fossil material is slightly enriched.

NORM

The Swiss Radioprotection Ordinance provides special criteria for the disposal of NORM⁸. Materials should not contain more than 100g of natural uranium or 10 g of natural thorium. Materials, which are not conform to one of the limit of exemption, are subject to the guidelines of the SRO, especially concerning the disposal of such materials.

Fossil species	^{nat}U (g/fossil)	^{nat}Th (g/fossil)
Limit of exemption	100	10
Fossil, Aceratherium – Humerus	0.032	0.001
Fossil, Aceratherium – Humerus	0.64	<0.001
Fossil, Aceratherium - Radius fragm.	0.01	<0.001
Fossil, Potamotherium - Cranium fragm.	0.001	<0.001
Fossil, Potamotherium - Radius dext.	0.08	0.005
Fossil, Rhinoceros – Femur	0.13	0.002
Fossil, Rhinoceros – Femur	0.08	0.001
Fossil, Rhinoceros – Calcaneus	0.17	0.004
Fossil, Rhinoceros -Costae fragm.	0.46	0.006
Fossil, Aceratherium – Humerus	0.032	0.001

Table 3 uranium and thorium content of the fossils

None of the fossils reached any limit of exemption. Therefore, all fossil samples are liberated from SRO.

Internal Dose estimation

A relevant dose could result from the internal corporation of radioactive dust from fossils, when such fossils were handled with, e.g. cutting, rasping etc. With the help of the individual conversion factors for adult persons for inhalation⁹ and the mean activity of the dose relevant radionuclides, a

⁸ SRO: Art. 10.2f

⁹ SRO: Annex 3

inhalative dose was estimated on the basis of an inhalation of 100 mg of fossil dust (see table 2). It can be clearly seen, that the most dose relevant nuclides are ^{227}Ac and ^{230}Th , followed by ^{234}U , ^{238}U and ^{231}Pa . In addition, although the ^{238}U -series is dominant in the analysed fossils the dose from ^{227}Ac contributes most to the whole dose. The inhalation of 100mg of dust would result in an dose of ≈ 45 mSv, this is much more than allowed as annual dose for the public (limit: 1 mSv/year) and even more than 20 mSv/year for people, which are professionally exposed to radiation.

Radionuclide	Decay series	ϵ_{inh} $\mu\text{Sv/Bq}$	Mean activity (Bq/g)	Dose (mSv/100mg)
^{235}U	^{235}U -series	6.1	0.37	0.2
^{231}Pa		89	0.33	2.9
^{227}Th		7.6	0.33	0.3
^{227}Ac		630	0.33	21
^{223}Ra		5.7	0.35	0.2
^{232}Th	^{232}Th -series	29	0.04	0.1
^{228}Ra		1.7	0.04	0.01
^{228}Th		32	0.04	0.1
^{224}Ra		2.4	0.04	0.01
^{238}U	^{238}U -series	5.7	4.2	2.4
^{234}U		6.8	5.7	3.9
^{230}Th		28	4.2	12
^{226}Ra		2.2	5.4	1.2
^{210}Pb		1.1	2.4	0.3
^{210}Po		2.2	2.4	0.5
Total dose by inhalation of 100 mg of dust				45

Table 4 Estimated dose contributions of the dose-relevant radionuclides for the inhalative incorporation of 100 mg of fossil dust. * mean dose rate measured at different sides of the object at a distance of 10cm. **d.w.: dry weight.

Conclusions

Collections of minerals or fossils may result in a rise of the radon contamination of the room air by emanation. That leads to rise of the annual dose for persons working in such an environment. A mean radon activity concentration of 300 Bq/m³ leads to an annual dose of about 10 mSv. Therefore, it is recommended to ventilate such rooms permanently with fresh air or to store uranium containing minerals and fossils in airtight containers or cabinets.

- In the present case, the permanent ventilation keeps the level of radon at about 400 Bq/m³, which is conform to the Swiss law.

A contamination by inhalation of dust from such objects has to be taken more seriously. As calculated with the data of nine investigated fossil samples, we estimated the dose by inhalation of 100 mg dust to about 45 mSv. This may happen when fossils are prepared without any precautions. In the present case, the preparation of fossils are executed in clean-benches, which have an independent air circulation system. Therefore, the uptake of dust should be as low as possible.

Rooms of a museum, where uranium containing minerals or fossils are stored, should be monitored for radon. Working places, which are situated in such store rooms are probably categorized as radon-exposed working-places. Consequently, a permanent personal dosimetry of the staff could be prescribed from the Federal authority. Any preparation of contaminated fossils should be executed with well-defined precautions (FFP3 mask, gloves, clean-bench as working place).

- In the present case, the mentioned precautions were realized.