

# Thermoluminescence dating of historical buildings as a tool for assessing natural radioactivity risk

Rosaria Galvagno, Alessia D'Anna, Anna Maria Gueli, Giuseppe Politi, Giuseppe Stella

*Department of Physics and Astronomy "E. Majorana", University of Catania, Via S. Sofia 64, 95123 Catania, Italy, [rosaria.galvagno@phd.unict.it](mailto:rosaria.galvagno@phd.unict.it); [alessia.danna@phd.unict.it](mailto:alessia.danna@phd.unict.it) <mailto:anna.gueli@unict.it>; [giuseppe.politi@unict.it](mailto:giuseppe.politi@unict.it); [giuseppe.stella@unict.it](mailto:giuseppe.stella@unict.it)*

**Abstract** – The absolute dating of historical buildings through thermally stimulated luminescence techniques involves also in situ and extra situ dosimetry techniques. The age calculation for brick sampled is obtained from the ratio between the absorbed dose through luminescence measurements and the annual dose through the U, Th and K contents and the environmental dose values at the sampling site.

The radioactive contents of the sample and the environmental dose values can be used not only for dating purposes, but also to make assessments related to the level of natural radioactivity present in building materials in the case of historic buildings. The present study considered available data of samples from six sites in eastern Sicily. The analyses performed revealed a correlation between the environmental dose and the latitude of the sites from which the samples came and between the K and Th contents.

## I. INTRODUCTION

Radiometric dating of a building by stimulated luminescence is currently based on the chronology obtained through Thermoluminescence (TL) and/or Optically Stimulated Luminescence (OSL) dating of bricks.

Referring to detailed literature regarding the TL dating technique the general equation used to determine the age, time from the last firing of the artefact until today, is the ratio between the Equivalent Dose (ED) and the annual Dose Rate (DR) [1].

The ED is the total dose accumulated from the last firing of terracotta samples, measured using emitted luminescence signals, while the DR is the quantity of the dose absorbed in one year and its value is determined by in situ and extra situ radioactivity measurements for evaluation of internal and external dose contribution.

In particular, for internal dose contribution evaluation, are determined the bricks radioactive contents of the principal Naturally Occurring Radioactive Materials (NORM), found in all the building materials on the earth

surface [2, 3, 4], as the natural decay series of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and of the  $^{40}\text{K}$  radioactive isotope. In each considered radioactive chain, unstable nuclei decay by emitting  $\alpha$ ,  $\beta$  or  $\gamma$  radiation until a stable lead is reached [5, 6]. External dose contribution due to environmental and cosmic dose rates, is obtained by in situ measurements using portable gamma spectrometer and/or Thermoluminescence Dosimeters (TLDs) [7].

Considering that all building materials contain radionuclides, and they are one of the most important sources of radiation to humans [8], literature data on luminescence dating can now also be exploited to provide information on the radioactive content of the samples analysed (bricks) and the environmental exposure data related to the context in which these samples are found. The information on the level of natural radioactivity content of building materials employed in the field of cultural heritage is useful for assessing whether there is a potential radiation risk in buildings constructed from these materials.

The present work is based on available data from thermoluminescence dating of historical buildings in eastern Sicily to assess both the environmental dose distribution and the U, Th and K contents of the analysed samples.

## II. MATERIALS AND METHODS

For the present work, experimental data from 6 different historical buildings in Eastern Sicily were chosen. In particular, the environmental dose and natural radioactive contents data of 77 brick samples from the Byzantine Cube churches of Santo Stefano in Santa Venerina (Catania) [9], Torre Cuba in Fontane Bianche (Syracuse) [9], Santa Domenica in Castiglione di Sicilia (Messina) [10] and Cuba of Malvagna in Malvagna (Messina) [9] were used, together with data from two further architectural structures in the city of Catania: Indirizzo Bath [11-13] and the Church of Sant'Agata La Vetere [14].

Details on the sampling sites, their exact geographical location, the considered number of samples, their age, and the references of the works from which the data were taken

are contained in Table 1 and in the next paragraph.

Table 1. Details of the sites from which the dated brick samples were taken.

Site	Location (Latitude)*	Nr of samples	Data (century)	Ref.
Santo Stefano	37.7°	3	V	[9]
		6	VIII	
		3	XI	
Torre Cuba	36.9°	3	II-III	[9]
		7	IV-V	
		2	VIII	
Santa Domenica	37.8°	4	XI-XII	[10]
		8	XIV-XV	
		1	XVI	
Cuba of Malvagna	37.9°	1	II	[9]
		3	VIII-X	
		3	XIV-XV	
Indirizzo Bath	37.5°	2	IV-V	[11-13]
		3	VII	
		5	XIV-XV	
		6	XVII	
Sant'Agata La Vetere	37.5°	9	V	[14]
		5	XIV	
		2	XVIII	

\*Only latitude is given in the table since longitude value of 15.1° is equal for all sites.

#### A. Sampling sites: Cube of Eastern Sicily, Roman Indirizzo Bath and Church of Sant'Agata La Vetere

Data from different types of architectural structures of historical and artistic interest were selected for the present work: the Cube and the Indirizzo Bath in Catania.

The Cubes, widely spread in the Eastern area of Sicily, are small buildings dating back to the early Middle Ages [15]. They are characterized by a recurring architectural feature, consisting of a central quadrangular room with apses on three sides of the structure. The characteristic presence of three apses gives such structures the name "tricora" or "triconco."

The central area of these structures is always covered by a dome, with the ritual function of recalling the vault of the skies.

The tricora plan owes its origins to pagan architecture: it turns out to be used in many Roman-era buildings as a bathhouse, mausoleum, or funerary building. Beginning in the 4th century, this type of structure is employed in Christian architecture as a place of worship, baptistry, or as a burial chapel.

The Etna area and the southeastern corner of Sicily turn out to be rich in surviving examples of these architectural structures, surely belonging to a larger set of buildings now lost.

In the Etna area one finds the Cuba of Santo Stefano, now in a ruined condition, while in the areas bordering the Alcantara valley are the Cuba of Malvagna and the Cuba of Santa Domenica, both of which can currently be visited, being in good structural condition.

In the northern surroundings of Syracuse, in the locality of Ognina, near Fontane Bianche, there is Torre Cuba, where it is possible to visit the underground room where the Byzantine Basilica is located.

The Indirizzo Baths are a thermal complex in the city of Catania. It represents the best preserved Roman thermal baths anywhere in Sicily and one of the best preserved in the Roman Empire [11].

The Church of Sant'Agata La Vetere is one of the oldest in the City of Catania. It has been destroyed and rebuilt several times due to eruptions and earthquakes that have affected the city. The structure is founded on the ruins of the Roman proconsul's palace and has undergone remodeling in different historical periods.

#### B. NORM concentration values measurement

The internal radioelement concentration of the brick samples was obtained using the Inductive Coupled Plasma Mass Spectrometry (ICP-MS) technique, through which it is possible to obtain information on the contents of <sup>nat</sup>U, <sup>232</sup>Th and <sup>40</sup>K.

#### C. Environmental dose contributions

To obtain the environment gamma dose measured and cosmic radiation coupled with each sampling site, different type of techniques was used. For the sites of Santo Stefano, Torre Cuba, Santa Domenica and Cuba of Malvagna measurements were made using very sensitive TL dosimeters: capsules containing LiF:Mg,Cu,P crystals (GR200A type) were placed in the exact sampling position of the bricks and left in that location for a different number of months.

The capsules used for these measurements were made of copper and were 6 mm thick, so that the contribution of alpha and beta decays of the natural radioisotopes of interest was negligible and only the gamma decay component was detected.

It should be noted that in each used capsules there were three TLD crystal, so that the obtained values were the weighted mean of the three measurements.

For the site Indirizzo Bath gamma measurements were carried out using a portable gamma spectrometer (InSpector™ 1000, Canberra) consisting of a, NaI scintillator coupled with a photomultiplier (PMT).

Only in the case of the Sant'Agata La Vetere Church both

TLDs (GR200A type) and portable gamma spectrometer (InSpector™ 1000, Canberra) were used to perform the environmental dose measurements. The results obtained through the two methodologies were in good agreement. Table 2 summarizes the techniques used, for each site, for the measurement of natural radionuclide concentrations of the sampled bricks and environmental dose assessment.

Table 2. Details on measurement methods of annual dose rate contributions.

Site	NORM concentration measurement	Environmental dose component
Santo Stefano	ICP-MS	TLDs
Torre Cuba	ICP-MS	TLDs
Santa Domenica	ICP-MS	TLDs
Cuba of Malvagna	ICP-MS	TLDs
Indirizzo Bath	ICP-MS	Portable gamma spectrometer
Sant'Agata La Vetere	ICP-MS	TLDs+Portable gamma spectrometer

### III. RESULTS

In Fig.1, the correlation matrix presents the relationships among distinct sample characteristics, including the content of U, Th, and K, the environmental dose, the obtained age of the sample, the latitude of the site, and the sampling location.

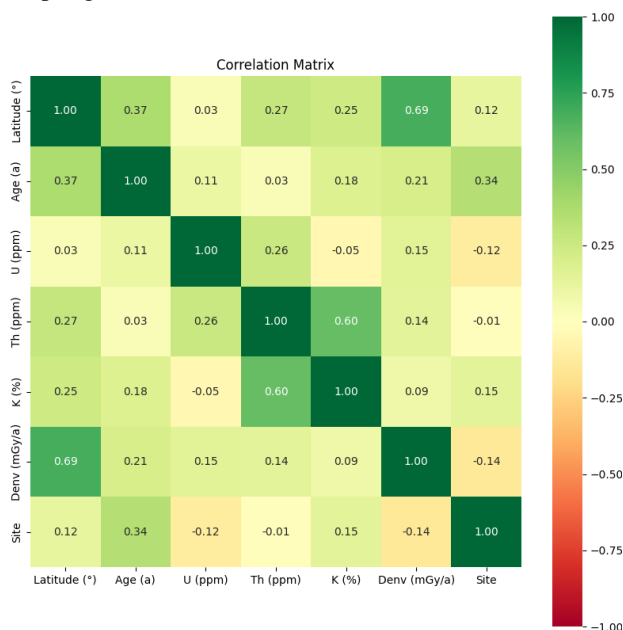


Fig. 1. Correlation matrix illustrating the pairwise correlations between various features within the dataset.

The correlation matrix proves to be a valuable statistical tool, facilitating the examination of the relationships between different features or variables within a dataset.

The correlation matrix displayed in this case employed the Spearman coefficient to calculate the correlations between the features. After excluding the values on the main diagonal, which represent the maximum correlation value of a feature with itself, the features that exhibit the highest correlation are the environmental dose with latitude (0.72) and the thorium content with potassium content (0.57). These correlations indicate a moderately strong relationship between these pairs of features. Conversely, the remaining values in the correlation matrix are considered insignificant, suggesting a lack of substantial correlations among the other variables.

Considering the correlation found, the mean values of the environmental dose of the six sites and the corresponding errors are plotted in a graph, shown in Fig.2, as function of latitude. The environmental dose increases with increasing latitude, always within the experimental error. The composition of the soil and rocks influences this result: in the area near the city of Catania, there is a presence of basaltic rocks originating from the activity of the Mt. Etna volcano, for which a high specific activity of the main NORM was measured compared to the average worldwide values [16].

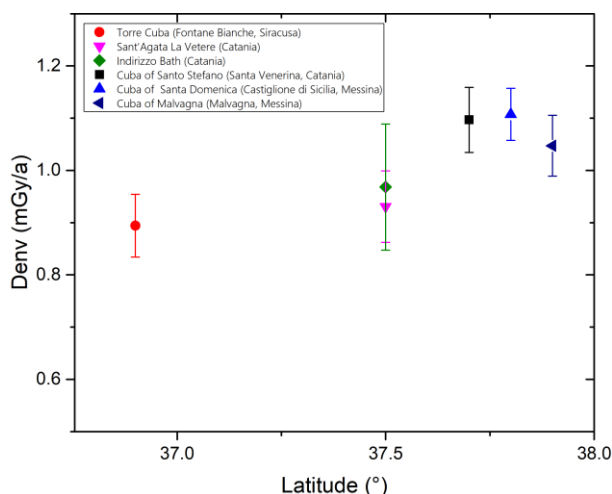


Fig. 2. Graph correlating environmental gamma dose with the site latitude.

At sites further away from Catania, such as Torre Cuba in Fontane Bianche and Cuba di Malvagna in Malvagna, the presence of basaltic rocks decreases and there is a greater composition of calcarenite in the soil. Calcarenite has a specific activity of natural radionuclides that is lower than that of basalt [17].

A Mann-Whitney U-test was performed to determine whether there are statistically significant differences between the environmental doses at the various sites.

Taking into consideration all possible pairs of dose values, p-values were determined. The reference value for this test is 0.05, assuming 95% confidence level. The results are shown in Table 3. In the table, acronyms were given to the locations of the six sites: *SV* stands for Santa Venerina, *FB* for Fontane Bianche, *CS* for Castiglione di Sicilia, *SLV* for Sant'Agata La Vetere, *I* for Indirizzo Bath and *M* for Malvagna.

Table 3. p-values calculated on the environmental doses of the sites.

SV						
FB	<0.05					
CS	0.519	<0.05				
SLV	<0.05	0.222	<0.05			
I	<0.05	0.694	<0.05	0.169		
M	0.328	<0.05	<0.05	<0.05	<0.05	
	SV	FB	CS	SLV	I	M

P-values marked in red are those for which there is no statistically significant difference between the feature under study. From a statistical point of view, the environmental dose values of the Santa Venerina, Malvagna and Castiglione di Sicilia sites appear to belong to the same population, as the p-value suggests that it is possible to confirm the hypothesis of no difference between the groups. The environmental dose of Torre Cuba, Sant'Agata la Vetere and Indirizzo Bath are, likewise, indistinguishable from a statistical point of view.

The results obtained by means of the U-test corroborate the trend of the experimental data, which is shown in Fig.2. Considering the averages and the corresponding experimental errors, the data are grouped into two. In the first group we find data from the Fontane Bianche site and the two Catania sites, while in the second group we find the Santa Venerina, Santa Domenica and Malvagna sites.

A further analysis was carried out concerning the correlation between potassium content and thorium content in the samples analysed from the different sites. The black curve in Fig.3 shows the relationship between the concentration of K and Th, which is found to vary within a narrow range, maintaining an overall constant trend. The fact that the K/Th ratio is constant means that as the K concentration increases, the Th concentration increases, as predicted by the positive correlation value between the two features.

#### IV. CONCLUSIONS

The objective of this study is to make assessments and draw possible conclusions about environmental dose trends in buildings of historical and artistic interest in the

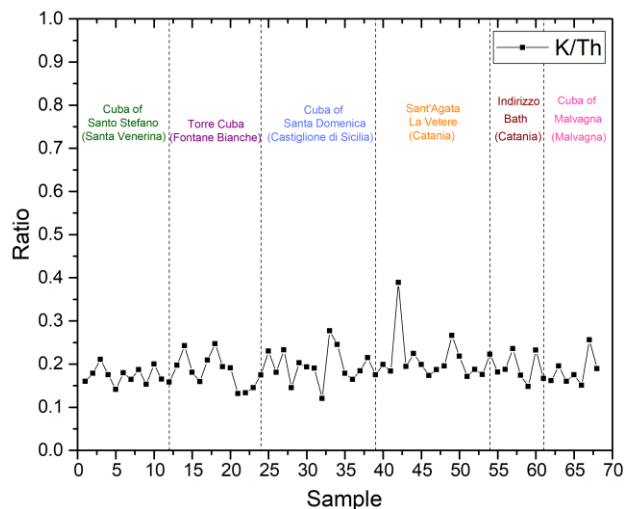


Fig. 3. K/Th ratio values for samples from the six sites.

geographical area under consideration. Concentration data for three of the main NORMs, namely U, Th and K, and environmental dose data obtained for samples analysed as part of absolute luminescence dating were used in this study. The samples considered came from six different sites in eastern Sicily.

Statistical analyses were conducted on the data referring to 77 samples. The correlation matrix between the various features characterizing each site was calculated, finding as a result a high correlation between two pairs of them: environmental dose and latitude and K and Th contents.

To study these correlations better, further analysis was carried out, precisely studying the distribution of mean  $D_{env}$  values as a function of latitude and finding that environmental dose values increase in areas with a prevalence of basaltic rocks in the Catania region and decrease as one moves away toward territories with other types of prevailing compositions (such as limestone in the Syracuse area).

By calculating the p-values between the environmental doses of the various sites, it was found that these divided into two statistically correlated groups: the first group containing values from the Santa Venerina, Castiglione di Sicilia and Malvagna sites; the second group containing data from the two Catania sites and the Fontane Bianche site.

The correlation between K and Th contents was studied in more detail by placing the K/Th ratio of the various samples in a graph. Little variation is observed, allowing the conclusion that the ratio is almost constant: thus, as the potassium content increases, so does the thorium content. The positive correlation between these two features had already been shown by the correlation matrix.

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