Search for $\alpha$ decay of naturally occurring Hf-nuclides using a Cs$_2$HfCl$_6$ scintillator

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Abstract

Residual radioactive contaminants of a caesium hafnium chloride (Cs$_2$HfCl$_6$) crystal scintillator have been measured in a low background setup at the Gran Sasso National Laboratory of the INFN, Italy. The total alpha activity of the detector is at the level of 7.8(3) mBq/kg. The results of direct studies of the $\alpha$ decay of naturally occurring Hf isotopes that have been performed using the “source=detector” approach are presented. In 2848 h of data taking, the $\alpha$ decay of $^{174}$Hf was observed with $T_{1/2} = (7.0 \pm 1.2) \times 10^{16}$ y.

Keywords: rare alpha decay; $^{174}$Hf; $^{176}$Hf; $^{177}$Hf; $^{178}$Hf; $^{179}$Hf; $^{180}$Hf; crystal scintillator; Cs$_2$HfCl$_6$; HP-Ge $\gamma$ spectrometer; source = detector approach; low background experiment; hafnium.

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1 Introduction

Since its discovery more than a century ago, $\alpha$ decay remains one of the most powerful tools to study nuclei and their structure. $\alpha$ decay is energetically favourable for naturally occurring heavy isotopes (from $^{142}$Ce to $^{238}$U), while the probability of the $\alpha$ particles tunnelling through the nuclear potential barrier is significantly reduced for nuclei lighter than the $^{209}$Bi. In fact, these light nuclei – their available decay energy is less than 3 MeV – undergo $\alpha$ emission with very long half-life ($\gtrsim 10^{14}$ y); therefore, these processes are extremely difficult to detect with conventional techniques. However, significant progress has been made in the field of search for rare $\alpha$ decays during the past decade. This was mostly triggered by the development and application of new experimental techniques, as well as by improving well-known ones. A recent detailed review on investigations of rare $\alpha$ decays and the achieved results is given in Ref. [1]. It should be noted that for some $\alpha$ active elements there are still no detector materials that may contain the element of interest in an amount significant enough to perform highly sensitive measurements with the “source = detector” approach.

Very recently there has been a significant renewed interest in crystal scintillators as the $\text{K}_2\text{PtCl}_6$ [2]; in fact, their properties include: a high light yield, a very good linear response at low energies and a good energy resolution. The $\text{Cs}_2\text{HfCl}_6$ (CHC) crystal – belonging to the same structure group – is one of the promising new scintillating materials for $\gamma$ spectroscopy offering a light output of more than 50000 photons/MeV, a 3.3% energy resolution at 662 keV [3], with an excellent ability for pulse shape discrimination (PSD) of the $\gamma(e)/\alpha$ scintillation signals [4]. Moreover, this is also the first scintillating material containing a high fraction of Hf ($\sim 27\%$ in mass) that can be easily produced using the Bridgman growing technique.

First investigations of the chemical purity of a CHC crystal using inductively coupled plasma mass spectrometry (ICP-MS) and of its radio-purity using an ultra-low background high purity germanium (HP-Ge) detector have shown that this compound is clean with respect to the U/Th radioactive chains (only limits were set at the level of few mBq/kg). However, some contamination with man-made $^{137}\text{Cs}$ ($\sim 1$ Bq/kg) and $^{134}\text{Cs}$ ($\sim 50$ mBq/kg), and cosmogenic $^{132}\text{Cs}$ ($\sim 25$ mBq/kg) and $^{181}\text{Hf}$ ($\sim 15$ mBq/kg) was measured in the sample [5]. Thus, due to its promising good radio-purity and to the combination of its outstanding scintillation features, the CHC crystal opens new possibilities in the search for the rare nuclear processes in natural
In this paper, we show the successful operation of a CHC crystal as low-background scintillator to investigate rare $\alpha$ decays of naturally occurring Hf isotopes, specifically of $^{174}$Hf.

We remind that the first and only measurement of the $^{174}$Hf $\alpha$ decay was carried out more than fifty years ago using an ionization chamber with thin and low mass HfO$_2$ samples. Only a preliminary indication of its detection was obtained due to an extremely low signal-to-background ratio, quoting as half-life the value $2.0(4) \times 10^{15}$ y [6] while theoretical predictions in various models quote a half-life value ranging from $3.5 \times 10^{16}$ y to $7.4 \times 10^{16}$ y [7–9], i.e. one order of magnitude higher.

Figure 1: Simplified scheme of the $\alpha$ decay of $^{174}$Hf to $^{170}$Yb. The energies of the excited levels and of the emitted $\gamma$ quanta are in keV (the relative intensity of the $\gamma$ quantum from each level is given in parentheses). The $\alpha$ decay schemes of all the naturally occurring Hf isotopes are reported in Ref. [10].

In order to detect such rare decays, it is necessary to use radio-pure materials to maximize the signal-to-background ratio. Thus, we give in this work, the chemical purity and the radio-active contamination of the used CHC crystal “as is” in the light of future applications in low-background experiments to investigate rare processes in Hf. Information about some $\alpha$ transitions of naturally occurring Hf isotopes with $Q_\alpha > 0$ are listed in Table 1. All the naturally occurring Hf isotopes can decay to g.s. or to excited levels of their daughter. Fig. 1 shows a simplified expected decay scheme of the $\alpha$ decay of the $^{174}$Hf isotope; the expected $\alpha$ decay schemes of all the naturally occurring Hf isotopes are reported in Ref. [10].
Table 1: Some potential $\alpha$ transitions of Hf isotopes and related information. Only naturally occurring isotopes (with natural abundance $\delta$) and with $Q_\alpha > 0$ between g.s. transitions or between g.s. and lowest bound level transitions (with spin/parity $J^\pi$) are listed. $E_\alpha$ is the kinetic energy of the alpha particle. $N$ is the number of nuclei in the CHC crystal used in this work. Experimental measurements (when available) and theoretical prediction of the half-live are reported in the last four columns. $T_{1/2}$ values have been calculated in Refs. [1,10], following the prescription in Refs. [7–9].

| Nuclide Transition | $J^\pi$ of Parent $\rightarrow$ Daughter Nuclei and its level (keV) | $\delta$ (%) | $Q_\alpha$ (keV) | $E_\alpha$ (keV) | $N$ | $T_{1/2}$ (y) |
|-------------------|-------------------------------------------------|-------------|-----------------|-----------------|-----|----------------|
| $^{171}$Hf $\rightarrow$ $^{170}$Yb | $0^+ \rightarrow 0^+$, g.s. 0$^+$ $\rightarrow$ 2$^+$, 842 | 0.16(12) | 2494.5(2.3) | 2437.6(2.2) | 1.0 $\times$ 10$^{19}$ | $2.0(4) \times 10^{15}$ $^{11}$ $^{12}$ $^{13}$ | $3.5 \times 10^{16}$ | $7.4 \times 10^{16}$ | $3.5 \times 10^{16}$ |
| $^{170}$Hf $\rightarrow$ $^{172}$Yb | $0^+ \rightarrow 0^+$, g.s. 0$^+$ $\rightarrow$ 2$^+$, 847 | 5.26(70) | 2254.2(1.5) | 2203.3(1.5) | 3.3 $\times$ 10$^{20}$ | $3.0 \times 10^{17}$ $^{10}$ | $2.5 \times 10^{20}$ | $6.6 \times 10^{20}$ | $2.0 \times 10^{20}$ |
| $^{172}$Hf $\rightarrow$ $^{171}$Yb | $7/2^- \rightarrow 5/2^-$, g.s. 7/2$^- \rightarrow 7/2^-$, 78.6 | 16.00(16) | 2245.7(1.4) | 2195.3(1.4) | 1.2 $\times$ 10$^{21}$ | $1.3 \times 10^{18}$ $^{10}$ | $4.5 \times 10^{20}$ | $5.2 \times 10^{20}$ | $4.4 \times 10^{20}$ |
| $^{173}$Hf $\rightarrow$ $^{174}$Yb | $0^+ \rightarrow 0^+$, g.s. 0$^+$ $\rightarrow$ 2$^+$, 76.5 | 27.28(28) | 2084.4(1.4) | 2037.9(1.4) | 1.7 $\times$ 10$^{21}$ | $2.0 \times 10^{17}$ $^{10}$ | $3.4 \times 10^{21}$ | $1.1 \times 10^{24}$ | $2.2 \times 10^{24}$ |
| $^{174}$Hf $\rightarrow$ $^{173}$Yb | $9/2^- \rightarrow 7/2^-$, g.s. 9/2$^- \rightarrow 9/2^-$, 104.5 | 13.62(11) | 1807.7(1.4) | 1767.6(1.4) | 8.6 $\times$ 10$^{20}$ | $2.2 \times 10^{16}$ $^{10}$ | $4.5 \times 10^{20}$ | $4.0 \times 10^{20}$ | $4.7 \times 10^{20}$ |
| $^{175}$Hf $\rightarrow$ $^{174}$Yb | $0^+ \rightarrow 0^+$, g.s. 0$^+$ $\rightarrow$ 2$^+$, 82.1 | 35.68(33) | 1287.1(1.4) | 1258.7(1.4) | 2.2 $\times$ 10$^{21}$ | $1.0 \times 10^{18}$ $^{10}$ | $6.4 \times 10^{18}$ | $5.7 \times 10^{18}$ | $9.2 \times 10^{18}$ |
| $^{176}$Hf $\rightarrow$ $^{175}$Yb | $0^+ \rightarrow 0^+$, g.s. 0$^+$ $\rightarrow$ 2$^+$, 82.1 | 35.68(33) | 1287.1(1.4) | 1258.7(1.4) | 2.2 $\times$ 10$^{21}$ | $1.0 \times 10^{18}$ $^{10}$ | $6.4 \times 10^{18}$ | $5.7 \times 10^{18}$ | $9.2 \times 10^{18}$ |
2 The experiment

2.1 The CHC crystal scintillator

The growth of the CHC crystal was done using the Bridgman technique. The initial compounds were from a commercially available feedstock with the highest available chemical purity of CsCl beads and HfCl$_4$ powder. The purity level of CsCl beads was 99.998%. To reach a similar purity grade of HfCl$_4$ powder, the compound was processed by three-fold purification (see e.g. Ref. [4]). Later, to prepare the CHC compound for the crystal growth, the stoichiometric mixture of purified HfCl$_4$ powder and CsCl beads was well mixed and placed into a quartz ampule sealed under vacuum. Then, the ampule was transferred to a two-zone vertical furnace to perform the crystal growth with a crystallization rate of 1 cm/day and applying a thermal gradient of 5°C/cm at the solid/liquid interface. A more detailed description of the purification of the starting material and the CHC crystal growth is given in Ref. [4]. A CHC crystal sample with a mass of 6.90(1) g, 22 mm diameter and 4.6 mm height ($\rho \sim 3.9$ g/cm$^3$), was cut from a 50 g boule and used in this study. Some general properties of CHC crystals are listed in Table 2.

Table 2: Some general properties of CHC crystal scintillators.

| Property                          | Value          |
|----------------------------------|----------------|
| Effective atomic number          | 58             |
| Density (g/cm$^3$)               | 3.9            |
| Melting point (°C)               | 820            |
| Crystal structure                | cubic          |
| Wavelength of emission (nm)      | 400–430        |
| Average decay time ($\mu$s)      | 4–5            |

2.2 The detector

The experiment was carried out at the STELLA (SubTErranean Low Level Assay) facility of the LNGS [14]. The CHC crystal scintillator was coupled with a 3-inch low-radioactivity photomultiplier (PMT, Hamamatsu R6233MOD), and placed above the end-cap of the ultra-low background HP-Ge $\gamma$ spectrometer GeCris (465 cm$^3$). Due to the longitudinal extent of the CHC
Figure 2: Schematic cross-sectional view of the experimental set-up (not in scale). There are shown the CHC crystal scintillator (1) coupled with a 3 inches PMT (2), the HP-Ge detector (3), which is separated by a cylindrical teflon ring (4). They are completely surrounded by a passive shield made by archaeological Roman lead (5), high purity copper (6), low radioactive lead (7). The whole set-up (with the exception of the cold finger for the HP-Ge detector) is enclosed in a plexiglas box (8) continuously flushed with HP-N₂ gas.
detector and of its PMT, the top part of the usual GeCris shield has been slightly re-arranged; no other modifications have been applied to the shield. A schematic cross-section of the experimental set-up is shown in Fig. 2.

The surface of the CHC crystal was covered with PTFE tape to improve the light collection. The passive shield was assembled (from the external to the internal part) with low radioactivity lead (∼25 cm), high purity copper (∼5 cm), and, in the inner-most part, with archaeological Roman-age lead (∼2.5 cm). The whole set-up – with the exception of the cold finger for the HP-Ge detector – was contained inside a plexiglas box and continuously flushed with high purity (HP) nitrogen gas to exclude radon close to the detectors.

![Figure 3: Typical energy distributions collected with the CHC detector for γ’s from $^{137}$Cs and $^{22}$Na sources. The fits of the 662 keV and 1275 keV peaks (using the asym–Gaussian function as shape adopted in Ref. [15]) are superimposed. The double arrows indicate the FWHM of the two fitted peaks.](image)

The signals from the PMT and the HP-Ge were acquired using a CAEN DT5720B digitizer taking 250 MSamples/s; these signals were recorded in a time window of 50 µs. An event-by-event data acquisition system stored the pulse shapes of the events. The idea was to use, as described in Section 4, a coincidence logic between the CHC and the HP-Ge detector, to study also the α decay of Hf isotopes to the first excited level, when also a γ-ray is emitted and could in principle be measured with the HP-Ge detector. In this way, any possible signal would be directly pointed out from the data. Thus, hereafter – unless otherwise stated – the energy spectra of events occurred in the CHC detector and in anticoincidence with the HP-Ge detector are considered.

The energy calibration and resolution of both detectors CHC and HP-Ge were determined using γ calibration sources with peak energies 59.5
keV ($^{241}\text{Am}$), 511.0 keV ($^{22}\text{Na}$), 661.7 keV ($^{137}\text{Cs}$) and 1274.5 keV ($^{22}\text{Na}$). In particular, the energy resolution of the CHC detector is: FWHM(keV) = 0.53(5) × $E^{0.73(2)}$, where $E$ is in keV. Fig. 3 shows the typical energy distributions measured by the CHC detector for $\gamma$'s from $^{137}\text{Cs}$ and $^{22}\text{Na}$ sources; there the fits of the 662 keV and of the 1275 keV peaks performed by adopting the asym–Gaussian function as shape (see Ref. [15]) are super-imposed. In fact, in certain cases an asymmetric shape can be expected, due to either e.g. a non-uniformity of the light collection in the detector volume or to K-escape peaks; for a complete discussion see Refs. [16–19]. To monitor

Figure 4: Spectrum of the $^{241}\text{Am}$ acquired by the CHC scintillator. In the inset the PSD plot of the $\beta/\gamma$ and $\alpha$ events is reported; see text. In red the $\alpha$ events, in blue the $\beta/\gamma$ events and in black the raw data. The superimposed fit (light green online) is performed using a non-Gaussian function as proposed in Ref. [15] for the peak and an exponential function to describe residual $\beta/\gamma$ events surviving the PSD selection.
the stability of the energy scale, the data were divided in several runs and
the stability in time of the energy spectra was verified.

Moreover, a preliminary dedicated energy calibration of the CHC crystal
scintillator was done deep-underground with a $^{241}$Am source in air to obtain
a first estimate of the quenching factor (Q.F.)$^3$ of the CHC. This source was
collimated and placed in front of the CHC detector at a distance of about
1.5 cm. Fig. 4 shows the spectrum of the $^{241}$Am source acquired with the
CHC scintillator. In the inset the PSD of $\beta/\gamma$ and $\alpha$ events (see section
3.2) is shown; the population with smaller mean time (red online) is mostly
due to external $\alpha$’s. The distribution of the alpha events was fitted with
a background model made of an exponential function (to describe residual
$\beta/\gamma$ events) plus an asymmetric Gaussian (asym-Gaussian) function for the
peak$^3$. The fit result (light green on-line in Fig. 4) provides an energy peak
centroid at 1061(12) keV (energy in $\gamma$ scale) which – considering also the $\sim$
1.5 cm of air between the source and the detector – gives a Q.F. $\sim$ 0.4 at
that energy.

3 Low background measurements of the CHC crystal

The PSD between $\beta/\gamma$ and $\alpha$ particles, and the time-amplitude analysis of
the fast sub-chains of decays from the $^{232}$Th family were applied in order to
evaluate the radioactive contamination of the CHC crystal scintillator and
the response of the detector to $\beta/\gamma$ particles. In particular, the data of the
radioactive contamination of the CHC crystal scintillator was used to build
a model of the background in order to derive an estimate of the half-lives of
the $\alpha$ decays of the Hf-isotopes, especially for the $\alpha$ decay of $^{174}$Hf.

$^2$The Q.F. describes the response of a scintillator to heavy ionizing particles; in detail,
it is the ratio between the detected energy in the energy scale measured with $\gamma$ sources
and the actual energy of the heavy ionizing particle. The Q.F. is an experimental feature
of a detector and it is strongly dependent on its nature, mechanisms of detection and
impurities.

$^3$Besides what mentioned above in the text, the asym-Gaussian shape of the peaks in
the case of external alpha’s is also due to the partial absorption of the alpha energy in the
medium before the CHC.
3.1 Measurements of residual contaminations by ICP–MS and by HP-Ge spectrometry

In Table 1 the isotopic composition of $^{\text{nat}}$Hf according to literature is shown. However, the isotopic abundance of $^{174}$Hf is known with poor precision. To overcome this problem, a sample of the CHC crystal, 11.8(1) mg, was analysed by means of ICP-MS. The measured abundances are summarized in Table 3; in particular, the obtained isotopic abundance of $^{174}$Hf is 0.156(6)%, considerably increasing the precision of the measurement. This has been obtained by dissolving and diluting the CHC sample to 100 $\mu$g/l of Hf. In this way, all the Hf isotopes were measured using the “digital mode” detector avoiding issues due to the Digital/Analogic detector cross calibration (ICP-MS mod 7500a by Agilent technologies was used for isotope composition determination). In general, when applying high dilution factor before ICP-MS measurements, the isobaric interferences related to the matrix are significantly reduced. Focusing our attention on the mass window of the $^{174}$Hf, it is affected by the $^{174}$Yb signal. But in the CHC sample the presence of the Yb was excluded by monitoring the $^{173}$Yb, which in the measured solution was very low and comparable to the procedural blank one. The values reported in table 3 are the average of five replicates and their uncertainties are computed with 68% confidence level. All values in the table are in agreement with those reported in literature.

Table 3: Isotopic composition of $^{\text{nat}}$Hf measured in a sample of the CHC crystal by ICP-MS.

| Isotope | Abundance (%) |
|---------|---------------|
| $^{174}$Hf | 0.156(6) |
| $^{176}$Hf | 5.18(5) |
| $^{177}$Hf | 18.5(1) |
| $^{178}$Hf | 27.2(1) |
| $^{179}$Hf | 13.9(1) |
| $^{180}$Hf | 35.2(2) |

Table 4 shows the level of impurities measured by ICP-MS. These results have been considered in order to identify the possible presence of isotopes interfering with the goal of present work (see later).
Table 4: Concentrations of trace contaminants in the CHC crystal as measured by ICP-MS analysis. The limits are at 68% C.L.

| Nuclide | Concentration (ppb) |
|---------|---------------------|
| $^{144}\text{Nd}$ | <2.4 |
| $^{147}\text{Sm}$ | 0.6(1) |
| $^{148}\text{Sm}$ | 0.4(1) |
| $^{151}\text{Eu}$ | 19(7) |
| $^{152}\text{Gd}$ | <0.02 |
| $^{180}\text{W}$ | <0.4 |
| $^{184}\text{Os}$ | <0.003 |
| $^{186}\text{Os}$ | <0.25 |
| $^{190}\text{Pt}$ | <0.02 |
| $^{209}\text{Bi}$ | <2 |

The radioactive contaminations in the CHC crystal were also been measured using the ultra-low background HP-Ge $\gamma$ spectrometer GeCris of the STELLA facility at LNGS in 841 h of data taking. The results are shown in Table 5.

There is no evidence of radionuclides from the natural decay chains of $^{235}\text{U}$, $^{238}\text{U}$ and $^{232}\text{Th}$ in the CHC crystal; the corresponding limits have been set at level of a few mBq/kg. The limits on activities of other commonly observed nuclides are also shown in Table 5. However, the CHC crystal is more significantly contaminated with man-made $^{137}\text{Cs}$ (0.74(8) Bq/kg) and $^{134}\text{Cs}$ (79(8) mBq/kg). In the case of the cosmogenic radionuclides $^{132}\text{Cs}$ and $^{181}\text{Hf}$ the upper limits are at the level of 15 mBq/kg and 11 mBq/kg, respectively.

Among the isotopes listed above, $^{134}\text{Cs}$ and $^{137}\text{Cs}$ are rather long-living nuclides with half-lives of 2.0652(4) y and 30.08 y, respectively; while the other isotopes have relatively short half-life values ($T_{1/2} = 6.480(6)$ d for $^{132}\text{Cs}$, and $T_{1/2} = 42.39(6)$ d for $^{181}\text{Hf}$) making them not problematic for exploring rare decays occurring in Hf isotopes. In a future low-background experiment with CHC detectors, it necessary to carefully check the initial CsCl compound and find a supplier whose material contains a minimal amount of $^{137}\text{Cs}/^{134}\text{Cs}$. Moreover, to reduce the contamination of the cosmogenic nuclides one should avoid the transportation of produced CHC crystals by
Table 5: Radioactive contaminations of the CHC crystal measured with the ultra-low background HP-Ge $\gamma$ spectrometer GeCris of the STELLA facility at LNGS. The uncertainties associated to the measured values are 1$\sigma$, while the upper limits are given at 95% confidence level (C.L.).

| Chain | Nuclide | Activity (mBq/kg) |
|-------|---------|------------------|
|       | $^{40}$K | $0.4(1)\times10^3$ |
|       | $^{44}$Ti | $10(4)$ |
|       | $^{60}$Co | $<25$ |
|       | $^{137}$Cs | $0.74(8)\times10^3$ |
|       | $^{132}$Cs | $<15$ |
|       | $^{134}$Cs | $79(8)$ |
|       | $^{181}$Hf | $<11$ |
|       | $^{190}$Pt | $<20$ |
|       | $^{202}$Pb | $<9.1$ |

| $^{232}$Th | $^{228}$Ra | $<12$ |
| $^{228}$Th | $<3.6$ |

| $^{238}$U | $^{226}$Ra | $<23$ |
| $^{234}$Th | $<0.80$ |
| $^{234m}$Pa | $<0.48$ |

| $^{235}$U | $^{235}$U | $<14$ |

airplane. Finally, it will be of benefit storing CHC crystals underground for one-two months before starting any low-background experiment. The above mentioned nuclides were present, in traces, also in a previous work concerning CHC crystals, roughly having the same radioactive level as measured here [5]. However, the crystal of our work contains significantly higher contamination of $^{40}$K at the level of $0.4(1)$ Bq/kg, and $^{44}$Ti with activity of $10(4)$ mBq/kg. These radionuclides were not observed in earlier measurements with CHC crystal on the HP-Ge detector and require further studies. However, it is worth to note that in the paper [20], the GeCris was used to measure SrI$_2$(Eu) and a contamination of the HP-Ge set-up by $^{44}$Ti (see fig. 9 and text of Ref. [20]) was detected. Thus, the same origin could be present in both cases.
3.2 Pulse-shape discrimination between $\beta/\gamma$ and $\alpha$ particles

Scintillation signals from events of different origin ($\alpha$ particles; $\gamma$ quanta or $\beta$ particles) can show different time profiles depending on the detector capabilities; this can be used to discriminate among them. In our case, we have used a pulse-shape discrimination (PSD) technique based on the event mean time (see e.g. [4, 21]). In particular, the time profile of each event is exploited to calculate its mean time according to:

$$\langle t \rangle = \frac{\sum f(t_k)t_k}{\sum f(t_k)}$$ \hspace{1cm} (1)

where the sum is taken over the time channels, $k$, starting from the origin of the pulse up to $8 \mu$s. Moreover, $f(t)$ is the digitized amplitude (at the time $t$) of a given signal. The scatter plot of the mean time versus energy for the data of the low background measurements is shown in Fig. 5; it demonstrates the pulse-shape discrimination ability of the CHC detector. The distribution of the mean times for the events with energies – using the $\gamma$ scale – in the range $(0.4 - 3.0)$ MeV is shown in the inset of Fig. 5. The spectra of $\beta/\gamma$ and $\alpha$ events selected by PSD analysis are given in Fig. 6.

3.3 Time–amplitude analysis of $^{228}$Th sub–chain and the derived Q.F.

The time–amplitude analysis (described e.g. in Ref. [22–24]) was used to select the events of the following decay sub–chain of the $^{232}$Th family: $^{224}$Ra ($Q_{\alpha} = 5789$ keV; $T_{1/2} = 3.66$ d) $\rightarrow$ $^{220}$Rn ($Q_{\alpha} = 6405$ keV; $T_{1/2} = 55.6$ s) $\rightarrow$ $^{216}$Po ($Q_{\alpha} = 6906$ keV; $T_{1/2} = 0.145$ s) $\rightarrow$ $^{212}$Pb.

To select these decays, firstly, we search for the pair of $\alpha$s ($^{220}$Rn – $^{216}$Po) and after we come back to search for the $\alpha$ from $^{224}$Ra. In fact, each $\alpha$ event with energy in the interval $(1.4 - 3.0)$ MeV ($\gamma$ scale$^4$) was used as trigger to search in the same energy interval – for a second $\alpha$ event ($^{216}$Po) in the subsequent time interval $(0 - 1)$ s (total efficiency 99.2%). This pair of $\alpha$s ($^{220}$Rn – $^{216}$Po) was used as trigger to search back for a third $\alpha$ from $^{224}$Ra. In this latter case, the time interval $(1 - 112)$ s and the same energy

$^4$The Q.F. of the $\alpha$ events in the CHC has been preliminary estimated in Section 2.2 and supported by the data in Ref. [4]. Taking into account this estimation the $\alpha$ particles of $^{220}$Rn are expected to fall in this energy region.
interval as above were considered (total efficiency 74.0%). Assuming the secular equilibrium of this sub-chain, an average activity of $^{228}$Th in the CHC crystal scintillator has been estimated: 100(50) $\mu$Bq/kg. In a data set accumulated over 2176 h with the CHC detector, the energies of the $\alpha$ peaks of $^{224}$Ra, $^{220}$Rn and $^{216}$Po, selected by the described time-amplitude analysis, are 2260(200) keV, 2540(200) keV, 2780(240) keV ($\gamma$ scale), respectively.

According to the result of the time–amplitude analysis, the Q.F. of the used CHC scintillator to $\alpha$ particles at the energies of $^{224}$Ra, $^{220}$Rn and
Figure 6: Energy spectrum measured by the CHC detector over 2848 h live-time (raw data; black histogram) and spectra of $\beta/\gamma$ (red dots on-line) and of $\alpha$ events selected by PSD (blue histogram on-line).

$^{216}$Po $\alpha$ decays is 0.39(4), 0.40(3), 0.40(3), respectively. Fig. 7 shows these Q.F. values and the global fit (red dotted line) following the prescription of Ref. [25], showing that an $\alpha$ particle produces about 1/2.5-th of the light produced by $\gamma$ quanta in the energy range (1–8) MeV. Note that hereafter the energy is in $\alpha$ energy and not in $\gamma$ scale. In conclusion, considering the model of Ref. [25] the Q.F. at 4 MeV is 0.36, exactly the same Q.F. value measured in Ref. [4]. In the following, the fit result according the model of Ref. [25] will be used.

### 3.4 Identification of Bi–Po events

The search for the fast decays $^{214}$Bi ($Q_\beta = 3270$ keV, $T_{1/2} = 19.9$ m) $\rightarrow$ $^{214}$Po ($Q_\alpha = 7834$ keV, $T_{1/2} = 164$ $\mu$s) $\rightarrow$ $^{210}$Pb (in equilibrium with $^{226}$Ra from the $^{238}$U chain) and the fast decays $^{212}$Bi ($Q_\beta = 2252$ keV, $T_{1/2} = 60.55$ m) $\rightarrow$ $^{212}$Po ($Q_\alpha = 8954$ keV, $T_{1/2} = 0.299$ $\mu$s) $\rightarrow$ $^{208}$Pb was performed with the
Figure 7: Dependence of the Q.F. on the energy of the $\alpha$ particles measured by the internal $\alpha$ decays of $^{224}\text{Ra}$, $^{220}\text{Rn}$, $^{216}\text{Po}$ of the CHC crystal (blue points). The model obtained as global fits of these data points following the prescription of Ref. [25] are also reported (red dotted line) with its 1$\sigma$ fit uncertainty (yellow filled band); the Q.F. for a CHC scintillator measured in Ref. [4] is also shown (cyan dot line).

help of the pulse-shape analysis of the double pulses within the same time window (50 $\mu$s). We found 11 events; 6 events have a time interval between the starting of the $\beta$ pulse and that of the $\alpha$ pulse ($\Delta T_{BiPo}$) less than 2 $\mu$s. The probability to have a $^{214}\text{Bi} - {^{214}\text{Po}}$ event in the windows (0.024 – 2) $\mu$s is 0.83%, while the detection efficiency in the same time window for $^{212}\text{Bi} - {^{212}\text{Po}}$ events is 93.6%. In the case of $^{214}\text{Bi} - {^{214}\text{Po}}$ events the time window (2 – 50) $\mu$s has to be considered, and the corresponding efficiency is 18.2%. Taking into account all this information one can estimate the activity of $^{226}\text{Ra}$ in the CHC crystal: $(0.39^{+0.12}_{-0.13})$ mBq/kg, and that of $^{228}\text{Th}$: $(91^{+25}_{-27})$ $\mu$Bq/kg. Thus, the latter is in good agreement with the result of the time-amplitude analysis.

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$^5$The lower limit is necessary to be safe when distinguishing two consecutive pulse profiles in the same acquisition window.
4 Results on the α decay of naturally occurring Hf isotopes

The spectrum of the α events, selected using the PSD analysis, is presented in Fig. 8; there the energy scale is in α energy having considered the Q.F. model of Ref. [25] as discussed in Section 3.3.

Figure 8: Energy spectrum of the α events selected by PSD from the data of the low-background measurements with the CHC crystal scintillator over 2848 h. The fit of the data by the model built from α decays of $^{238}$U and $^{232}$Th with daughters is shown by blue solid line (individual components of the fit are shown too). The energy scale is in α energy having considered the Q.F. discussed in Section 3.3.

The α energy spectrum below 4 MeV will be discussed later; while the α energy spectrum above 4 MeV has been fitted by using a model which includes the α peaks of $^{232}$Th, of $^{238}$U and of their daughters in order to study these contaminants. Besides this, this analysis is useful to have an additional check of the adopted Q.F. model. Later, we will focus the analysis in the energy range of interest to study the Hf α decays. The equilibrium of the $^{232}$Th and $^{238}$U chains is assumed to be broken in the CHC crystal; therefore, the activities of the following nuclides and related sub-chains (father–last daughter in the following): $^{232}$Th→$^{228}$Ra, $^{228}$Th→$^{208}$Pb and $^{238}$U→$^{234}$U→$^{230}$Th,

6In this case the peak shapes are considered Gaussian to simplify the fit process and to reduce the number of free parameters (also taking into account the relative low number of histogram bins with respect to the number of peaks).

7The equilibrium can be broken in the chains because of the different chemical properties of the nuclides in U/Th chains and of the relatively large half-lives of some nuclides in the chains.
228\textsuperscript{Th}–220\textsuperscript{Ra}, 226\textsuperscript{Ra}–210\textsuperscript{Pb}, and of the sub-chain 210\textsuperscript{Pb}–210\textsuperscript{Bi}–210\textsuperscript{Po}–206\textsuperscript{Pb}, are free parameters of the fit. The energy resolution takes into account the above-mentioned dependence on energy, as measured by calibration. Moreover, the activities of 228\textsuperscript{Th} and 226\textsuperscript{Ra} were fixed to results of the time-amplitude and of the double pulse (see Sections 3.3 and 3.4) analyses.

Considering Fig. 8 one can identify five $\alpha$ structures associated with the following $\alpha$ peaks \cite{11,12}: (i) $^{216}\textsuperscript{Po}$ ($Q_\alpha = 6906$ keV); (ii) $^{218}\textsuperscript{Po}$ ($Q_\alpha = 6115$ keV) + $^{212}\textsuperscript{Bi}$ ($Q_\alpha = 6207$ keV) + $^{220}\textsuperscript{Rn}$ ($Q_\alpha = 6405$ keV); (iii) $^{210}\textsuperscript{Po}$ ($Q_\alpha = 5407$ keV) + $^{228}\textsuperscript{Th}$ ($Q_\alpha = 5520$ keV) + $^{222}\textsuperscript{Rn}$ ($Q_\alpha = 5590$ keV) + $^{224}\textsuperscript{Ra}$ ($Q_\alpha = 5789$ keV); (iv) $^{234}\textsuperscript{U}$ ($Q_\alpha = 4858$ keV) + $^{230}\textsuperscript{Th}$ ($Q_\alpha = 4770$ keV) + $^{226}\textsuperscript{Ra}$ ($Q_\alpha = 4871$ keV); (v) $^{232}\textsuperscript{Th}$ ($Q_\alpha = 4082$ keV) + $^{238}\textsuperscript{U}$ ($Q_\alpha = 4270$ keV). The fit result, in the energy interval (3.8–7.8) MeV, is shown in Fig. 8. The fit gives the activities of $^{238}\textsuperscript{U}$, $^{210}\textsuperscript{Po}$, $^{232}\textsuperscript{Th}$, $^{226}\textsuperscript{Ra}$ and $^{228}\textsuperscript{Th}$ in the crystal, while – because of a not sufficient separation between the $^{234}\textsuperscript{U}$ and $^{230}\textsuperscript{Th}$ peaks – one can estimate only the total activity of $^{234}\textsuperscript{U}$ and $^{230}\textsuperscript{Th}$; the values are listed in Table 6. Considering all $\alpha$ events, the total internal $\alpha$ activity in the CHC crystal is at the level of 7.8(3) mBq/kg.

When adopting the claimed half-life of Ref. \cite{6} (also reported in Table 1) for the $^{174}\textsuperscript{Hf}$ $\alpha$ decay, the expected number of events – within 2848 h of data taking with the used CHC crystal – is about 1100 counts. Thus, considering that the measured $\alpha$ events are 553(23) in total, even ascribing all of them to $^{174}\textsuperscript{Hf}$ $\alpha$ decay (despite the analysis reported above), one can safely rule out the result of Ref. \cite{6}; in fact, even in such an unlike hypothesis, the $T_{1/2}$ value derived from the present experimental data would be $4.01(17) \times 10^{15}$ y,
i.e. is about 4.5 $\sigma$ far from the value of Ref. [6]: $T_{1/2} = 2.0(4) \times 10^{15}$. Thus, the $T_{1/2}$ value given in Ref. [6] is safely rejected. Let us now perform a more refined determination of the $T_{1/2}$ value of the $^{174}$Hf $\alpha$ decay supported by our data.

Since the $Q_\alpha$ of $^{174}$Hf is 2494.5(2.3) keV, the most problematic dangerous radionuclides – considering their natural isotopic abundances, their $Q_\alpha$ values and their half-lives – in the search for the $\alpha$ decay of $^{174}$Hf are: $^{144}$Nd, $^{147}$Sm, $^{148}$Sm, $^{152}$Gd, $^{186}$Os, $^{190}$Pt, $^{209}$Bi. Their main properties are listed in Table 7. In particular, $^{190}$Pt and $^{209}$Bi could contribute in the energy region around 3 MeV, while $^{144}$Nd, $^{147}$Sm, $^{148}$Sm, $^{152}$Gd and $^{186}$Os contribute to the energy region of interest. Taking into account the measured contaminants in Table 4, the expected counts for all isotopes are reported in Table 7. Thus, only $^{147}$Sm may give a significant effect with 36(6) counts.

The background model in the energy interval (1.1 – 3.9) MeV, where the $^{174}$Hf $\alpha$ decay is expected, is made by an exponential function (to describe residual $\beta/\gamma$ events), and suitable asym–Gaussian functions to describe the $\alpha$ decay of $^{147}$Sm ($Q_\alpha = 2311.2(10)$ keV), $^{174}$Hf ($Q_\alpha = 2494.5(2.3)$ keV) and the events in the energy range (3.0-3.9) MeV. These events have been assumed to be degraded $\alpha$ events from possible surface and other contamination. The FWHM of the peaks was fixed taking into account the dependence on energy as reported in Section 2. For the case of asym–Gaussian used to model the

| Nuclide  | $Q_\alpha$ (keV) | $T_{1/2}$ (y) | Isotopic Abundance (%) | $E_\alpha$ (keV) | Expected Counts |
|----------|-----------------|---------------|------------------------|-----------------|-----------------|
| $^{144}$Nd | 1906.4(17) | 2.29(16)$\times 10^{15}$ | 23.798(19) | 1854.8(17) | <0.007 |
| $^{147}$Sm | 2311.2(10) | 1.060(11)$\times 10^{11}$ | 15.00(14) | 2249.9(10) | 36(6) |
| $^{148}$Sm | 1986.9(10) | 7(3)$\times 10^{15}$ | 11.25(9) | 1934.6(10) | 3.6(1)$\times 10^{-4}$ |
| $^{152}$Gd | 2204.4(10) | 1.08(8)$\times 10^{14}$ | 0.20(3) | 2147.8(10) | <1$\times 10^{-3}$ |
| $^{186}$Os | 2820.4(13) | 2.0(11)$\times 10^{15}$ | 1.59(64) | 2761.0(13) | <6$\times 10^{-4}$ |
| $^{190}$Pt | 3252.6(6) | 6.5(3)$\times 10^{11}$ | 0.012(2) | 3185.5(6) | <0.1 |
| $^{209}$Bi | 3137.3(8) | 2.01(8)$\times 10^{19}$ | 100 | 3078.4(8) | <4$\times 10^{-7}$ |
degraded α events the left tail of the function is used as free parameter, instead σ is limited by the FWHM energy dependence.

Figure 9: Energy spectrum of α events selected by the pulse-shape discrimination from the data of low-background measurements with the CHC crystal scintillator over 2848 h. The energy scale is in α energy having considered the Q.F. discussed in Section 3.3 (left) The fit of the data by the model built from α decays of the 174Hf (red line) and of the 147Sm plus degraded alpha particles and an exponential function (to describe residual β/γ events) is shown (blue solid line online). The yellow band is the background model with respect to the the signal of the α decay of the 174Hf isotope. (right) The fit of the data by a modified model similar the previous one but considering just one peak (instead of two) in the energy (2.2 – 2.6 ) MeV.

The fit, in the range (1.1 – 3.9) MeV, provides the area of the peak searched for with $\chi^2/n.d.f.=0.87$ (P-value = 38.7%) and 31.7(5.6) events. The counts for the peak near 2.3 MeV are 29.5(5.4) in very good agreement with that expected for 147Sm reported in Table 7. The Q$_\alpha$ of 147Sm and 174Hf determined by the fit procedure show a slight variation (for both in the same direction) of the mean value ($\sim$ 5%) consistent with the uncertainty of the adopted Q.F. model discussed in Section 3.3. In addition to the $\chi^2$ test, another independent statistical test has been applied: the run test (see e.g. Ref. [26]); it verifies the hypothesis that the positive (above the fit value) and negative (under the fit value) data points are randomly distributed. The lower and upper tail probabilities obtained by the run test are 94% and 12% respectively.

The data in the range (2–3) MeV could be explained in principle by one single peak. In order to study this possibility we performed a fit of same data
as before, but considering only one peak in the energy (2 – 3) MeV instead of two (see Fig. 9–right); this fit yields a $\chi^2$ probability of 1.7.

To summarize, the analysis support that the data are statistically in good agreement with the assumed model, in particular with the assumptions of signals potentially due to $^{147}$Sm and $^{174}$Hf $\alpha$ decays (first and second peak in Fig. 9–left respectively). To compute the half-life we use the following formula:

$$T_{1/2} = \ln 2 \cdot N \cdot \epsilon \cdot t / S,$$

where: i) $N$ is the number of potentially $\alpha$ unstable nuclei; ii) $\epsilon$ is the PSD efficiency that corresponds to 99% (see above); iii) $t$ is the measurement time; iv) $S$ is the number of events of the effect searched for. According to all this, the $T_{1/2}$ value for the $\alpha$ decay of $^{174}$Hf is:

$$T_{1/2} = (7.0 \pm 1.2) \times 10^{16} \text{ y}$$

An attempt to improve the experimental sensitivity for $^{174}$Hf, $^{176}$Hf, $^{177}$Hf, $^{178}$Hf, $^{179}$Hf $\alpha$ decay either to the ground state or to the first excited level has been done. The $^{180}$Hf $\alpha$ decay has not been studied due to a too high background in its energy region of interest. The lower limit of half-life is calculated using formula (2) where $S$ is replaced by lim $S$, the number of events of the effect searched for which can be excluded at a given confidence level (in the present work all half-life limits are given with 90% C.L.).

To estimate the lim $S$ counts of the $\alpha$ decay of Hf isotopes to the ground state, the $\alpha$ spectrum, in the range (1.1–3.9) MeV, was fitted by a model composed by the global fit of Fig. 9–left plus an asym–Gaussian function for the signal searched for and taking into account the $Q_\alpha$ of the transition (see Table 1). Table 8 reports the respective counts (all compatible with zero) together with the lim $S$ values calculated according the Feldman-Cousins procedure [27]. For these cases, the detection efficiency is reported in Table 8 and is mostly due to PSD, taking into account that all the $\alpha$’s are fully contained in the CHC detector. The lower limits half-life are also listed. The values span in the range $(0.58 – 3.2) \times 10^{20} \text{ y}$. These are (except for the case of $^{174}$Hf and $^{179}$Hf) the first-achieved lower limits of transitions towards g.s. present in literature.

We reasonably assume that all the $\alpha$’s are fully contained in the CHC detector.
Table 8: Half-life lower limits on α decay of $^{174}$Hf, $^{176}$Hf, $^{177}$Hf, $^{178}$Hf, $^{179}$Hf to the ground state or to the first excited level of relative daughter obtained from analysis of the data recorded with the CHC crystal scintillator in coincidence with the HP-Ge detector. All the limits are given at 90% C.L.

| Nuclide Transition | Parent, Daughter Nuclei | Energy Level (keV) | Efficiency (ε) (%) | Counts | lim S | $T_{1/2}$ Limit (y) |
|--------------------|--------------------------|--------------------|--------------------|--------|------|---------------------|
| $^{174}$Hf $\rightarrow$ $^{170}$Yb | $0^+ \rightarrow 2^+$ | 84.3 | 0.11 | 0 | 2.30 | $1.1 \times 10^{15}$ |
| $^{176}$Hf $\rightarrow$ $^{172}$Yb | $0^+ \rightarrow 0^+$, $0^+ \rightarrow 2^+$ | 78.7 | 0.06 | 0 | 2.30 | $9.3 \times 10^{19}$, $1.8 \times 10^{16}$ |
| $^{177}$Hf $\rightarrow$ $^{173}$Yb | $7/2^- \rightarrow 5/2^-$, $7/2^- \rightarrow 7/2^-$ | 99 | 0 | $-4.4 \pm 2.1$ | 0.80 | $3.2 \times 10^{20}$, $7.5 \times 10^{16}$ |
| $^{178}$Hf $\rightarrow$ $^{174}$Yb | $0^+ \rightarrow 0^+$, $0^+ \rightarrow 2^+$ | 76.5 | 0.04 | 0 | 2.30 | $5.8 \times 10^{19}$, $6.9 \times 10^{16}$ |
| $^{179}$Hf $\rightarrow$ $^{175}$Yb | $9/2^+ \rightarrow 7/2^+$, $9/2^+ \rightarrow 9/2^+$ | 104.5 | 0.65 | 0 | 2.30 | $2.5 \times 10^{20}$, $5.5 \times 10^{17}$ |

Table 9: Half-lives on the α decay of Hf isotopes measured in this work in comparison with previous measurements (when possible) and with the theoretical predictions. All the limits are given at 90% C.L.

| Nuclide Transition | Parent, Daughter Nuclei and its Energy Level (keV) | Experimental present work | Theoretical Values | $T_{1/2}$ Limit (y) |
|--------------------|-------------------------------------------------|--------------------------|--------------------|---------------------|
| $^{174}$Hf $\rightarrow$ $^{170}$Yb | $0^+ \rightarrow 0^+$, g.s. $0^+ \rightarrow 2^+$, 84.3 | $7.0 \pm 1.2 \times 10^{16}$ | $6.5 \times 10^{16}$ | $3.4 \times 10^{16}$ |
| $^{176}$Hf $\rightarrow$ $^{172}$Yb | $0^+ \rightarrow 0^+$, g.s. $0^+ \rightarrow 2^+$, 78.7 | $9.3 \times 10^{13}$ | $3.0 \times 10^{15}$ | $1.3 \times 10^{15}$ |
| $^{177}$Hf $\rightarrow$ $^{173}$Yb | $7/2^- \rightarrow 5/2^-$, g.s. $7/2^- \rightarrow 7/2^-$, 86.6 | $3.2 \times 10^{10}$ | $1.3 \times 10^{13}$ | $4.9 \times 10^{9}$ |
| $^{178}$Hf $\rightarrow$ $^{174}$Yb | $0^+ \rightarrow 0^+$, g.s. $0^+ \rightarrow 2^+$, 76.5 | $5.8 \times 10^{13}$ | $2.0 \times 10^{17}$ | $7.1 \times 10^{11}$ |
| $^{179}$Hf $\rightarrow$ $^{175}$Yb | $9/2^+ \rightarrow 7/2^+$, g.s. $9/2^+ \rightarrow 9/2^+$, 104.5 | $2.5 \times 10^{13}$ | $2.2 \times 10^{13}$ | $4.7 \times 10^{10}$ |
| $^{180}$Hf $\rightarrow$ $^{186}$Yb | $9/2^+ \rightarrow 7/2^+$, g.s. $9/2^+ \rightarrow 9/2^+$, 104.5 | $6.4 \times 10^{13}$ | $2.2 \times 10^{13}$ | $4.1 \times 10^{10}$ |

To study the α decay of Hf isotopes to the first excited level, the emitted γ-rays detected by the HP-Ge detector in coincidence with the α energy released in the CHC have been studied. No signal in coincidence was detected,
thus, 2.30 counts at 90% C.L. have been considered as lim S. In Table 8 the detection efficiencies for the coincidences in these decay channels have been estimated by simulating the experiment with EGS4 code \[28\] and including the PSD efficiency for the $\alpha$ detection; the $T_{1/2}$ limits are spanning in the range $10^{15}$–$10^{17}$ y. All the results obtained, in comparison with previous measurements and with theoretical predictions, are summarized in Table 9. It is worth to note that potentially more stringent limits on such processes, than the caution ones given above, could be reached studying just the alpha spectrum acquired with the CHC detector and exploiting Monte Carlo techniques.

5 Conclusions

To study the $\alpha$ decay of naturally occurring hafnium to the ground state and the first excited state a CHC crystal scintillator was used in coincidence with a HP-Ge detector in 2848 h of live time. The results rules out the $T_{1/2}$ value of the $\alpha$ decay of $^{174}$Hf given in Ref. \[6\]. In particular, we found that the $\alpha$ decay of $^{174}$Hf to the ground state has been definitely observed with a $T_{1/2} = (7.0 \pm 1.2) \times 10^{16}$ y. This value is in good agreement with the theoretical predictions reported in Table 9.

No signal was detected for $\alpha$ decay of $^{174}$Hf to the first excited state and for $\alpha$ decay of $^{176}$Hf, $^{177}$Hf, $^{178}$Hf, $^{179}$Hf either to the ground state or to the first excited level of daughter nuclides. The derived lower limits of the half-life for these decays are reported in Table 8. In particular, the lower limits for the transitions of $^{176}$Hf $\rightarrow$ $^{172}$Yb ($0^+ \rightarrow 0^+$) and $^{177}$Hf $\rightarrow$ $^{173}$Yb ($7/2^- \rightarrow 5/2^-$) are very close to the theoretical predictions and are (except for the cases of $^{174}$Hf and $^{179}$Hf) the first lower limits of transition between g.s. (see Table 9).

Except for the $\alpha$ decay of $^{174}$Hf for the transition $0^+ \rightarrow 2^+$, all other limits ($\sim 10^{16}$–$10^{20}$ y) are very far from the theoretical predictions.

To improve the sensitivity by more than one order of magnitude compared to the present measurements, giving the possibility to observe the alpha decay $^{176}$Hf $\rightarrow$ $^{172}$Yb ($0^+ \rightarrow 0^+$, g.s.), a larger CHC crystal $\sim 100$ g (or the enrichment of the CHC crystal with the Hf isotope of interest) could be used and the $^{147}$Sm contamination reduced by a factor $\simeq 10$. Moreover, in a future low-background experiment with CHC detectors, it is necessary to reduce as much as possible the amount of $^{137}$Cs/$^{134}$Cs.
We have also evaluated an average quenching factor for alpha particles, modelled according to the prescription of Ref. [25], and reported in Fig. 7; it varies in the range 0.3–0.4. Dedicated measurements, with α sources and calibrated absorbers, possibly in vacuum, are needed to better study the Q.F.

Finally, the CHC crystal scintillator shows a very interesting PSD capability as shown in Fig. 5 and low U/Th contamination of few mBq/kg.

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