Surveying silk fibre degradation by crystallinity determination: a study on the Tang dynasty silk treasure from Famen Temple, China

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ABSTRACT When Chinese archaeologists opened an unknown vault under the collapsed pagoda of Famen Temple near Xian (Shaanxi Province, NW China) in 1987, they found a vast amount of valuable silk textiles. The degraded textiles were part of a treasure comprising hundreds of artifacts deposited by Tang dynasty (AD 618–907) emperors as a gift to the temple. Run as a bilateral German-Chinese project, the Roemisch-Germanisches Zentralmuseum Mainz established a textile conservation laboratory in Shaanxi´s provincial capital Xian in 2001, joining numerous other laboratories that have existed there since the early 1990s.

This preliminary study represents part of an ongoing investigation programme that accompanies the conservation work. The Tang dynasty silk is generally in a very poor state of preservation as a result of its long burial period. Large sections have only survived as an amorphous brown mass of fibre debris. Some parts are better preserved, however, offering the unique opportunity to study the whole range of degradation stages on ancient silks.

This preliminary scientific investigation focuses on the determination of the silk fibres' crystallinity and its relation to the ageing process. As we know from modern material, silk is mainly crystalline, albeit in a somewhat amorphous state. The methods of investigation used were X-ray diffraction (XRD) using synchrotron radiation, which is a new way to determine crystallinity of ancient silk fibres; and polarized Fourier transform infrared spectroscopy (FTIR) for the determination of crystallite orientation. Both methods were specifically devised to gain information on small single fibres.

Keywords: silk, degradation, synchrotron study, polarized IR spectroscopy, Famen, China

Introduction

Silk is rarely found on excavations, even in China where the majority of the world's silk textiles had been manufactured in antiquity. Although the degradation of *Bombyx mori* silk fibres has been studied on more recent silks (Becker *et al.* 1997; see also pp. 44–7, 143–50 and 151–8 in this volume), there is still a lack of data regarding ancient silks from burial environments.[1] For the present study, a set of silk fibres exhibiting different states of preservation from a single burial context was available. These were taken from Chinese silk textiles dating to the 9th century.

While it is not possible to reverse decay processes in silk fibres, a more detailed understanding of the ageing mechanisms may help when deciding upon appropriate treatment protocol and determining optimum conditions for the storage and display of ancient, as well as more recent, silk artifacts.

Silk is a semi-crystalline protein fibre therefore a study of its crystallinity may lead to a more detailed knowledge of the degradation process. Instead of investigating the bulk material in the form of silk powders, however, we decided to choose methods that could give information on single fibres – X-ray diffraction (XRD) using synchrotron radiation and polarized infrared microspectroscopy.

Silk from Famen Temple

The silk fibres came from textiles that are currently being treated as part of a large bilateral conservation project between China and Germany, with major financial support from the German government. In 2001, the Roemisch-Germanisches Zentralmuseum Mainz established a textile conservation laboratory in Shaanxi´s provincial capital Xian. Housed in the rooms of the Shaanxi Archaeological Institute, the facility was designed for the conservation treatment of the famous silk textiles from Famen Temple, 120 km west of Xian. The silks had turned up in 1987 during the excavation of a collapsed pagoda, when a hitherto unknown vault in the temple base was detected (Fig. 1).

The vault contained one of the most significant treasures of the Tang dynasty (AD 618–907), including a vast number of precious metal items, porcelain and silk. These would have been personal gifts from the Tang emperors to the Buddhist shrine (Koch 1995). The value of this collection lies in the fact that it has remained undisturbed and that it is accompanied by an exact historical background: a stele that once blocked the entrance of the vault lists all the items and dates in detail.

According to the ancient list, the textile remains include not only large fabrics that cover the boxes of Buddhist relics,

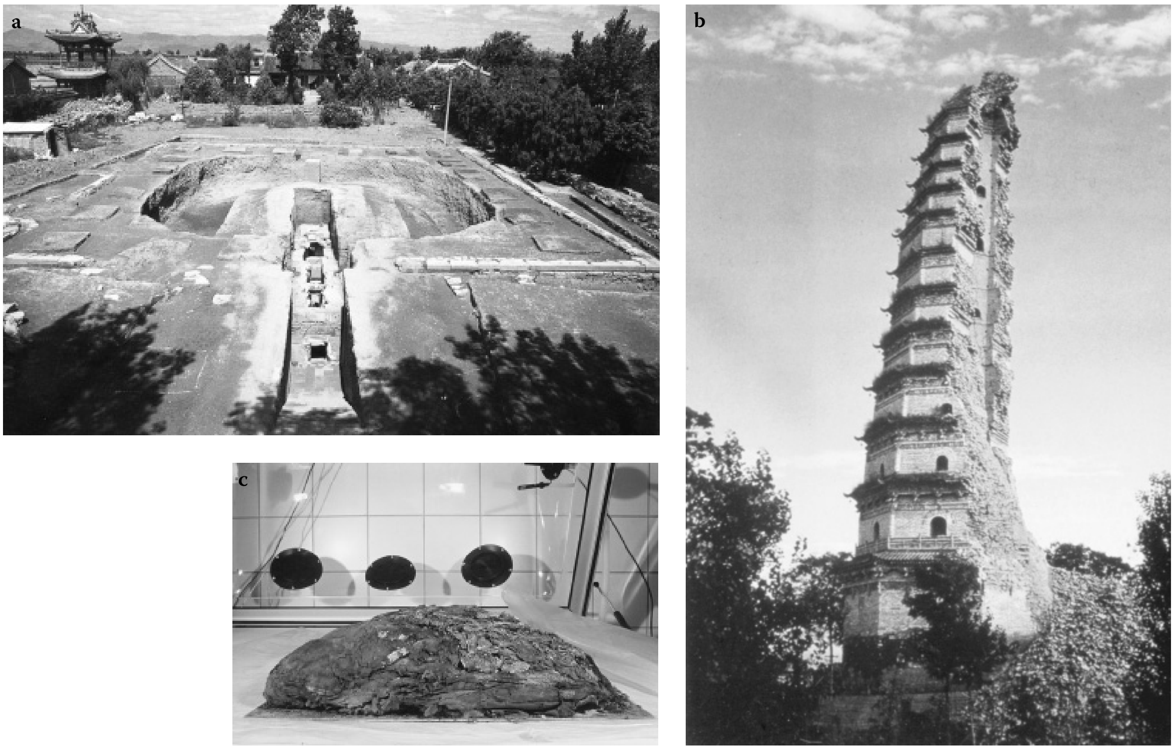

Figure 1 (a) The silk textiles investigated were found in this underground vault (left) together with hundreds of other valuable artifacts. (b) The vault was detected during excavations in 1987 when the site of the pagoda of Famen Temple was cleared after it had been half destroyed by heavy rains in 1981. (c) This bundle of heavily degraded silk dating to the 9th century was found in the underground vault of Famen Temple, China. It is built up from several hundred layers of finely woven silk fabric, some of which form amorphous brown fibre debris while other segments still look quite intact.

but also smaller textiles such as handkerchiefs and full monk's clothing (Han in press). Weaved with precious metal threads, covered by splendid embroideries and painted in many colours, the famous Famen silk fabrics are of immense scientific value to specialists in the field of art history and textile technology. The poor preservation state of the silks, however, has inhibited any handling for research purposes or even exhibition.

The burial environment in an underground humid vault has led to rather pronounced deterioration of the fibres, not aided by bits of mortar, bricks and other building materials that have affected the remains. After excavation in 1987, extensive fungal attack took place despite ethylene oxide being used in an attempt to prevent mould growth. In particular, some of the larger bundles of textile were badly affected. Generally, the fine, delicate woven structures have deteriorated into amorphous brown masses of fibre debris. Some parts are more intact, however, displaying their original brown-golden colours. Nevertheless, even these better preserved parts disintegrate when touched. A set of samples was chosen from different fabrics in order to monitor their crystalline characteristics and correlate this with their visual degradation state.

Protein chemistry and crystallinity

A silk fibre from a silkworm cocoon consists of two filaments: the fibroin brins, which are glued together by a soluble protein-rich gum, sericin. One cocoon can comprise 3,500 m of a single fibre with filaments 15–25 μm thick (Robson 1985). When processing silk for textile use, the sericin is removed by hot water during the degumming process and the fibres, now single fibroin filaments, are spun into a thread.

Fibroin is a protein. Proteins are formed when a large number (by definition > 100) of different amino acids combine by polycondensation to build a long chain (Arni 1995). The intra-chain bonds between two amino acids are called peptide bonds. The amino end ($-NH_2$) of one molecule links to the carboxyl end ($-COOH$) of another molecule, releasing one water molecule (condensation). The sequence of different amino acids in one chain is defined as its primary structure. A predominant motif of the silk fibroin primary structure may be described as a sequence of the rather simple amino acids, glycine, alanine and serine (abbreviated as GAGAGS). Tyrosine is the next most common component. The secondary structure of a protein describes the conformation of the chain, which is determined by intermolecular secondary bonding. The latter are mostly hydrogen bonds between oxygen and nitrogen atoms of neighbouring chains. In the case of silk, a 'pleated sheet' structure results. In turn, the sheets stack to form a three-dimensional, well-ordered, crystalline structure.

The tendency towards crystallisation is more pronounced for peptide chains containing smaller side groups that can be closer together, whereas the amino acids with bulkier side groups are generally part of a more irregular, amorphous structure. In silk, both types occur simultaneously, forming a mixture of crystalline and less ordered amorphous regions, and so the fibroin structure is described by the 'fringed micelle' model (see Fig. 2). Compared to other proteins, silk has a relatively high degree of crystallinity with fibroin β-sheet crystallites aligned along the fibre axis. The crystalline regions account for the high tensile and tear strength characteristic of silk fibres (Tímár-Balázsy and Eastop 1998). The amorphous regions are more open to all sorts of agents that cause alteration such as oxygen, humidity and salts, and other studies have shown that silk deterioration starts here (Crighton 1993).

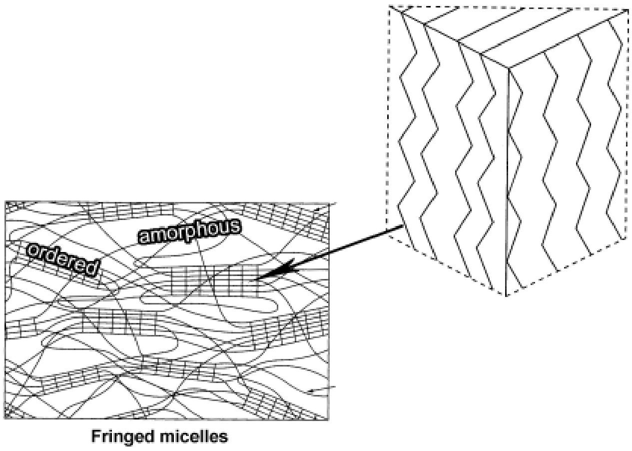

Figure 2 The silk protein fibroin consists of different amino acid chains that have combined to form pleated sheets. In the crystalline segments of silk these sheets appear as an orderly three-dimensional arrangement.

Samples

In this preliminary study, we wanted to test whether the selected methods (synchrotron diffraction and polarized IR spectroscopy) would be suitable for investigating the crystallinity of ancient silk. A small set of fibres was chosen according to the visual degradation characteristics of the material. Among them, some looked less aged and felt more elastic to the touch (sample FS 8-1b, Fig. 3) while others were from sections of silk bundles which were beginning to deteriorate, where the colour was darker and fibre lengths were restricted due to breakage on the joints of weft and warp threads. The most decayed samples came from fabric specimens whose structure was already lost with dark, very short fibre fragments being all that remained (e.g. FS 8-1a, Fig. 3). All samples were of the same colour (brown) to minimise the effect of a possible influence of the dye component on degradation.

- FS 1-1b: small particles, not flexible, no sheen and a dull brown colour
- FS 1-1c: more flexible than b with a bright sheen and a warm gold-brown colour
- FS 8-1a: amorphous, very fragile powder of fibre fragments
- FS 8-1b: flexible fibre from a section with a distinct fabric structure visible
- FDS 042-F1: fibre from a dry fabric that is starting to disintegrate from the edges
- Modern habutai silk as a reference

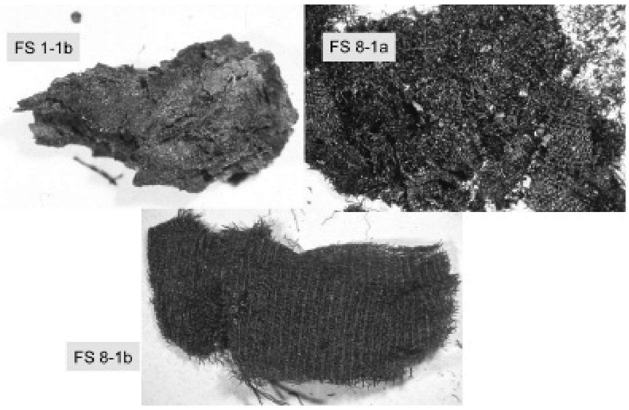

Figure 3 Samples were chosen according to their visual appearance, representing different stages of degradation.

Methods

Diffraction studies by synchrotron radiation

The most common methods for investigating the crystallinity of materials take advantage of the diffraction of X-rays. More accurate and detailed results are available from synchrotron radiation (Riekel and Vollrath 2001), which is introduced here as a new approach to studying silk decay processes. Apart from other advantages, synchrotron X-rays are extremely bright and intense.

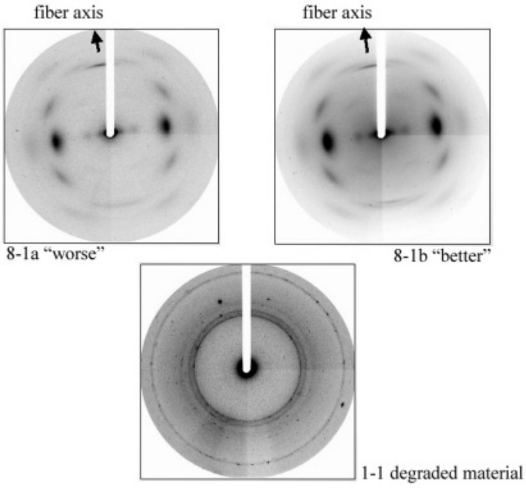

Figure 4 XRD patterns of different samples. Only the most degraded sample (FS 1-1) shows the typical faint and irregular spot shapes typical for non-crystalline materials.

The experiments were performed at the microfocus beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble.[2] Here a synchrotron beam with a diameter of 5 μm was directed to a fibre mounted on a sample holder. This allowed not only the investigation of single fibres but also different sections of one fibre. The resulting diffraction pattern should be a set of distinct regularly arranged spots in the case of any crystalline structure surviving in the silk fibres. The diffraction patterns obtained from three samples are given in Figure 4.

Despite the fact that visually, sample FS 8-1a appeared more amorphous, the diffraction pattern did not differ significantly from that of 8-1b (flexible fibre of better condition). In both cases, the pattern looked more or less regular and the single spots quite sharp. Sample FS1-1b, which was a fibre fragment taken from the edge of a brown dry piece of fabric, revealed a pattern of spots with an irregular hazy contour. These initial experiments suggest that the crystalline regions in a silk protein polymer may remain intact even if degradation processes have already caused a loss of integrity and decreased mechanical performance. Only in the final stages of deterioration, when degradation is sufficiently severe, are the crystalline regions also affected.

Infrared microspectroscopy

Molecules do not only interfere with X-rays – interaction with infrared (IR) radiation also results in effects that yield valuable information about the molecular structure of a compound. The IR beam is absorbed by molecules, which start to vibrate resulting in a reduction in the intensity of the beam. In the IR spectrum of a material, the relative beam intensity is plotted against the energy of the beam. A characteristic set of peaks is produced, each being assigned to a specific vibrational movement of the molecule or a segment of it. Crystallinity will influence the nature of the spectrum. Ordered arrangements may give sharper and more distinct peaks and the position of a peak may change with decreasing order.

The silk fibroin IR spectrum is dominated by peaks arising from the vibrations of the peptide links in the backbone. The amide I band is assigned to the peptide C=O stretching vibration with a small contribution from N–H in-plane bending. For crystalline β-sheets (like silk) this band lies near 1615 cm^{-1}, while for α-helices (like wool) and for a random coil arrangement it is around 1655 cm^{-1}.

By using a polarized IR beam it is possible to determine orientation information. A peak will only appear in the polarized IR spectrum of silk if the fibroin crystallites are aligned with the 'vibrational' direction of the beam. At any other angle, the peak will become weaker and may even disappear completely.

Four samples were chosen for the IR studies: FS8-1b (also used in the synchrotron studies mentioned above), FDS 042 F1, FS 1-1c, and a modern habutai silk as a reference.

Analytical procedure

Silk spectra were acquired using a Perkin Elmer AutoImage microspectroscopy system. The fibres were flattened in a diamond compression cell and then laid on a barium fluoride window. Transmission spectra were recorded of single fibres as an IR polarizer was successively rotated in 15° steps through 180°. Spectra were recorded over the range 4000–700 cm^{-1} at a resolution of 8 cm^{-1} for 32 or more scans, and were subsequently processed using Grams 32/v6 software. In each case, triplicate analyses were undertaken.

The friable nature of the archaeological silk specimens led to problems with handling the samples and preparing them for IR spectroscopic analysis; only the more pliable of the brittle specimens could be studied. To some extent, the problems were surmounted by turning to IR microspectroscopy rather than attenuated total reflectance (ATR) spectroscopy. This did not solve all the problems, however, suggesting that polarized IR spectroscopy is not best suited to microstructural analysis of the most fragile silks.

Degree of crystallinity

In order to assess the ratio of crystalline compared to amorphous regions in a silk fibre, the position of the amide I band was investigated in some detail because, as mentioned above, the position of the peak in the spectrum is different for crystalline β-sheet structures and random coils.[3] Since the amide I band for the crystalline β-sheets lies at 1615 cm^{-1} while that for α-helices and random coils is around 1655 cm^{-1}, the intensity ratio I_{1615}/I_{1655}, measured from standard spectra, can be used to define an IR crystallinity index, X. The higher the index X the higher the ratio of crystalline regions would be in a specific silk fibre.

Results

All the silks have shown the characteristic spectrum of a *Bombyx mori* silk fibre.

Table 1 shows the average value for X as well as the range achieved by different measurements.

Table 1 Results of the polarized Raman study with X representing the degree of crystallinity of a single fibre. Comparing the X-value of modern habutai silk against degraded fibres from Famen indicates that crystallinity is still high even for ancient silks.

	Habutai	FS 8-1b	FDS 042 F1	FS 1-1c
X	0.90	0.91	1.18	0.83
Range	0.85–1.10	0.90–0.91	–	–

The habutai silk was used as a standard for fresh non-altered silk protein. The X-value for the habutai silk ranges from 0.85 to 1.10, the variability in part being an inherent characteristic of silk but also reflecting experimental error. The X-values for the three samples from Famen spread around 1 and fall more or less into the range covered by modern silks.

Orientation of crystallites

Another question linked to crystallinity is the problem of preferred orientation of the crystallites. Are they aligned in a special direction and parallel to some extent or do they form a random distribution? If the crystalline segments of the protein structure were randomly distributed, the resulting spectrum should be identical for every direction of a polarized IR beam irrespective of the fibre orientation. If some structural features

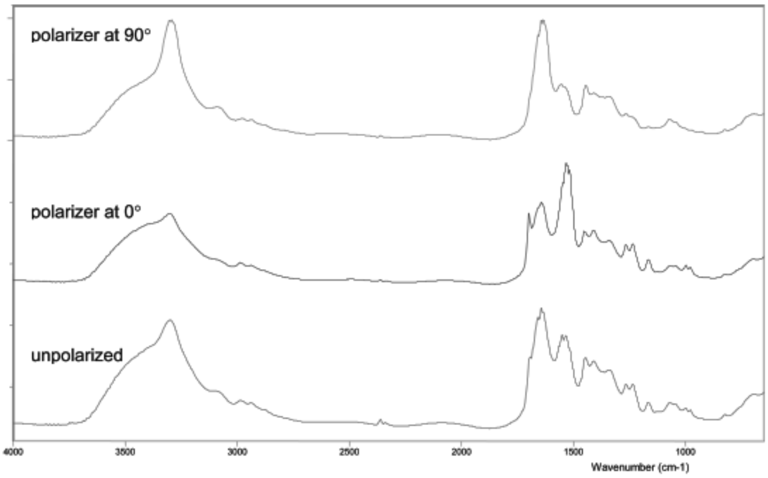

Figure 5 Unpolarized and polarized IR absorbance spectra for a silk fibre from the Famen specimen FS1-1c. The amide I peak at 1615 cm^{-1} dominates the standard spectrum in the fingerprint region. In this case, the response to polarized radiation indicates that there is still a small degree of ordering of the silk fibroin along the fibre axis.

were preferentially aligned then the associated IR peaks should be more pronounced in one direction of the polarized beam than another. By polarizing the IR radiation so that the electric vector is restricted to one direction and recording the IR spectrum as the fibres are rotated, the fibroin crystallite orientation becomes visible in the spectrum.

The spectral extremes should be reached when the silk fibres are aligned parallel (0°) and perpendicular (90°) to the electric vector. This is because the carbonyl groups of the amide bond running across the β-sheets in crystallites with a strongly preferred orientation are aligned *perpendicular* to the electric vector of the beam in the one case, but *with* it in the other. The absorption band at 1615 cm^{-1} is strong when the fibre is perpendicular to the electric vector.

Results

For recording the polarized spectra, the beam is restricted to one direction while the fibres are rotated.

Based on the X-value an orientation parameter, Ω, was defined which is the ratio of X values determined from spectra recorded with the IR polarizer set at 90° and 0°, so that $\Omega = X_{90}/X_0$. If Ω is high, which means that the β-sheet amide band at 1615 cm^{-1} is dominant compared to the α-helix/random coil band at 1655 cm^{-1}, then a large proportion of the peptide carbonyl groups is aligned with the electric vector of the incident IR beam. As shown in Table 2 this is the case for the modern habutai silk with Ω = 1. 57, but now the difference between modern habutai silk and the degraded Famen samples is more pronounced: while the ancient silk fibres cluster around Ω = 1, the value for modern habutai silk is much higher. This means that the new silk fibres show strong preferential orientation of the crystalline fibroin along the fibre axis, while the more degraded Famen silks have lost much of this crystallite ordering. Due to difficulties arising from the fact that fibre debris is hard to prepare for analysis, the most degraded samples could not be investigated.

Table 2 Results of the polarized Raman study with Ω representing the spatial ordering of crystallites within a single fibre. A marked difference exists between Ω of modern and naturally degraded samples.

	Habutai	FS8-1b	FDS 042 F1	FS 1-1c
Ω	1.57	0.95	1.07	0.94
Range	1.30–1.84	0.91–0.99	0.9–1.2	0.77–1.2

Conclusions

Both synchrotron diffraction studies and IR spectroscopy have proved useful for crystallinity studies on silk fibres. The samples ranged from modern fresh silk habutai to ancient fibres exhibiting very different stages of degradation based on visual assessment. The ancient fibres came from the Tang dynasty silk treasure from Famen Temple in China dating to the 9th century.

Both methods have shown that the crystalline portions of the protein structure remain quite unchanged until degradation becomes extreme and the fibres have lost their typical textile qualities such as sheen and flexibility. The XRD pattern, here using synchrotron radiation, does not change much with proceeding alteration; only the strongly altered sample gave a more hazy diffraction pattern with irregular contours. The same holds true when one looks at the ratio of crystalline to amorphous regions by means of IR spectroscopy. Data proved that the overall crystallinity is quite similar to modern habutai silk.

One factor that does appear to change when degradation proceeds, however, is the orientation of the crystallites. Results from polarized IR spectroscopy indicate that modern silk protein has a much stronger preferential orientation of the crystalline fibroin sections along the fibre axes than the ancient samples. So the data support the hypothesis that silk deterioration is initiated in the amorphous regions of fibroin and furthers our understanding of the silk degradation process.

While there may be no 'cure for the disease', with increasing knowledge of the mechanisms and factors influencing silk deterioration, preventive conservation may be more appropriately refined. In any case, defining the condition of valuable artifacts and monitoring their deterioration is crucial. Both of the methods we have investigated offer analysis at the level of a single fibre for the objective assessment of aged silks.

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Notes

1. In a study on microbial degradation, modern silk fibres were used (Seves *et al.* 1998).
2. For the basics of synchrotron radiation and experimental set-up on beamline ID 13 see www.esrf.fr/UsersAndScience/Experiments/ SCMatter/ID13.
3. *Cf.* TCC FTIR-report 12-2003 by Sophia Lahlil.

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