Radiological Impact of Building Material: Characterization of a Village Entirely Built out of Stone in Tuscany, Italy

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Abstract. Tuscany, with its mixed geology, offers a great variety of stones that are used to build entire villages. In this paper, two of these building materials are considered: Rosso Ammonitico and Pietra Serena. In particular, the activity concentration of ²²⁶⁹Ra, ²³²⁵Th and ⁴⁰⁰K have been analysed in order to estimate the value of the gamma index. In addition to this, the X-ray fluorescence spectroscopy has been carried out to obtain a chemical characterization of the stones. Although these kind of stones are not subjected to radiological characterization, the approach used was the one reported in Radiation Protection 112, also implemented in the Italian Legislative Decree 101/2020, because of their lithographical peculiarity and their employment in construction.

1. Introduction

Gamma radiation emitters represent a source of external radiation both indoor and outdoor. Principally, environmental radioactivity constitutes the biggest portion of the external radiation dose absorbed by the world population [1,2] and the most important radioactive elements are ²³⁵⁸U, ²³²⁵Th and their progeny, and ⁴⁰⁰K. In particular, the last element can be found in soil and rocks, therefore its distribution throughout the territory highly depends on the geology of the region of interest [3-5]. The most abundant element of the ²³⁵⁸U series found in soil is ²²²⁶Rn, a radioactive gas characterized by a half-life of 3.8 days. Radon constitutes the highest quota of internal exposure since, as well as its progeny (²¹⁸Po, ²¹⁴⁹Pb, ²¹⁴⁰Bi and ²¹⁴⁰Po), emits alpha particles that can have a negative impact on health, as DNA damages heavily depend on the track of the particles [6-8]. Since people’s lifetime is almost completely spent indoors [9], the analysis of activity concentration of radionuclides found in building materials (BM) is considered crucial from a radiological standpoint. In fact, while several studies have investigated indoor air quality [10-13], many others have focused their
attention on the radionuclides in BM. For example, our team is working on a characterization campaign of rural villages that are completely built with typical stones of the Italian territory [14-16]. In this paper, the activity concentration of radionuclides found in Rosso Ammonitico and Pietra Serena stones are investigated. These two types of rocks, characteristic of the northern part of the Tuscany Region in Italy, are used as a BM since the Etruscan-Roman period [17]. Tuscany, a region of central Italy, is characterized by peculiar geology, ranging from the Apuan Alps to the hills of the Crete Senesi. The local villages reflect the complexity of the lithological types found in this territory since each of them has a unique architecture, style, and local BM [18].

BM were taken into consideration by the European Commission for the first time in 1999 when the Radiation Protection 112 (RP112) [19] was published. In this document, the gamma index (I_{γ}), a tool to assess the health risk due to the exposure of the radionuclides found in these materials, is first mentioned. The norm states that the value of this index must be lower than 1 for the material to be considered safe to use in a structural context. Years later, in 2013, the RP112 document will constitute the base for the European Directive 59/2013/EURATOM [20], in which there is a first characterization of the BM, listed in Annex XIII (Table 1).

### Table 1. List of types of BMs of interest for the content of gamma-emitting radionuclides reported in annex XIII [20].

| Origin of building materials | Types of building materials |
|-----------------------------|-----------------------------|
| Natural materials           | Alum-shale. |
|                             | Building materials or additives of natural igneous origin, such as: |
|                             | granitoides (such as granites, syenite and orthogneiss), porphyries; tuff; pozzolana (pozzolanic ash); lava |
| Materials incorporating residues from industries processing naturally-occurring radioactive material | fly ash; |
|                             | phosphogypsum; |
|                             | phosphorus slag; |
|                             | tin slag; |
|                             | copper slag; |
|                             | red mud (residue from aluminium production); |
|                             | residues from steel production |

Additionally, the Directive offers a reference level to limit human exposure and assess health hazards through the calculation of the effective dose given by the measured radionuclides. The importance of these investigations is confirmed by documents that offer a database of all the radiological characteristics of the BM, such as the ISTISAN report 17/36 [21], which contains a list of the activity concentration values of different radionuclides found in about 23,000 samples, among which bulk materials and their elements, and other materials employed in several European Countries.

From the Italian regulatory standpoint, the Legislative Decree 101/2020, Article 29 [22], implements the European Directive 59/2013/EURATOM and provides the reference level to limit the risk of exposure to radionuclides found in different BM. Furthermore, the Italian Decree adopts, in Annex II, the same list of the BM of Directive 59/2013/EURATOM.

Although the stones analysed in this paper are not listed in this annex, the investigation of the radionuclides found in them is incredibly interesting. In fact, as previously mentioned, both Rosso Ammonitico and Pietra Serena are employed to build entire villages. Moreover, these stones are typical of a region with complex lithography, which characterization can be considered fundamental to add new materials to those already recorded in the ISTISAN report. Therefore, their analysis has an elevated resonance from a radiological point of view.

In this work, the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K for both stones have been estimated to calculate the I_{γ}. In addition to this, X-ray fluorescence spectroscopy has been carried out to obtain the chemical-physical composition of the samples in question.
2. Materials and methods

2.1. Sampling area
The stones analysed in this paper are the Rosso Ammonitico (Figure 1a) and the Pietra Serena (Figure 1b). The former is a limestone, commonly employed as a decorative stone, that can be found in the Tuscan Nappe in the northern part of the Italian region. This material was also used as a BM to create some villages. For instance, the village of Sassorosso, which literally means “red stone”, is completely built from blocks of Rosso Ammonitico [23]. This limestone is characterised by a fine grain of reddish colour [17]. Since it has marine origins, this nodular stone is full of ammonite fossils and its durability depends on the presence of the gaps between the nodules [24]. Conversely, Pietra Serena is a quartz-feldspar sandstone that can be found along the Apennine ridge. Used exclusively as a BM in many Tuscan cities, such as Arezzo, Cortona, and Fiesole, this stone is characterized by grains of heterogeneous composition (quartz, igneous stones, and biotite) and a clay matrix made of chlorite, illite and kaolinite [25-29]. Given the roughness of its surface, the Pietra Serena, which means sky-coloured stone, is also employed in the street paving of most villages in Tuscany. Nevertheless, throughout the sixteenth century, this material has been extensively used for ornament, given its particular grey-white colour [17].

Figure 1. a) Rosso ammonitico stone, b) Pietra Serena stone

2.2. Samples preparation
After their collection, the samples were prepared accordingly the UNI EN ISO 18589-2:2015 [30]. The stones were reduced to fine powder by grinding, using PM 100 Retsch, and sieving. Subsequently, the powder has been dried in the DIGITRONIC Selecta 2005141 oven at 105°C for a duration of two hours and the powered samples have been homogenised. Lastly, the obtained material has been weighted and airtight closed into a Marinelli Becker for 30 days to let the $^{226}$Ra reach the secular equilibrium with its daughters, effectively ensuring a correct measurement [14].

2.3. XRF spectroscopy measurements
The X-ray fluorescence spectroscopy (XRF) is the chemical-physical analysis of the stones considered in this study. It was performed using a portable device composed of:

- Rhodium anode X-ray generator (V=40 kV, I=0.2 mA),
- FAST SDD® X-ray detector,
- Electronic chain that supplies both power and signal processing.

The exposure time for the experiment was 300 s and the detector used in this study was composed of an 8 mm beryllium window, coupled with helium flushing, that assured the detection of light elements [31]. The quantitative analyses of the measurements, carried out at INFN CH-Net infrastructure, were performed with the software bAxil™.
2.4. Gamma spectroscopy
The gamma spectroscopy has been carried out using the High Purity Germanium (HPGe) detector, produced by the ORTEC company, composed of a beryllium window characterized by a 48% of relative efficiency. This detector presents an energy resolution of 2.16 keV for 1.33 MeV. The analyses of the spectra, obtained with the ORTEC DSPECT-LF unit and the MCA Emulator Software, were performed with the GammaVision Spectrum Analysis Software. To reduce the background signal given by the external environmental radiation, a lead shield, characterized by a thickness of 10 cm, was placed around the detector. Afterwards, the minimum detectable activity (MDA) has been calculated with a 95% confidence level [32]. The counting time for both the samples and the background radiation was equal to 24 hours to obtain a good statistic and, to accurately study the gamma-spectrum, the transition energies for $^{238}$U, $^{232}$Th, and $^{40}$K were estimated. The full energy peaks employed in the determination of the activity concentrations of the samples were: 63.2 keV and 92.5 keV for $^{234}$Th ($^{238}$U), 186 keV for $^{226}$Ra, 46.5 keV for $^{210}$Pb ($^{238}$U), 911.1 keV and 968.9 keV for $^{228}$Ac ($^{232}$Th), and 1461 keV for $^{40}$K [16].

The standard error was calculated considering the following elements:

- The error related to the counting,
- The gamma emission probability,
- Energy and efficiency calibration,
- Mass of the sample.

2.5. Gamma index estimation
The estimation of the gamma-index ($I_\gamma$), which was deemed necessary in BM [33,34], was carried out accordingly to the Directive 2013/59/EURATOM [21], implemented by the Italian Legislative Decree 101/2020 [22], using the following equation:

$$C_{Ra}/300 \text{ Bq kg}^{-1} + C_{Th}/200 \text{ Bq kg}^{-1} + C_{K}/3000 \text{ Bq kg}^{-1}$$  \hspace{1cm} (1)

Where $C_{Ra}$, $C_{Th}$, and $C_{K}$ indicate respectively the activity concentration of $^{226}$Ra, $^{232}$Th, and $^{40}$K in the BM.

3. Results and conclusion
3.1. XRF measurements
The chemical composition of the samples was obtained through the XRF analyses, and the results are reported in the following table (Table 2).

|       | MDL | Rosso Ammonitico | Pietra Serena |
|-------|-----|------------------|---------------|
| Al$_2$O$_3$ | 5   | 12 ± 2           | 5 ± 2         |
| SiO$_2$   | 2   | 42 ± 2           | 42 ± 2        |
| K$_2$O    | 0.2 | 2.75 ± 0.07      | 0.50 ± 0.03   |
| CaO       | 0.1 | 34.4 ± 0.2       | 40 ± 0.2      |
| TiO$_2$   | 300 | 0.91 ± 0.04      | 0.32 ± 0.02   |
| MnO       | 150 | 0.117 ± 0.007    | 0.29 ± 0.01   |
| Fe$_2$O$_3$ | 0.01 | 8.22 ± 0.04     | 11.4 ± 0.05   |
| Co$_3$O$_2$ | 10  | 26 ± 4          | 31 ± 3       |
| NiO       | 40  | 77 ± 11          | 71 ± 10      |
| ZnO       | 60  | 142 ± 22         | 293 ± 25     |
| As$_2$O$_3$ | 50  | n.d.            | 61 ± 17     |
Table 3. Activity concentration of the radionuclides of interest and gamma index

| Radionuclide | Activity Concentration (Bq/kg) | $I_\gamma$ |
|--------------|--------------------------------|------------|
| $^{226}\text{Ra}$ | 17.3 ± 1.4 | 113.3 ± 6.6 | 487.4 ± 19.5 | 0.78 ± 0.04 |
| $^{232}\text{Th}$ | 2.8 ± 0.6 | 14.91 ± 2.07 | 8.3 ± 0.8 | 0.09 ± 0.01 |

Table 4. Activity concentrations of building materials listed in the ISTISAN report [21].

| Building Material | $^{226}\text{Ra}$ (Bq/kg) | Mean | $^{232}\text{Th}$ (Bq/kg) | Mean | $^{40}\text{K}$ (Bq/kg) | Mean |
|-------------------|---------------------------|------|--------------------------|------|------------------------|------|
| Rosso Ammonitico  | Limestone_1                | 11   | 2                        | 22   |
|                   | Limestone_2                | 65   | 6                        | 46   |
|                   | Limestone_3                | 76   | 8                        | 47   |
| Pietra Serena     | Sandstone_1               | 33   | 32                       | 530  |
|                   | Sandstone_2               | 14   | 13                       | 230  |

As it is possible to observe, some of the activity concentrations of the examined stones exceed the reference values indicated in Table 4. In particular, the Rosso Ammonitico stone shows high values of both $^{226}\text{Ra}$ and $^{40}\text{K}$, while Pietra Serena is characterized by extremely low levels of radioactivity. One of the most probable causes is that, although they are similar in nature, the analysed stone and the ones listed in the report have different origins. In fact, the analysis of the radioactive content in these BM must be contextualized paying particular attention to the geological setting of the Region of interest. Although the ISTISAN report [21] contains a plethora of different information on the BM commonly used in the European Union, it severely lacks the data on stones used in several sampling areas, such as the Pietra Serena. Particularly interesting is the study of the Sassorosso village, since, as previously mentioned, it is completely built out of the Rosso Ammonitico. According to the calculated activity concentrations of the radionuclides found in this stone, the radioactivity level is way above the reference value, effectively marking this zone as an alert from the radiological standpoint. Conclusion The study of the concentration activity of radionuclides that can be found in BM is becoming more and more important from the radiation protection point of view. In fact, the guideline for this analysis is elucidated in both the RP112 [19] and the European Directive 2013/59/EURATOM [20]. The stones analysed in this paper, Rosso Ammonitico and Pietra Serena, are both found in the northern part of the Tuscany Region in Italy. Although these stones are not used just for decoration but also as BM, they
are not listed in Annex II of the Italian Decree 101/2020, where all the materials for which the evaluation of the $I_\gamma$ is deemed mandatory are recorded [22]. However, even if the $I_\gamma$ values are not considered alarming for the safety of the population, the study of the radioactivity levels of the collected samples is noteworthy, since they belong to rural villages entirely built with these fascinating materials. In fact, there are other studies that have deepened the analysis of the activity concentration of radionuclides in peculiar BM with which villages have been built throughout Italy, to offer a mapping of the territory [14-16].

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