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X-ray Dating of a Turin Shroud's Linen Sample

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Abstract: On a sample of the Turin Shroud (TS), we applied a new method for dating ancient linen threads by inspecting their structural degradation by means of Wide-Angle X-ray Scattering (WAXS). The X-ray dating method was applied to a sample of the TS consisting of a thread taken in proximity of the 1988/radiocarbon area (corner of the TS corresponding to the feet area of the frontal image, near the so-called Raes sample). The size of the linen sample was about 0.5 mm × 1 mm. We obtained one-dimensional integrated WAXS data profiles for the TS sample, which were fully compatible with the analogous measurements obtained on a linen sample whose dating, according to historical records, is 55–74 AD, Siege of Masada (Israel). The degree of natural aging of the cellulose that constitutes the linen of the investigated sample, obtained by X-ray analysis, showed that the TS fabric is much older than the seven centuries proposed by the 1988 radiocarbon dating. The experimental results are compatible with the hypothesis that the TS is a 2000-year-old relic, as supposed by Christian tradition, under the condition that it was kept at suitable levels of average secular temperature—20.0–22.5 °C— and correlated relative humidity—75–55%—for 13 centuries of unknown history, in addition to the seven centuries of known history in Europe. To make the present result compatible with that of the 1988 radiocarbon test, the TS should have been conserved during its hypothetical seven centuries of life at a secular room temperature very close to the maximum values registered on the earth.

Keywords: X-ray dating; WAXS; Turin Shroud (TS); cellulose degradation; linen yellowing; relative humidity; room temperature

1. Introduction

The Turin Shroud (TS) is the most-studied archaeological object in the world [1,2]. The TS is an ancient linen cloth, 4.4 m long and 1.1 m wide, which wrapped the corpse and encoded the image of a tortured man, who was scourged, crowned with thorns, crucified, and pierced by a spear in the chest. In agreement with the Christian tradition, many researchers are convinced that the TS is the sepulchral cloth of Jesus Christ; however, in 1988, the Shroud was radiocarbon dated by three famous laboratories [3] and attributed to the year 1325 Anno Domini (AD), with an uncertainty of ±65 years, implying that the TS should be a Medieval artifact. This result has been widely criticized [4,5] for both procedural and statistical problems, as was recently confirmed by the statistical analyses of raw data made available to the scientific community after only about thirty years and a legal action [6]. A regression analysis of data on the TS carbon dating has shown their statistical heterogeneity, together with the implausibility of the spatial allocations of some measurement samples [4–6]. Moreover, the ^{14}C dating results remain controversial, especially because of the likely non-negligible carbon contamination of the textile [6,7]. This contamination could be due to many factors, including environmental ones [8,9].

Moreover, other dating methods agree in the assignment of the TS to the first century AD [5,10–12]. Spectroscopic methods, based on Fourier Transform Infrared spectroscopy/Attenuated Total Reflectance [10] and Raman spectroscopy [11], date the Shroud

to 300 Before Christ (BC) $\pm$ 400 years and 200 BC $\pm$ 500 years, respectively. The mechanical multi-parametric method, based on an analysis of five parameters, including the breaking load and Young's modulus and the loss factor, after an adequate calibration based on the results of two dozen samples of known age, dates TS as 400 AD $\pm$ 400 years old [12]. Estimates of the kinetic constants for the loss of vanillin from lignin suggest that TS has an age range from 1300 to 3000 years [5]. A recent numismatic analysis [13] proposes that TS was already present in 692 AD.

A new method for dating ancient linen threads by inspecting their structural degradation by means of Wide-Angle X-ray Scattering (WAXS) [14] was recently applied to small linen samples taken from ancient fabrics, previously dated with the radiocarbon method. Our work showed that when the ancient fabrics are preserved by environmental contamination—i.e., when they were kept in the tombs where they were found—X-ray and ^{14}C dating agree well [14].

The aim of this work is to apply this new dating method for ancient linen fabrics to a TS linen sample. In Section 2, we describe the material and present the method that was adopted for the analysis, which was detailed in [14]. In Section 3, we summarize the X-ray experimental results obtained for the TS sample. In Section 4, we resume the main formulae [14], which were used to date the natural aging of linen cellulose, discussing their implications for TS X-ray dating. Finally, in Section 5, we report on the conclusions.

2. Materials and Methods

2.1. Samples and WAXS Characterization

The size of the TS linen sample was about 0.5 mm $\times$ 1 mm (see Figure 1a). The TS sample consisted in a thread taken in proximity of the 1988/radiocarbon area (corner of the TS corresponding to the feet area of the frontal image, near the so-called Raes sample).

WAXS experiments were performed at the X-ray Micro Imaging Laboratory (XMI-LAB) of the CNR-IC on all the linen samples reported in Table 1. Experiments on samples A, D, FII, LII of Table 1, were published in [14].

Table 1. Linen samples used for X-ray dating of the TS sample. Sample name, description and age are reported in [3,10,11,14] and re-assumed here. AD = Anno Domini; BC = Before Christ. HR = Historical Record.

Sample Name	Linen Sample Description of Fabric (Provenience)	Year of Manufacture Obtained by Dating [with the Bibliographic Reference in Square Brackets]
A	New fabric, bleached (Italy)	2000 AD [10,11,14]
D	Medieval fabric, ^{14}C dating, Fayyum (Egypt)	544–605 AD [10,11,14]
FII	Fabric ^{14}C and HR dating (Siege of Masada, Israel)	55–74 AD [10,11,14]
LII	Fabric ^{14}C dating, Egypt	3500–3000 BC [10,12,14]
TS	Fabric and fibers from Turin Shroud	1260–1390 AD [3] 700 BC–100 AD [10] 700 BC–300 AD [11] 0–800 AD [12] 1000 BC–700 AD [5] Before 692 AD [13]

Figure 1a,b show the optical microscope photographs of the analyzed TS sample. Figure 1c displays the 2D WAXS pattern measured on the sample.
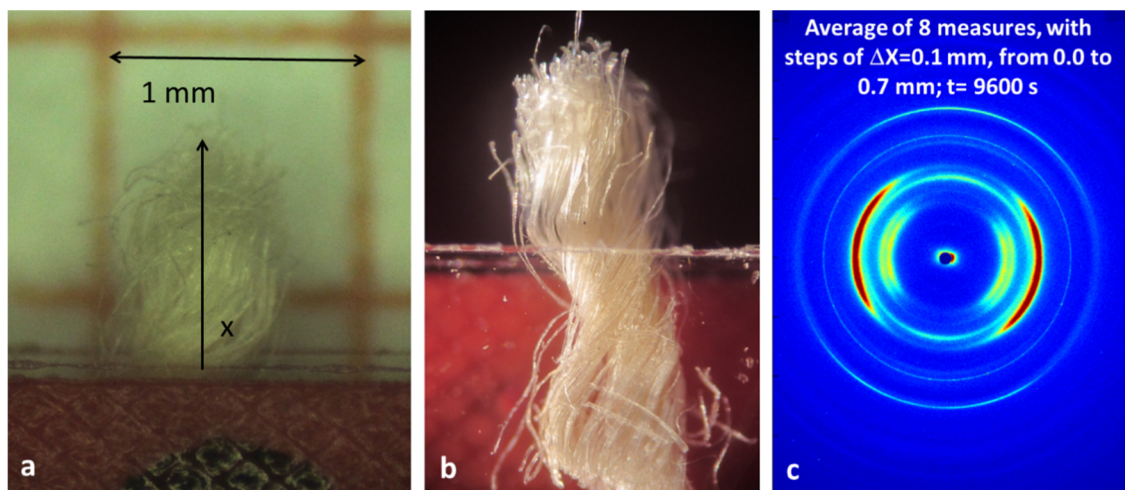
Figure 1. (**a**,**b**) Optical microscope photographs of the TS sample. (**c**) 2D WAXS pattern measured on the TS sample.

The laboratory is equipped with an Fr-E+ SuperBright rotating copper anode microsource ($\lambda = 0.154$ nm, 2475 W) coupled with a focusing multilayer optics Confocal Max-Flux (CMF 15–105) to a small/wide-angle X-ray scattering SAXS/WAXS (SWAXS) three-pinholes camera equipped for X-ray scanning microscopy. An image plate detector (250 mm × 160 mm, with 100 μm effective pixel size) with an offline Rigaku RAXIA-Di reader was employed to collect WAXS data. WAXS data were collected for each linen sample, directly mounted on the sample holder with an acquisition time ranging from 1200 to 1800 s. The spot size at the sample position was about 200 μm. The image plate detector was placed about 10 cm from the sample, giving access to a range of scattering vector moduli ($q = 4\pi \times \sin\vartheta/\lambda$) from 1.5 to around 35 nm^{-1}. Two-dimensional (2D) patterns were converted into one-dimensional (1D) data profiles after the calibration procedure.

Analyses were repeated several times on the same sample. The 2D WAXS pattern shown in Figure 1c was obtained by summing the scattered X-rays from 8 different positions on the sample along the x-axis shown in Figure 1a, moving the sample 0.1 mm for each measurement, with a collection time of 1200 s for each step and a total measurement time of 9600 s for the whole WAXS pattern. WAXS patterns on other linen samples (A, D, FII, LII of Table 1) were previously measured with the same experimental set-up and have already been published [14].

2.2. Chain Breaks in Cellulose Due to Natural Aging

Cellulose consists of linear, polymeric chains of cyclic (anhydroglucose) units, whose number per chain is called Degree of Polymerization (*DP*) [14]. During polymerization, the chains of cellulose molecules are organized in both crystalline and amorphous regions, in micro-fibrils, and, finally, into fibres. The depolymerization, i.e., the increase in the number of Chain Breaks (*CB*), is the main mechanism of cellulose degradation. The natural aging process that degrades cellulose over thousands of years can be accelerated in suitable ovens by increasing the temperature to the maximum number of *CB* within a few thousand hours [15–18].

The *CB* at any aging time *t* and the normalized asymptotic value obtained for very long aging times is given by [14]:

$$CB_{nor}(t, T_r) = 1 - \frac{1}{\omega_{DP}^* + (1 - \omega_{DP}^*) \times exp[a_{TDP}(T_o, T_r) \times k_{DP}(T_o) \times t]}. \quad (1)$$

Here, ω_{DP}^* is the *DP* maximum fractional loss; $k_{DP}(T_o)$ is the reaction rate at $T_o = 90 + 273.15$ K, i.e., at the oven temperature T_o at which the accelerated degradation process

has been measured by other authors [15–18]; *t* is the aging time. The Arrhenius shift factor $a_{TDP}(T_o, T_r)$ has the following expression [15]:

$$a_{TDP}(T_o, T_r) = exp\left[\frac{E_{DPa}}{R} \times \left(\frac{1}{T_o} - \frac{1}{T_r}\right)\right],$$ (2)

where *R* is the gas constant (8.314 J/mol/K). T_r is the estimated average room temperature at which the linen fabric was preserved over the centuries (i.e., the local secular average room temperature).

The normalized Aging Parameter (*AP*) determined in the following section can be considered an experimental evaluation obtained by the WAXS of the ratio between *CB* at any aging time *t* and the normalized asymptotic value obtained for very long aging times, as expressed by Equation (1) [14].

3. Results

The 2D WAXS pattern shown in Figure 1c was integrated in the azimuthal angular range of 10 degrees around the hk0 equatorial fiber–diffraction axis, as in [14], for the other 2D WAXS patterns measured on the linen samples of Table 1. These integrated profiles are indicated with I-profiles in the following. In Figure 2, we added the TS I-profile, obtained using the WAXS pattern shown in Figure 1c, to the I–profiles published in Figure 3 of [14], rescaling the TS measured intensity to have the same integral in the q-range 1.5–4.0 nm^{-1}, i.e., in the region of the incident beam tail. The rescaling of all the profiles to the same integrated intensity in the region of the incident beam tail, allows for variations in the scattered intensity due to the eventual variations in the incident beam intensity to be eliminated.
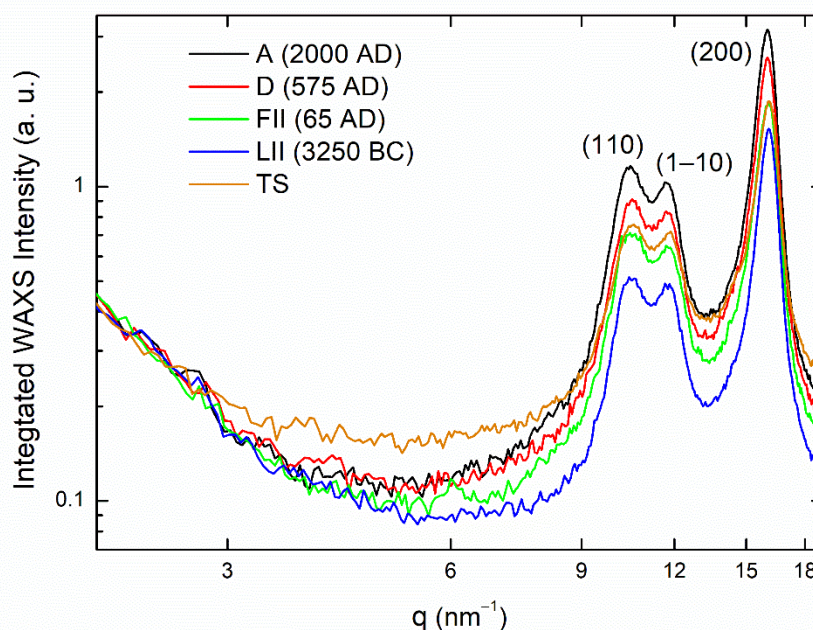

Figure 2. Integrated WAXS profiles (I-profiles) after integration in the angular sector of 10 degrees, around the hk0 equatorial fiber–diffraction axis. A, D, FII and LII are the same profiles of Figure 3 of [14]. I-profiles have been rescaled to have the same integrated intensity in the q-range 1.5–4.0 nm^{-1}. See main text for further details and Table 1 for symbols.

The result obtained for the TS (orange curve), compared with the I-profile obtained for sample A (Figure 2, black curve), FII (Figure 2, green light curve), D (Figure 2, red curve) and LII (Figure 2, blue curve), by means of a qualitative inspection, indicates that the TS diffraction peak intensities are very close to those of the FII sample I-profile, taken from a

sample whose Historical Record (HR) and ^{14}C dating is 55–74 AD: the FII sample taken from a linen fabric found in the archaeological ruins of the Siege of Masada (Israel).

　　To be quantitative in our analysis, we need to consider that the measurements for the TS sample were made after several months, after replacement of the anode filament, and realignment of the focusing optics. This explains the new incident beam's profile in the q-range 1.5–4.0 nm^{-1}, i.e., in the region of the incident beam tail used to perform an intensity scaling of the WAXS I-profiles, as described in [14]. To evaluate the change in the incident beam's profile in the q-range 1.5–4.0 nm^{-1}, we repeated the WAXS characterization for the A-sample of Table 1. This procedure allows the TS I-profile to be placed on the correct intensity scale regarding the measurements that were obtained for other linen samples [14]. The result is shown in Figure 3, which shows the integrated WAXS profiles (I-profiles), extracted from the relevant 2D patterns, after integration in the angular sector of 10 degrees, around the hk0 equatorial fiber–diffraction axis. The A-sample black curve is the same profile already shown in Figure 3 in [14].
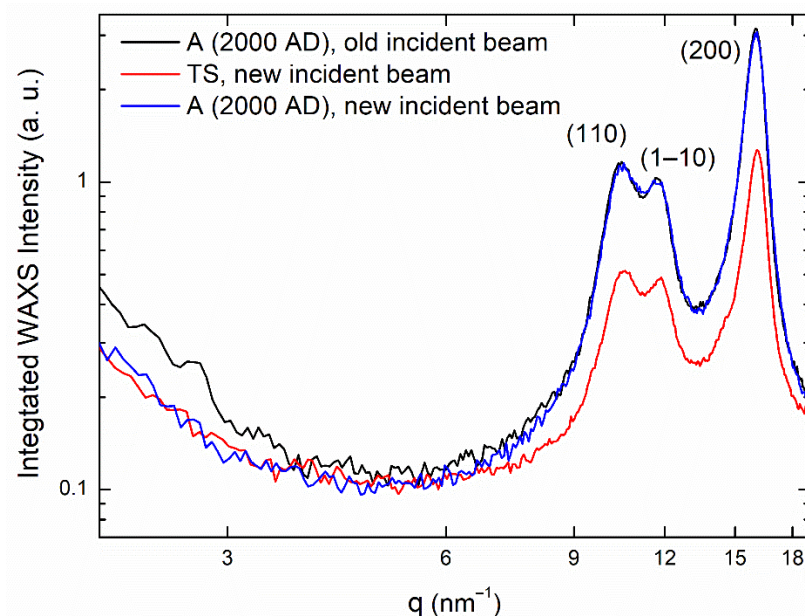

Figure 3. Integrated WAXS profiles (I-profiles) after integration in the angular sector of 10 degrees, around the hk0 equatorial fiber–diffraction axis, in arbitrary units. The A-sample black curve is the same profile of Figure 3 in [14]. The blue curve is the I-profile measured on the same A-sample with a new incident beam, scaled to have the same integrated intensity under the (110) and (1–10) diffraction peaks in the I-profile measured in [14].

　　The blue curve is the I-profile, measured on the same A-sample with a new incident beam. It was scaled to have the same integrated intensity under the (110) and (1–10) diffraction peaks in the I-profile measured in [14]. The TS I-profile was rescaled to have the same integrated intensity, in the q-range 1.5–4.0 nm^{-1}, of the blue I-profile obtained on sample A with the new incident beam.

　　The Aging Factor (*AF*, as defined in [14]), for the TS and A I-profiles of Figure 3 were reported in Table 2, together with the *AF* values that were published for the A, D, FII and DII samples, reported in Table 1 of [14]. Table 2 summarizes some experimental quantities obtained by WAXS: the scattered intensity, integrated below the (110) and (1–10) diffraction peaks, $<I>_{q \in [9,13]}$, in the scattering vector q-range = 9.0–13.0 nm^{-1}; the maximum intensity in the entire q-range, dominated by the intensity of the (200) peak (I_M); the minimum background intensity between the (1–10) and (200) diffraction peaks (I_m). The symbol $< \ldots >$ stands for the average of the scattered intensities in the indicated q-range. $<I>_{q \in [9,13]}$ stands for the intensity in an angular sector of 10 degrees around the hk0 axis,

averaged in the scattering q-range from 9 to 13 nm^{-1}, referred to in the following as I_D. The experimental data analysis is described in detail in [14].

Table 2. Data obtained from analysis of the integrated WAXS profiles [14]. AD = Anno Domini; BC = Before Christ. OIB = Old Incident Beam; NIB = New Incident Beam. Scattering vector q-values are given in nm^{-1}.

Sample Name	Linen Sample Description of Fabric (Provenience) Beam	Year of Manufacture	Scattered Intensity under the (110)–(1–10) Peaks	Maximum Main Diffraction Peak Intensity	Minimum Main Diffraction Peak Intensity	Main Diffraction Peak: Max-to-Min Ratio	Aging Factor
			I_D $<I>_{q \in [9.0,13.0]}$	I_M $I_{(200)}$	I_m $I_{q = 13.3}$	R_{Mm} I_M/I_m	AF $\frac{I_M}{I_m} \times \frac{1}{I_D}$
A	New fabric, bleached (Italy) OIB	2000 AD	0.996 ± 0.008	4.186 ± 0.009	0.517 ± 0.005	8.1 ± 0.1	8.1 ± 0.1
D	Medieval fabric, ^{14}C dating, Fayyum (Egypt) OIB	544–605 AD	0.833 ± 0.008	3.57 ± 0.01	0.460 ± 0.002	7.76 ± 0.04	9.3 ± 0.1
FII	Fabric ^{14}C and HR dating (Siege of Masada, Israel) OIB	55–74 AD	0.641 ± 0.008	2.41 ± 0.01	0.366 ± 0.004	6.58 ± 0.07	10.3 ± 0.2
LII	Fabric ^{14}C dating, Egypt OIB	3500–3000 BC	0.649 ± 0.007	2.76 ± 0.01	0.367 ± 0.002	7.52 ± 0.05	11.6 ± 0.1
A	New fabric, bleached (Italy) NIB	2000 AD	0.997 ± 0.009	4.10 ± 0.01	0.500 ± 0.006	8.2 ± 0.1	8.2 ± 0.1
TS	Thread from TS NIB	To be determined from WAXS data	0.496 ± 0.010	1.69 ± 0.01	0.336 ± 0.004	4.97 ± 0.09	10.0 ± 0.2

The aging factor *AF* obtained for the TS sample confirms that it is comparable to that of the FII sample, whose HR dating corresponds to the Siege of Masada (55–74 AD). The *AP* value, derived from WAXS-measured values for the TS sample, obtained as in [14] and calculated using the minimum and maximum *AF* values reported in Table 1 of [14], is

$$AP_{TS} = (10.0 - 7.56)/(11.6 - 7.56) = 0.60 \pm 0.02 \tag{3}$$

4. X-ray Dating of the TS Sample

AP can be considered as an experimental evaluation obtained, by the WAXS of the ratio between *CB* at any aging time *t* and the normalized asymptotic value obtained for very long aging times [14], as reported in Equation (1):

$$AP = CB_{nor}(t, T_r) \tag{4}$$

Equation (4) allows for an evaluation of the natural aging time *t* of fabric threads. *t* can be directly calculated from: the measured *AP* value; the *DP* activation energy E_{DPa}, and the *DP* maximum fractional loss ω^*_{DP}; the estimated average room temperature T_r at which the linen fabric was preserved over the centuries. In [14], for linen, we obtained: $E_{DPa} = 118.9 \pm 0.8$ kJ/mole; $\omega^*_{DP} = 0.953 \pm 0.001$. For $T_o = 273.15 + 90$ K, the reaction rate k_{DP} of the linen *DP* degradation, usually given in hours^{-1}, denoted as h^{-1}, is reported to be $k_{DP}(273.15 + 90) = 0.0022$ h^{-1} [16]. The *DP* degradation's reaction rate also depends on the humidity [19]. The value of 0.0022 h^{-1} was determined at a relative humidity value, $H_r = 50\%$ [16]. A variation in the relative humidity in the typical range of the average annual values registered almost everywhere on the earth's surface, ranging from 50% to

80%, causes almost linear variations in the degradation rate (see Figure 5 of [19]). An 10% increment in the relative humidity, from 50% to 60%, causes a k_{DP} increment of 10% [19]. Thus, variations of k_{DP} can be put almost linearly proportional to variations of the annual relative humidity's values, in the whole range of our interest, i.e., 50–80%. The average relative humidity values H_r of the localities of Egypt and Israel from which the samples used in [14] were kept for many centuries are all around $55 \pm 5\%$. This, in turn, caused a k_{DP} increment of only about 5%, from 0.0022 h^{-1} to 0.0023 h^{-1}, as used in [14], since, in measurements of the accelerated aging of cellulose [16], the relative humidity of the oven was kept constant at $H_r = 50\%$.

Other localities, for example in Italy, Turin, where the TS was kept for many centuries, are characterized by average relative humidity values $H_r = 75 \pm 5\%$. In this case, we should expect a k_{DP} value 1.5 times the value measured at a relative humidity $H_r = 50\%$, i.e., a k_{DP} of about 0.0033 ± 0.0001 h^{-1}. This increment is important, but it plays a less important role regarding the secular average room temperature T_r in affecting the natural aging of linen, since the dependence on the temperature is realized through an exponential factor, as shown in Equation (2), whereas k_{DP} is a multiplicative factor. To provide a quantitative indication of the different role of relative humidity and room temperature in affecting the natural aging of cellulose, from Equations (1)–(4) we found that the same natural aging process for the cellulose constituting linen would be obtained if one increased the average relative humidity from 50% to 75% and, at the same time, reduced the secular average room temperature by about 2.5 °C, e.g., from 22.5 °C to 20 °C. Indeed, to obtain the same rate of natural aging at T_{r1}, k_{DP1} and T_{r2}, k_{DP2} from Equations (1) and (2) it is sufficient to satisfy the following condition

$$T_{r2} - T_{r1} = \frac{R T_{r1} T_{r2}}{E_{DPa}} \times ln\left[\frac{k_{DP1}}{k_{DP2}}\right], \tag{5}$$

where the temperature is expressed in Kelvin. The previous numerical example can be derived from Equation (5).

Thus, relative humidity is less important than the room temperature in affecting natural aging of cellulose. Nevertheless, high humidity promotes new life: molds, fungi, bacteria, insects, etc., which are more effective at destroying cellulose with respect to natural aging due to the action of the room temperature. Therefore, ancient linen fabric are, usually, only well preserved in semi-desert or desert climates, as for the linen samples found in the tombs of the mummies analyzed in [14]. Conversely, this preservation of fabrics in other parts of the world, where the relative humidity can be much higher than semi-desert climates, is not guaranteed. Relics are an exception, due to their religious importance: they are also well preserved in geographical regions characterized by high relative humidity values; however, this slightly affects the rate of natural aging, and this finding has to be taken into account through Equation (5).

Moreover, it could be argued that some historically documented fires were suffered by the TS [12]. These accidental events could have influenced the aging of the cellulose constituting its linen fibers. To verify this eventuality, we measured the WAXS maps of linen samples before and after exposure to a temperature of 200 °C in an oven for half an hour, without any control of the relative humidity, which became very low during the fabric's exposure at these temperatures, as happens in real accidental fires. After this thermal treatment, the WAXS map of the samples was unaltered, as shown by the integrated profiles reported in Figure 4, but the yellowing of the linen was very pronounced, as was also seen in the experiments discussed in [20], where a detailed study about the linen yellowing, as a function of both the oven temperature and the time permanence in the oven, was performed.
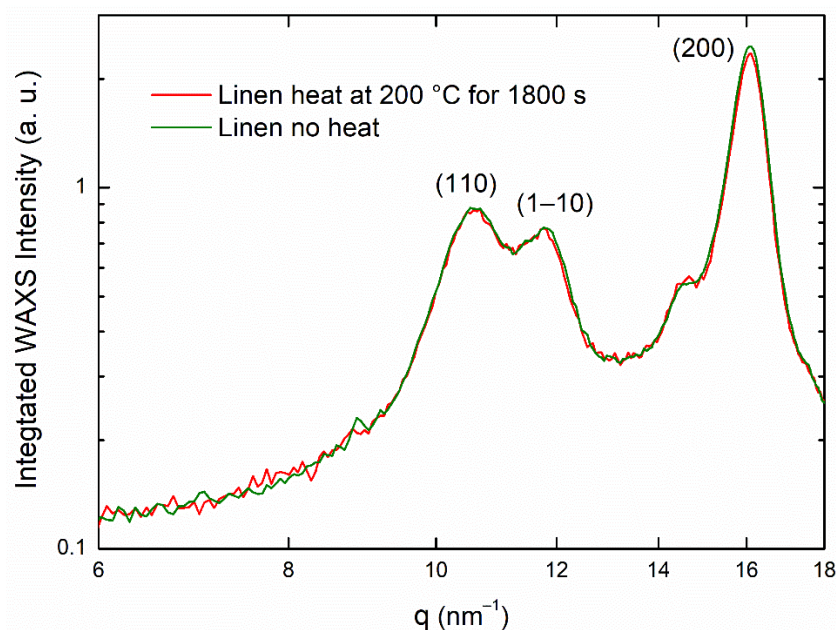
Figure 4. Integrated WAXS profiles (I-profiles) after integration in the angular sector of 10 degrees, around the hk0 equatorial fiber–diffraction axis. The red curve is the I-profile obtained after exposing a piece of linen in oven at a temperature of 200 °C for half an hour. The green curve is the I-profile before the thermal treatment.

The reason that a thermal shock at 200 °C does not affect the natural aging level of cellulose is related to the fact that, during a fire, the relative humidity becomes very low, reducing the reaction rate k_{DP} of the linen *DP* degradation by at least one order of magnitude. The only visible effect on the linen is its yellowing, caused by surface oxidation of fibers. Indeed, detailed experimental tests have demonstrated that a few minutes at a temperature of 200 °C could be enough to cancel out the TS image [20], due to the high level of yellowing of the fabric. Moreover, our WAXS experimental tests allow any contribution of the thermal shocks caused by historically documented fires to the secular natural aging of the TS fabric to be excluded.

Figure 5 shows the Equation (4)'s prediction regarding the natural aging of the cellulose constituting the linen of the TS sample. From documented history, we know that, from the XIV century, this was kept in France for about two centuries and at Turin (Italy) for about five centuries [12]. The secular average room temperature of Turin is of 12.5 ± 0.5 °C, and the average relative humidity is 75 ± 5% [21]. The European secular average room temperature is even smaller than that of Turin, at around 8.5–9 °C [22]. Even assuming seven centuries of history, always at a secular temperature of 12.5 ± 0.5 °C and an average relative humidity of 75 ± 5%, from Equation (2), we can obtain that the total *AP* would be very low, equal to 0.027 (black curve of Figure 5) of the order of the experimental error Δ*AP* = 0.02 with which the AP_{TS} was determined. The ^{14}C dating of the TS suggests it is seven centuries old [3]. Consequently, the ^{14}C dating of TS is fully incompatible with the TS X-ray dating (green dashed lines in Figure 5), because historical documents regarding TS' presence in France and at Turin (Italy) for a total of seven centuries, would lead to a maximum final value of $AP \leq 0.027$, which is much lower than the measured value of $AP_{TS} = 0.60 \pm 0.02$. Seven centuries would be enough to cause the measured value of $AP_{TS} = 0.60 \pm 0.02$ only in the hottest region of the world. The magenta curve is the prediction for Mali (Africa), one of the hotter regions of the world. For example, in the years 1901–1930, it was characterized by an average temperature of 27.8 °C [23]. Secular average room temperatures in the last seven centuries should be smaller than this value. Relative humidity in Mali is also only 40–45%. The magenta curve in Figure 5 was plotted for the highest annual value, $H_r = 50\%$, for that region, to allow for maximum *DP* degradation.
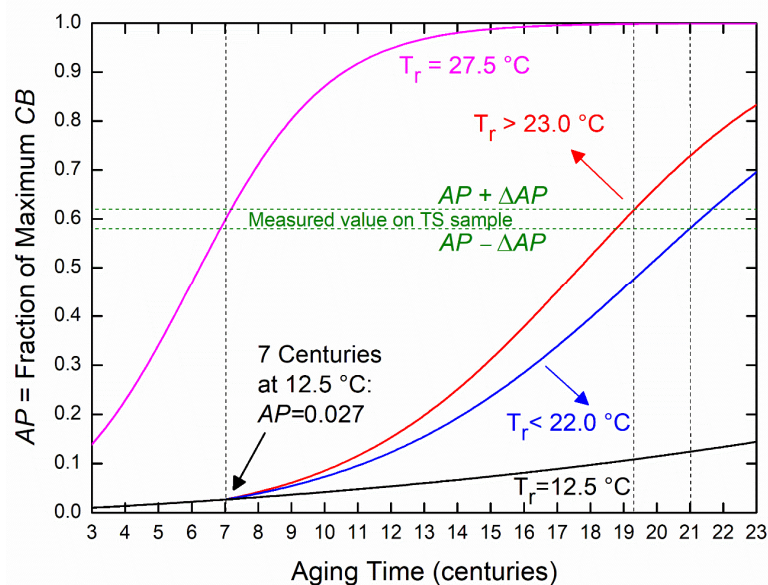
Figure 5. Prediction obtained by Equation (4) for the natural aging of the cellulose constituting the TS sample. Seven centuries at 12.5 °C, i.e., at the secular average temperature of Turin (Italy), would provide a very low final AP (black curve), of the order of the experimental error ΔAP. Seven centuries is the ^{14}C dating of the TS. Therefore, the ^{14}C dating of TS is incompatible with the natural aging of its cellulose, as evaluated by the X-ray analysis (green dashed lines), which is $AP_{TS} = 0.60 \pm 0.02$. To ensure compatibility with this experimental value, we have to assume an average secular temperature of $T_r = 22.5 \pm 0.5$ °C and an average relative humidity of $55 \pm 5\%$, leading to a total natural aging time of 20.2 ± 0.8 centuries. For $T_r < 22.0$ °C, the TS linen would be more ancient (blue curve) than 20 centuries. For $T_r > 23.0$ °C, the TS linen would be less ancient (red curve). The magenta curve is the prediction for Mali (Africa), one of the hotter regions of the world [23].

Therefore, to obtain an AP value of the order of 0.60 ± 0.02 (measured value), we necessarily need to assume additional centuries of history for the TS. Adding to the seven centuries of European history of the TS, further centuries of history in any place in the world characterized by an average secular temperature of $T_r = 22.5 \pm 0.5$ °C and an average relative humidity of $55 \pm 5\%$ will lead to a total natural aging time of 20.2 ± 0.8 centuries. For $T_r < 22.0$ °C, the TS linen would be more ancient (blue curve in Figure 5) than 20 centuries old. For $T_r > 23.0$ °C, the TS linen would be less ancient than 20 centuries (red curve in Figure 5).

Thus, an X-ray evaluation of the natural aging of the cellulose composing the TS linen implies that it would be less than 2000 years old only if, for some centuries, before the last seven centuries in Europe, it was kept in a geographical region of the world characterized by a higher average secular temperature than about 23 °C. The other possibility—T_r <22 °C—would be compatible with Christian tradition, leading to a TS age of more than 20 centuries.

In principle, the hypothesis that the TS fabric, for many centuries, could have endured an average secular room temperature higher than about 23 °C at an average relative humidity of $55 \pm 5\%$ is possible, since there are linen fabrics, such as sample NII of [14], taken by a mummy in Engedi (Israel), that were preserved for many centuries at an average secular temperature of about 23.5 °C and relative humidity values of $55 \pm 5\%$. However, under the hypothesis that the TS is much less than 20 centuries old, it would be quite curious if it was always kept in localities in the world characterized by very high secular average temperatures. The European secular average room temperature is around 8.5–9 °C [22], much lower than 23 °C. This simple consideration also seems to exclude the hypothesis that the TS linen is much less than 20 centuries old.

5. Conclusions

More than 30 years ago, it was argued that the measurement of the depolimerization of the cellulose constituting the linen of the TS could have offered the possibility of dating its fabric [24]. This was the aim of this work. In particular, the WAXS analysis presented here, for the natural aging of the cellulose in the linen of a TS sample, allows us to conclude that it is very probable that the TS is a relic of about 20 centuries old, even if we only have European historical documentation for the last seven centuries. Since the ^{14}C dating [3] does not agree with our results, or with the dating obtained by other works (see Table 1), a more accurate and systematic X-ray investigation of more samples taken from the TS fabric would be mandatory to confirm the conclusions of our study. In this regard, it is very interesting to note that X-ray dating can be realized on half-mm-sized samples and, contrary to ^{14}C dating, the WAXS allows for repetitive measurements to be taken of the same sample. Therefore, many laboratories could repeat the X-ray dating on the same samples, and the procedure would also be blinded, because submillimetric or millimetric samples of linen fabric are indistinguishable, compared to the cm-sized samples needed for ^{14}C dating, which prevented a blind measurement protocol from being carried out in the 1988–1989 ^{14}C study [3]. Indeed, the particular TS weaving was clearly identifiable, invalidating the achievement of a blind analysis procedure. As a result, the bias in the 1988–1989 ^{14}C analyses occurred, as was demonstrated for this famous relic [6].

Our tests on the effects of a thermal shock on the linen, obtained by measuring the WAXS patterns before and after a thermal treatment in the oven of a linen piece at a temperature of 200 °C for 30 min, allow for an increment in the natural aging due to the action of accidental fires, which have surely characterized the history of the TS fabric [12], to be excluded. In particular, detailed experimental tests about the yellowing of the linen have demonstrated that a few minutes at a temperature of 200 °C could be enough to cancel out the TS image [20].

Moreover, it is interesting to point out that our analysis has shown that, in order for the TS fabric to be about 20 centuries old, it should have necessarily been kept at an average secular temperature of about 22.5 ± 0.5 °C and an average relative humidity of 55 ± 5% for 13 centuries preceding the XIV century. From Equation (5), it follows that if the average relative humidity was of the order of 75 ± 5%, to obtain the same value of the measured natural aging of 0.60 ± 0.02 for the TS sample, the average secular room temperature should be about 20.0 ± 0.5 °C. Therefore, from our WAXS characterization it follows that we have a range of allowed secular average room temperatures of 20.0–22.5 °C, correlated with a range of average relative humidity values of 75–55%, as climate constraints, for the TS to be a 20-centuries-old relic. These physical constraints on the secular average room temperature and the average relative humidity, obtained by measuring the natural aging of the cellulose of the TS sample, here realized through WAXS characterization, could help historians test their hypotheses throughout the possible locations in the world and historical periods in which the TS could have been kept during the 13 centuries before its documented history in Europe.

Finally, since X-ray dating indicates that the TS is older than its seven centuries of European history, we can also argue that it was fortunate that the TS was carried to Europe seven centuries ago. Indeed, our analysis has shown that, from the XIV century until today, the natural aging of the cellulose of the TS linen has been very low, due to the low secular European average room temperatures, thereby preventing the TS body image from fully disappearing, which would have happened at an average secular room temperature of 22.5 °C. Indeed, Equation (4) implies that, under the hypothesis that the TS is 20 centuries old, after 20 centuries at an average value of T_r = 22.5 °C and a relative humidity of 55%, a natural aging of about 90% would have already occurred; this value is much higher than the 60% that was experimentally determined for the TS sample. Therefore, by chance, only the recent history of the TS in Europe has prevented the TS linen from fully yellowing and the TS image from fully disappearing, thus preserving a puzzle that is very difficult for science to solve. New WAXS analyses on the natural aging of the cellulose in linen

could allow for the correct age of the TS to be determined, which is a fundamental piece of this puzzle.

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