THE SUDARIUM OF OVIEDO: A STUDY OF FIBER STRUCTURES

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Abstract
The Sudarium of Oviedo has been studied intensively with a petrographic (polarizing) microscope. It is composed of pure flax fibers, and they show the same characteristics as the Shroud of Turin. The technology used to prepare the linen cloth appears to be identical to that described for Roman times by Pliny the Elder (*Natural History* XIX, 3, 16-18).

Flax fibers are mostly crystalline cellulose, and the crystals have a fibrillar structure. The fibers are birefringent between crossed polarizers; however, the birefringence changes depending on the past history of the material. Perfect, new flax fibers show extinction (the segments between growth nodes are perfectly black) at two angles as the microscope stage is rotated. Strained or irradiated fibers show zones of birefringence at other angles. Fibers from the Sudarium show many defects caused by different kinds of radiation.

The evidence indicates significant age for the material. It seems to have similar defect types and populations as the Shroud of Turin. The two cloths must be roughly the same age.

Observations

Figure 1 shows a photomicrograph of representative fibers from the Sudarium (100X, parallel illumination, in 1.515-index oil). The fibers are flax. Flax has a characteristic structure that looks like small lengths of bamboo, with straight segments separated by wider growth nodes. These fibers are relatively supple and do not show any significant microbial decay. The color can still be called white, unlike very old linen samples. An important characteristic is the presence of residual deposits of lignin at the growth nodes of the flax fibers. This indicates a mild bleaching method, unlike the method used in Egypt, which used natron (a very alkaline form of sodium carbonate that is found in natural deposits in Egypt). Approximately the same amount of residual lignin is a notable characteristic of the Shroud of Turin. Also visible is a blue cotton fiber that lies across the flax fibers. Cotton is easily identified on the basis of its tape-like structure and periodic reversals. The dye appears to be indigo. The fiber may have some historical importance, but I can not pursue the question.

Cellulose is composed of long chains of glucose molecules. It is largely crystalline, and the crystals are long on a microscopic scale. They lie parallel side by side in the structure of a fiber. The crystals are not, however, very rigid or stable compared with most inorganic crystals (e.g., quartz). They are held together by hydrogen bonds. Anything that can rupture the bonds in the structure will cause a defect in the crystal, and defects change the way polarized light travels through a crystal. The defects can be seen with a polarizing microscope. Figure 2 shows some modern flax fibers between crossed polarizers.

Figure 1: Flax fibers from the Sudarium of Oviedo, 100X in 1.515 oil. Observe the dark rings around the fibers. They are lignin that was not removed during bleaching.

Parts of the fibers lie at an angle to the plane of polarization and they show bright birefringence. A horizontal length in the middle of the view is parallel to a plane of polarization, and it is dark. The bright rings are growth nodes. Notice that the dark segments are very dark.

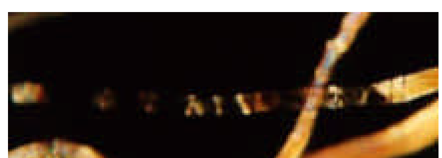

Figure 2: Segments of modern flax fibers, polarized.

Figure 3 shows a few fibers from the Sudarium between crossed polarizers. Notice that the lengths between growth nodes are *not* perfectly black. Something has disturbed the order of the crystals, causing birefringence. Some of the birefringence appears in bright streaks of different lengths and brightness that penetrate the fibers at different angles and for different distances.

The general haze in the background was caused by energetic electromagnetic radiation. Any wavelength of light that is more energetic than green can cause such defects. Very energetic gamma rays, x rays, and ultraviolet light cause the same kinds of dispersed, foggy defects.

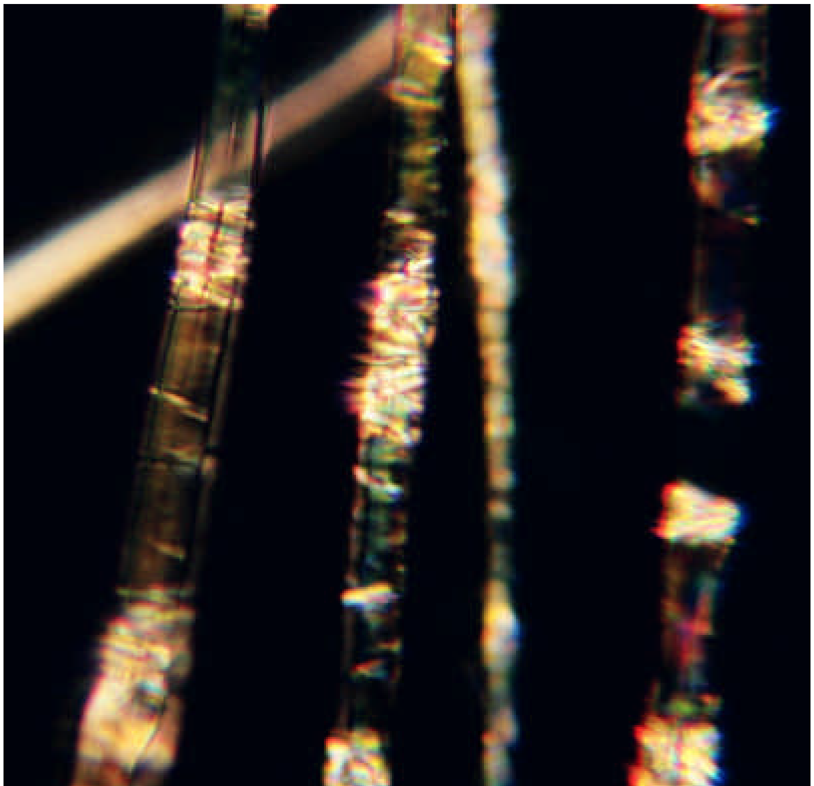

Figure 3: Fibers from the Sudarium, polarized, 800X in 1.515 oil.

The defects we see in the Sudarium indicate significant age. The environment at the surface of the earth is bombarded by a significant amount of natural radiation. A relatively small fraction of this is from cosmic rays; most comes from natural terrestrial radiation. Primary cosmic rays are very energetic, but very few reach the earth. They interact with the atmosphere to produce showers of secondary cosmic rays. Most of the secondary cosmic rays reaching the surface of the earth are muons; however, they do not produce any significant effects in matter. Some secondary cosmic rays can affect matter. Of the energetic, ionizing particles, about 85% are protons (hydrogen nuclei) and 12% are alpha particles (helium nuclei). The largest amount of natural radiation is alpha particles that come from radon (Rn). Radon is produced by the radioactive decay of naturally-occurring thorium (in rocks and soil), it is a heavy, inert gas, and it collects in low places in buildings. It can easily diffuse into storage containers such as reliquaries. Alpha particles are extremely effective at causing defects in materials, but they do not penetrate very far in either gases or solids. Only Rn atoms near a fiber when they disintegrate will have an effect on the cellulose. Evidence for all of these types of radiation can be seen in figure 3.

Defects change with age. Free radicals react with other materials and each other, and strained "high-free-energy" zones age more rapidly than unstrained ones. Dark streaks of the same dimensions as fresh defects can be observed in old fibers. Some are quite clear in figure 3. The decay of birefringent zones and ion tracks seems to indicate significant age. There is not yet enough data to use the observation for age estimation.

A flax fiber integrates defects as a function of time. They have properties similar to the dosimeters used in nuclear and x-ray laboratories. Older linens have been bombarded by several different kinds of radiation, and they tend to contain more defects than newer ones. Different kinds of defects are produced by the different kinds of radiation. I must assume that the different kinds of defects decay at different rates. Light and heat also produce characteristic defects, and both kinds accelerate aging [Robert L. Feller, Accelerated aging : photochemical and thermal aspects, The J. Paul Getty Trust, 1994, 292 pages]..

A flax sample from about 2000 BC is shown in figure 4. Because samples keep receiving radiation all of the time, very old fibers will show some bright birefringent defects. However, as figure 4 shows, old samples appear to show more dark defects than light ones. They are also very inhomogeneous. The dark defects appear to be voids, and the fibers are relatively brittle.

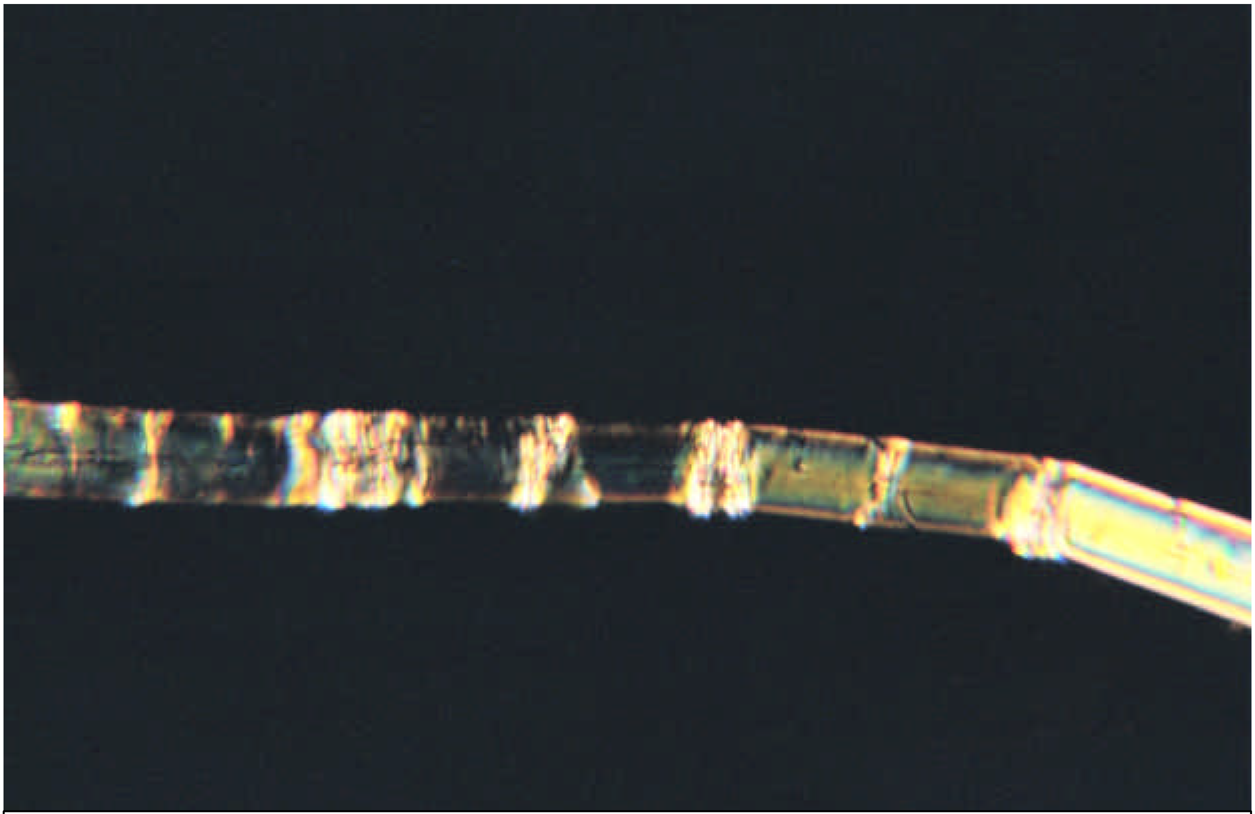

Figure 4: Flax fiber from ca. 2000 BC, 800X, polarized. It shows many dark defects, and it is quite inhomogeneous.

A sample from AD 1620 is shown in figure 5 for comparison. The cloth this came from was not well cared for, and it shows a significant amount of microbiological decay. However, the defect population is not nearly so high as that shown in figure 4, and there are not so many dark defects.

Figure 6 shows a fiber that is still embedded in the adhesive of the sampling tape I used in 1978. The sample was taken from the image area at the back of the ankle on the Shroud of Turin. This view can be compared with the center fiber in figure 3. The types and populations of defects appear to be identical. The flax in the two samples is certainly very similar in structure and production technology. The poor resolution of the image is a result of the fact that the fiber is submerged in the adhesive of the sampling tape, and the Mylar backing of the tape is becoming crystallized with age.

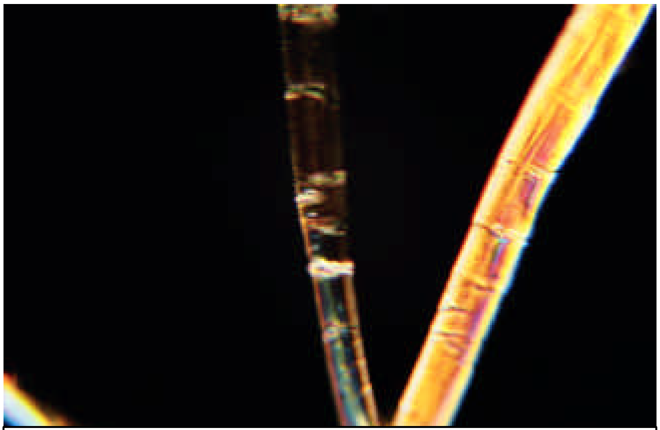

Figure 5: Flax fibers from AD 1620, 800X, polarized.

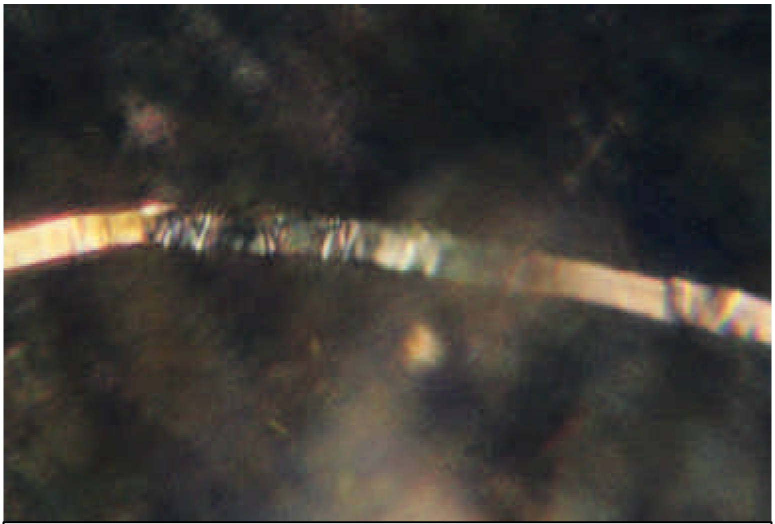

Figure 6: An image fiber from the back of the ankle of the Shroud of Turin, 800X polarized.

I observed that all very old samples of linen failed to give the normal microchemical test for lignin. Lignin on the Shroud of Turin failed to give the test. It was obvious that the lignin degraded with time. This suggested that lignin degradation could be used for age estimation.

It is often possible to estimate the ages of organic materials by observing their extent of degradation. This is a method I used repeatedly in estimating the safety of military high explosives. The estimates can often be quite accurate.

Rates of all kinds of chemical reactions are modeled with an exponential equation called the Arrhenius expression:

$$\frac{da}{dt} = kf(a)Ze^{-E/RT}$$

Rates can be predicted from amounts of reactants (a is the fraction reacted at any time t) and known, measured chemical kinetics constants (k, the rate constant; Z, the Arrhenius frequency factor; E, the Arrhenius activation energy; R, the gas constant; and T, the absolute temperature in degrees Kelvin). The f(a) is called the "depletion factor," and it depends on the physical state of the reactant, the type of reaction, and/or the number of molecules involved in the reaction. Any chemical process involved in linen aging will have properties in accordance with this equation.

I tried to measure the rate at which vanillin was evolved from lignin in order to estimate the age of the Shroud of Turin. A definitive measurement could not be made within the time available (up to 24 months). The numbers presented below can be used only for estimations. We used the time until the phloroglucinol/HCl spot test for lignin (actually vanillin available in the lignin) failed at 40, 70, and 100ºC. The observations gave the following Arrhenius predictive model.

$$k = 3.7x10^{11} e^{-\frac{29,600}{1.987T}}$$

Depending on storage temperature and any intermittent excursions in temperature, it would have required at least 1300 years for all traces of vanillin to be evolved, but at lower normal temperatures (e.g., in cold stone buildings) it could have required as much as 3000 years.

Although the information was useful in the Shroud of Turin context, where a radiocarbon date had claimed a medieval age, it is no help for the Sudarium. The documented age of the Sudarium is within the outer limits of the vanillin-based age estimation.

An important potential source of confusion:

Flax fibers are very stiff; i.e., they have a relatively high modulus of elasticity when compared with other natural fibers. This makes them very difficult to spin and weave with machinery. Flax had to be handled by hand into modern times. Even now, machine spinning and weaving results in defects in the fibers. These defects may be called slip planes or mechanical twinning. Such features are common in organic crystals that have been involved in pressing, extrusion, or drawing, and they can be recognized. Tension causes the formation of defects that closely resemble those made by protons; however, they all form at the same angle across the fibers. It is often possible to see their intersections with the fiber surface. Figure 7 shows an example. I broke this fiber from an AD 1620 sample by tension, and two slip planes are clearly visible at the right end of the dark segment. Modern linen samples show many such defects in nearly all of the material.

Figure 7: Slip planes caused by tension at the broken end of a flax fiber, 800X polarized. The defects intersect the surface, showing small steps.

Conclusions:

The Sudarium of Oviedo shows all of the physical and chemical properties of a very old sample of linen. The types of radiation damage observed in the crystals of its cellulose are very similar to other old linens of known age. Many small deposits of residual lignin can be observed at the growth nodes of the flax fibers. This is probably characteristic of linen samples made in Palestine during Roman times, as described by Pliny the Elder. The technology is certainly not the type used during medieval times in Europe or through the millennia in Egypt. I conclude that there is a finite probability that the Sudarium is related in time and location to the Shroud of Turin.