« Penny and Tim Hays Open Their "Just in from the East" Gallery

Richard Laursen on What Analysis of Dyes in Textiles Can Tell You and What It Cannot

On April 27, 2019, Richard Laursen,

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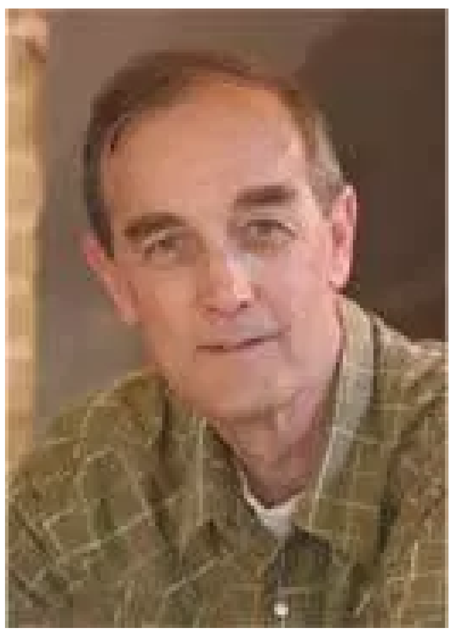

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a research chemist, emeritus at Boston University, gave a program to members of the International Hajji Baba Society, here at the Textile Museum in Washington, DC,, describing what analysis of dyes used in textiles can tell you and what it cannot.

Richard gave an illustrated lecture and a virtual version of that follows:

You can click on any image is this virtual version to get a somewhat larger version.

I will sometimes cue you to do that.

Slide 1

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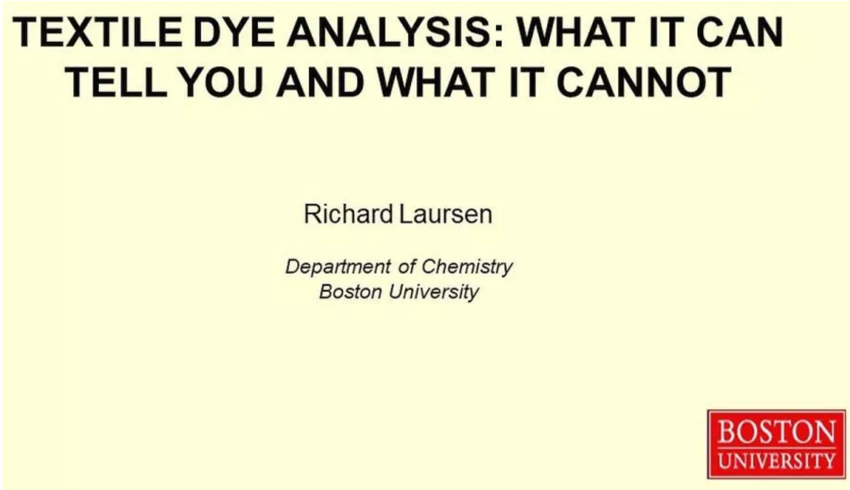

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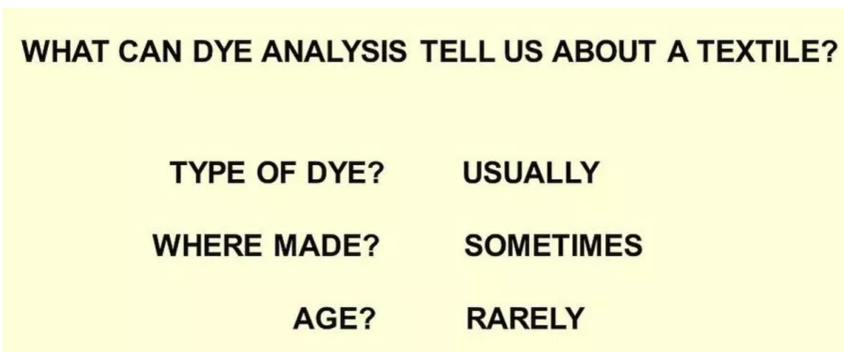

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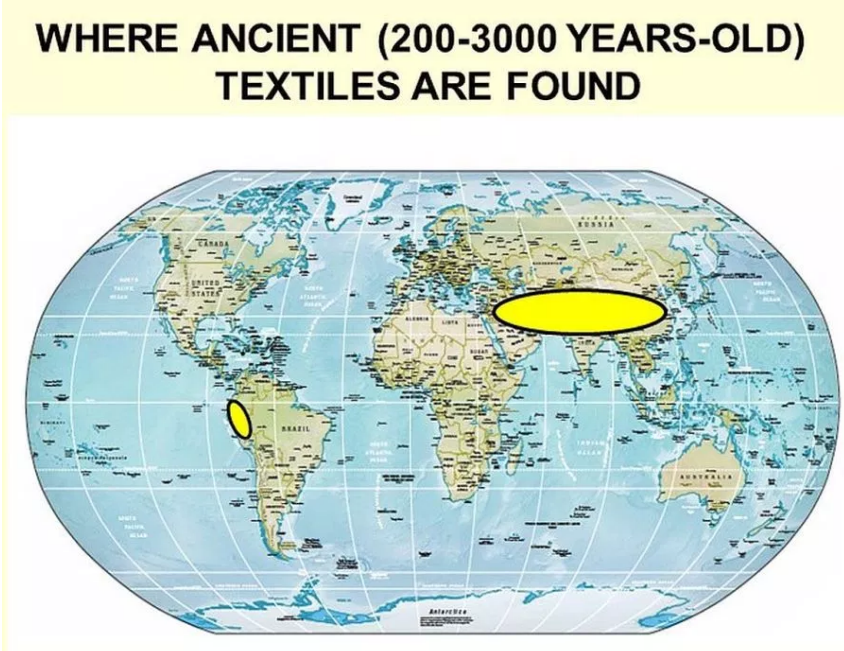

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The yellow ovals indicate where the bulk of the textiles came from. This is particularly true for ancient textiles because textiles are organic materials, which are usually destroyed (eaten) by fungi and other microorganisms found in soil and elsewhere. All living organisms require water and moderate temperatures to thrive, so ancient textiles are generally found in arid locations and in some tombs where they are not in contact with soil and/or water. Therefore, most of the textiles we have analyzed come from arid parts of Asia and the Andes of South America.

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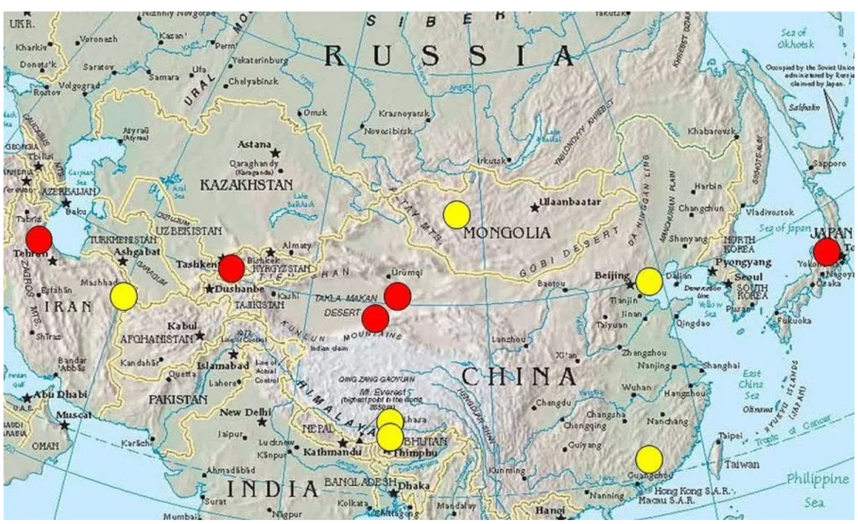

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The circles indicate where some of our samples have come from. I will talk about the red ones.

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First I will discuss the analytical methods we use.

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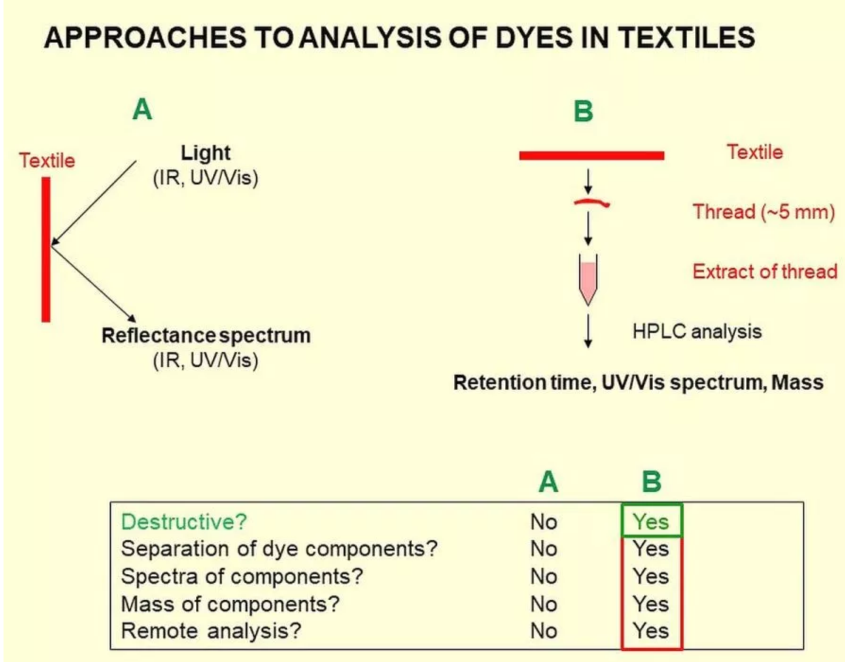

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There are two basic approaches to textile dye analysis. In method A, some sort of light is shown on the textile and the reflected light is analyzed. In method B, a small sample of the textile is removed, and extracted to remove the dye. The extract containing the dye is analyzed by high performance liquid chromatography (HPLC), which separates the components in the dye, and allows spectrometric and mass analysis of each.

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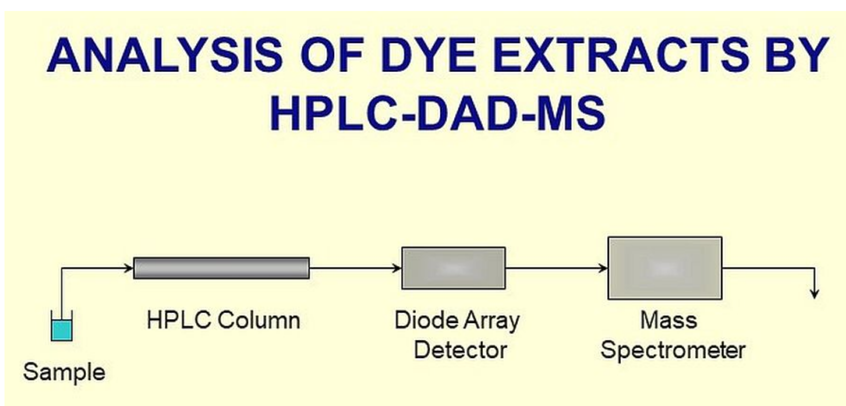

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This slide outlines the components of the analytical system we use. The sample is loaded onto the HPLC column, through which appropriate solvents are pumped to elute (wash) the separated components out. Each component is then analyzed by a Diode Array Detector (DAD) and by a Mass Detector (MD).

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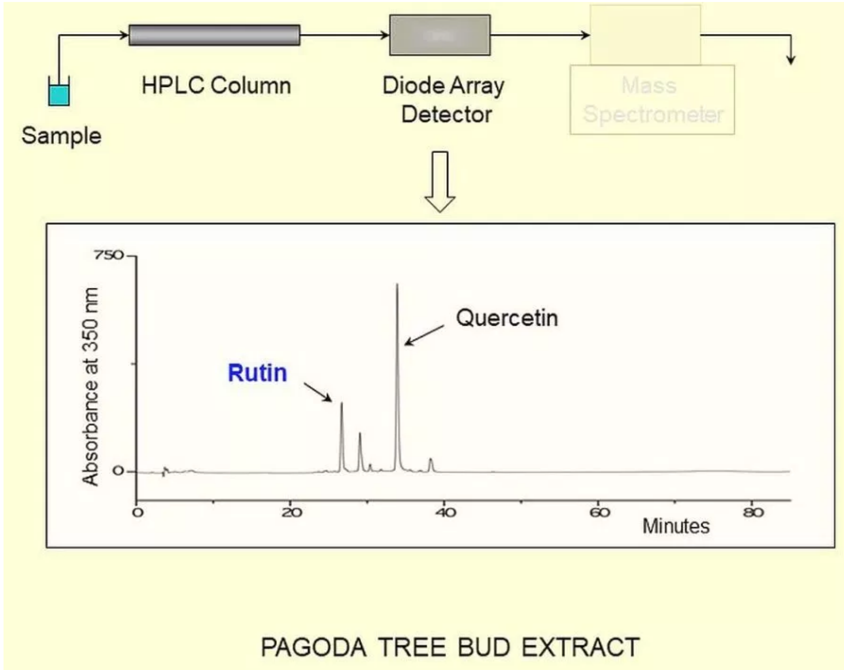

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The lower panel shows an elution profile, which is obtained after the separated components have passed through the DAD, only. Each peak represents a dye component—in this case of an extract of the yellow dye from pagoda tree leaves.

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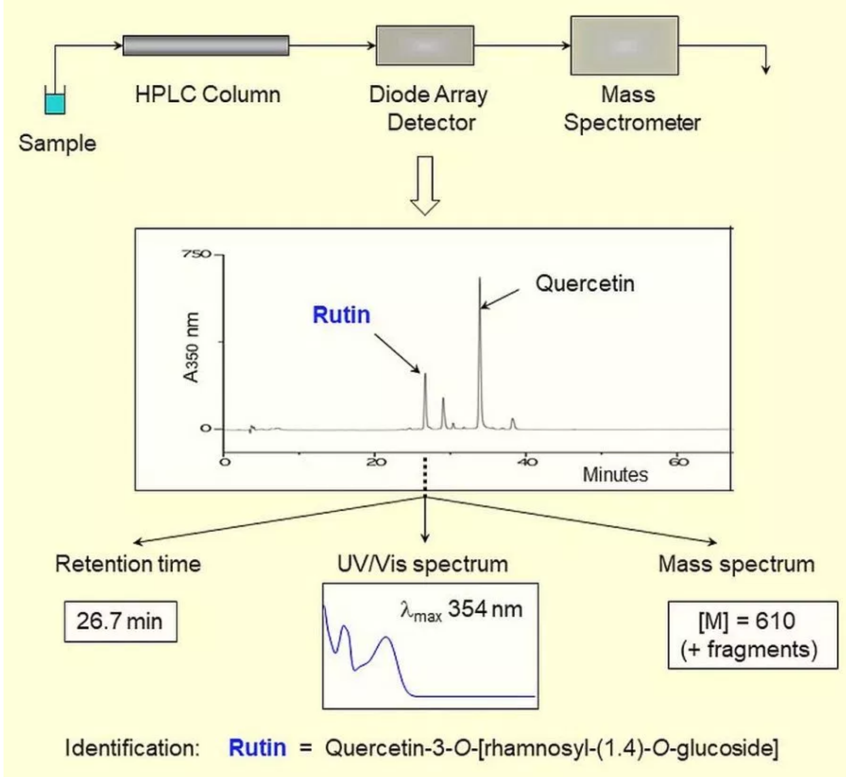

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From this type of analysis (method B) one can provide three types of information that characterize a particular dye component: (1) the retention time, which gives information about the polarity of each component, (2) the UV/Visible spectrum, which gives much information about the color and the class of the dye component, and (3) the molecular mass (molecular weight) of the compound. With three types of information, it is generally possible to identify a compound. In addition, the profile or pattern of compounds acts as sort of a "fingerprint" often allowing one to identify the plant or animal the dye came from. None of this possible using method A.

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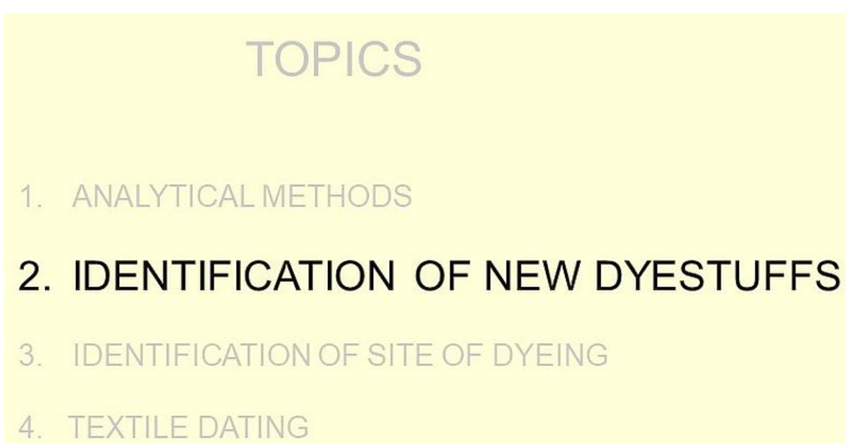

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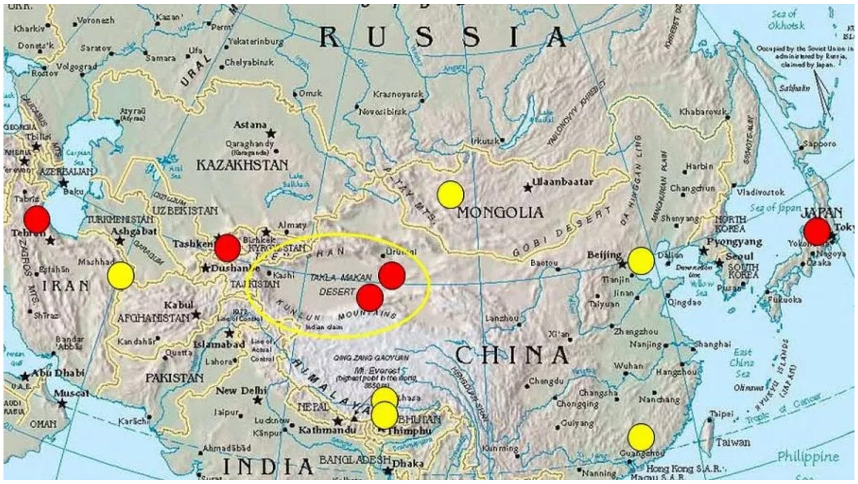

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One of the first textiles we analyzed came from fragments from Cherchen, a former village in the Taklamakan Desert region in Xinjiang, China. This is indicted by a yellow oval.

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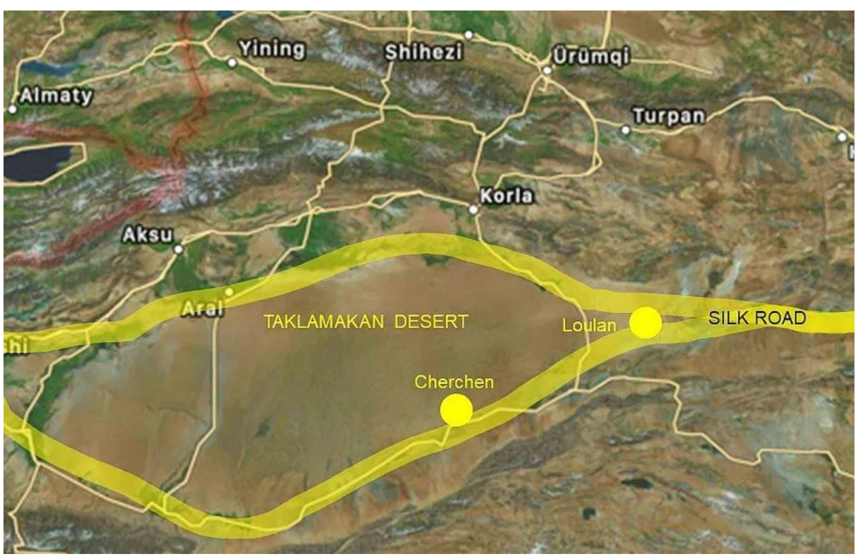

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This is an enlargement of the Taklamakan region. The yellow lines indicate portions of the old Silk Road that linked Europe and China. Traders in ancient times had to travel between oases either north or south of the desert. Cherchen was one of the oasis towns.

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Slide 14

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During the 1990s, archaeologists discovered, in a cemetery near Cherchen, the mummified remains of a man who had been buried nearly 3000 years ago. He was not buried in a tomb, but in a hole in the ground, but out of contact with the soil, and so he desiccated rather than decomposed.

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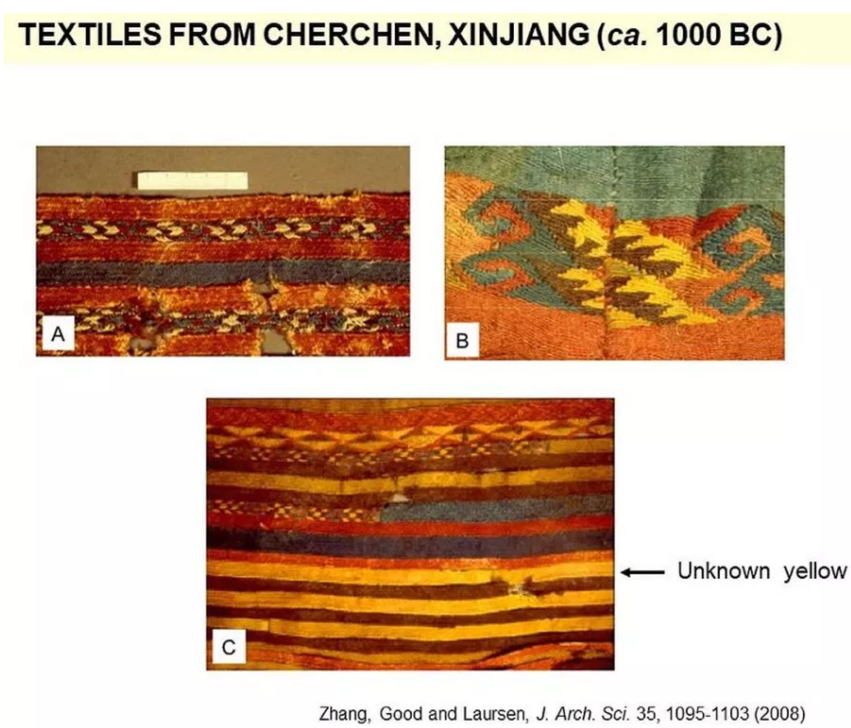

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Near the Cherchen Man were some textiles, which also survived nearly three millennia. Analysis of one of the yellow dyes revealed a dye compound that had never been reported before.

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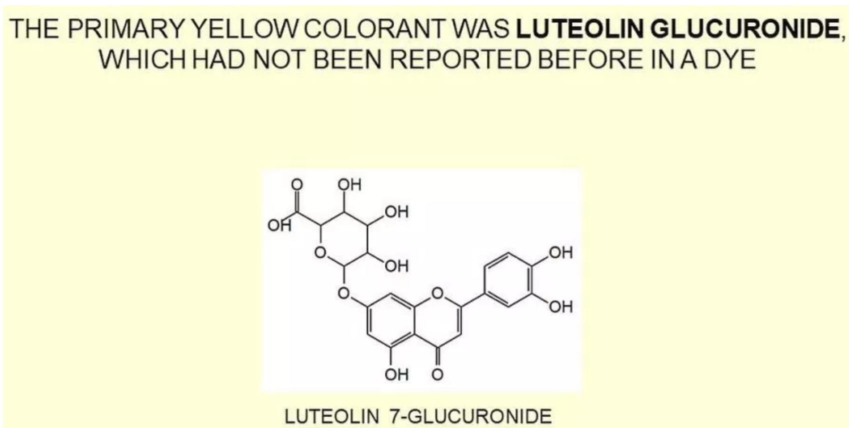

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The structure of this dye remained a mystery for several years, but eventually we deduced that it is probably the yellow flavonoid, luteolin glucuronide.

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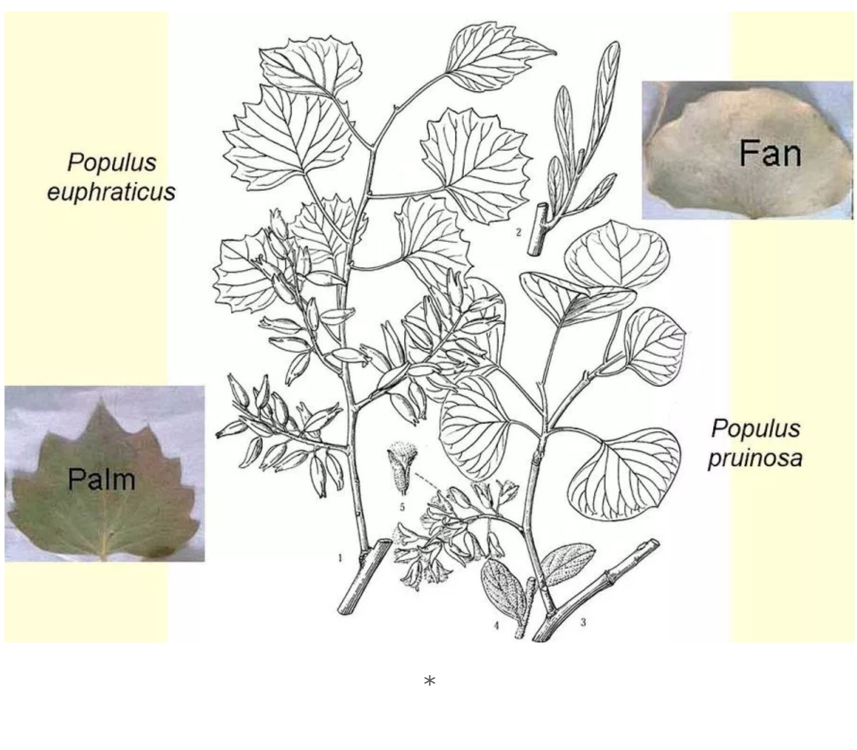

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All green plants also contain flavonoids (whose function may be to protect the chlorophyll in the plants from photo-oxidation; over 8,000 flavonoids have been chemically characterized so far), so dyers often used local plants as a source of yellow dyes—provided the plants contained sufficient concentrations of the flavonoids. It turns out that one of the plants that grows in profusion in the Taklamakan region is certain species of poplar tree. Two of these are *Populus euphaticus* and *Populus pruinosa* that have deep roots that allow them to grow along riverbeds that are filled with water from nearby glaciers in the spring but are dry in summer. The leaves of both these species of poplar tree contain luteolin glucuronide, so they may have been used to produce the yellow dye seen.

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We also found the same yellow dye in a sample (from the Victoria and Albert Museum in London) from Loulan, a former village in the Taklamakan region (see slide13).

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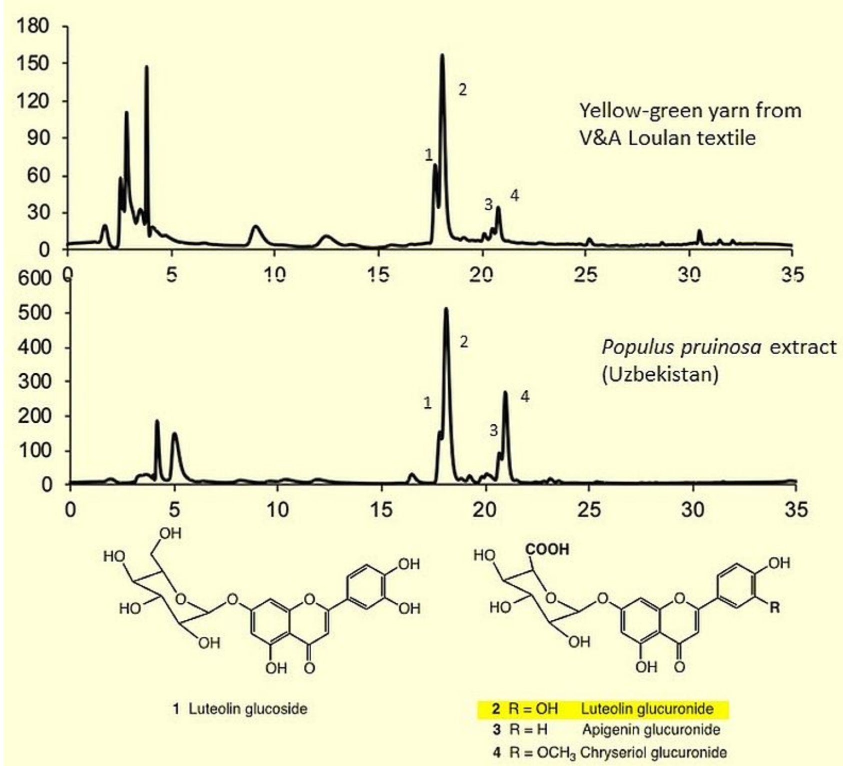

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This slide shows profiles of a yellow-green dye (flavonoid + indigo) from the V&A Loulan fragment and of an extract of *Populus pruinosa*, which are very similar. The peaks at < 5 minutes are "garbage" peaks and can be ignored.

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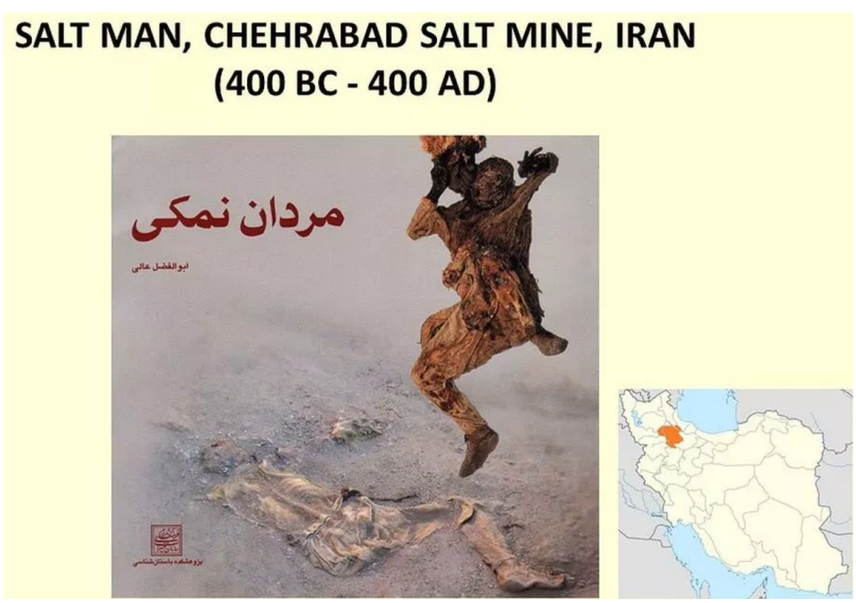

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During the past 25 years or so, archaeologists in Iran have found the mummified remains of 5 or 6 men in the Chehrabad salt mine

near Zanjan, Iran, that dates back to about 400 BC. Apparently these are the remains of miners who were killed when earthquakes brought the roof down on them. Other organic artifacts were found, too. These objects (including the miners) were well preserved because not only was the mine dry, but also because salt is a good preservative. These artifacts are interesting also because they belonged to poor people, rather than potentates who were often buried in tombs wearing special clothing, etc., so the dyes in these objects give a picture of what average/poor people were wearing.

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Slide 21

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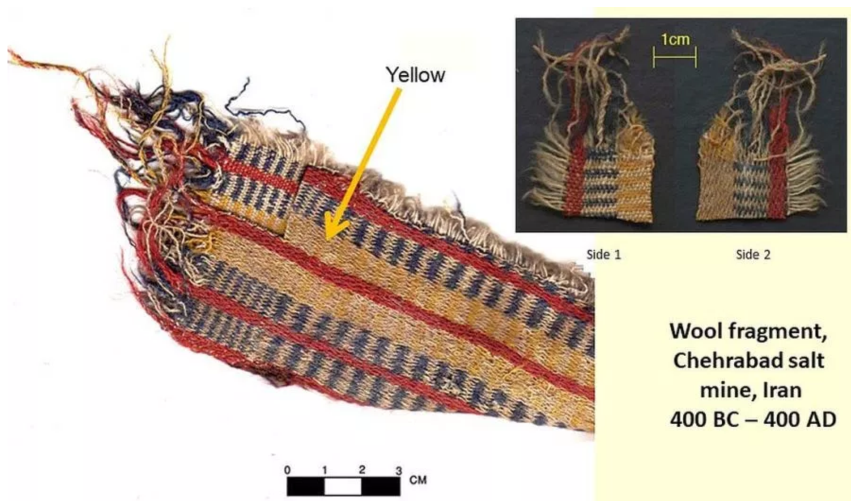

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The object we analyzed was a multi-colored belt of some sort. The left-hand side of this slide shows part of the original object, and the right-hand inset, the front and back views of the (relatively huge) sample we received. [One can also see in the original where our sample was cut out.]. The blue and red colors were from indigo and madder (*Rubia tinctorum*), respectively].

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Slide 22

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This slide shows in the background, the Chehrabad salt mine. In the yellow dye we found an unusual flavonoid sulfate (see inset). It turns out that this compound is found in many species of tamarisk, which is one of the few plants that flourish in dry, saline locales. We suspect that this may have been used to make the yellow dye, because it was readily available locally and the people who used it probably were too poor to buy something more expensive. Flavonoid sulfates have been reported in only one other dye plant—in Peru.

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Slide 23

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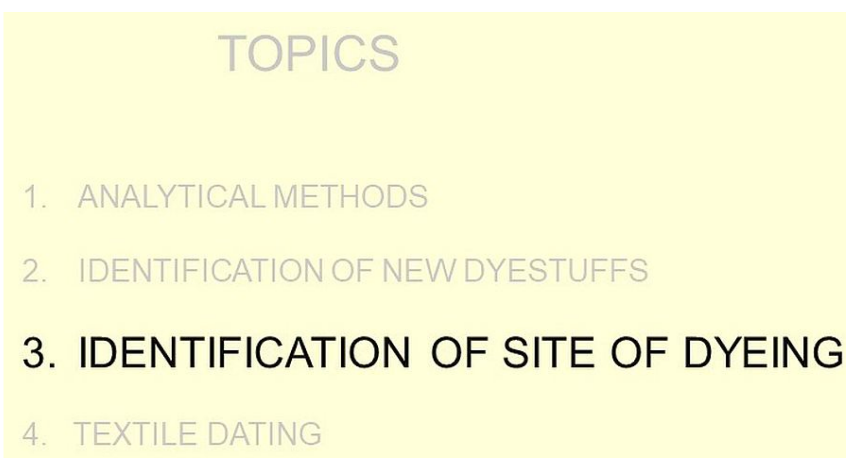

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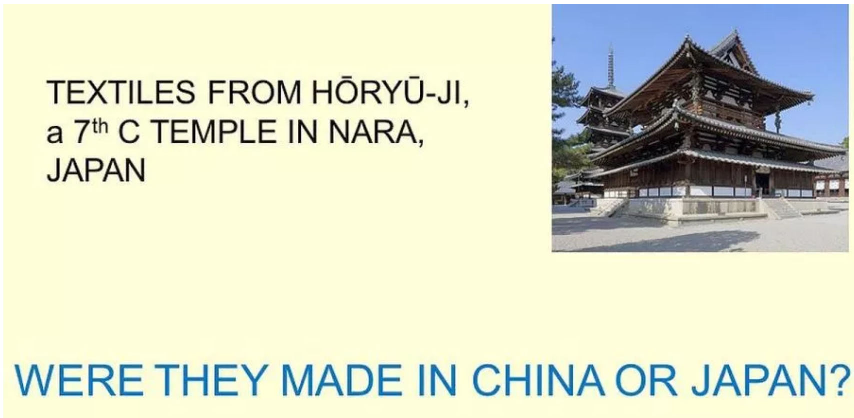

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Horyu-ji is a Buddhist temple founded in 607 AD and is the oldest wooden building in Japan. A number of textiles have been stored there for centuries. In the seventh century, the Tang Dynasty, in China, was close to its cultural apex and many things were imported into Japan from China.

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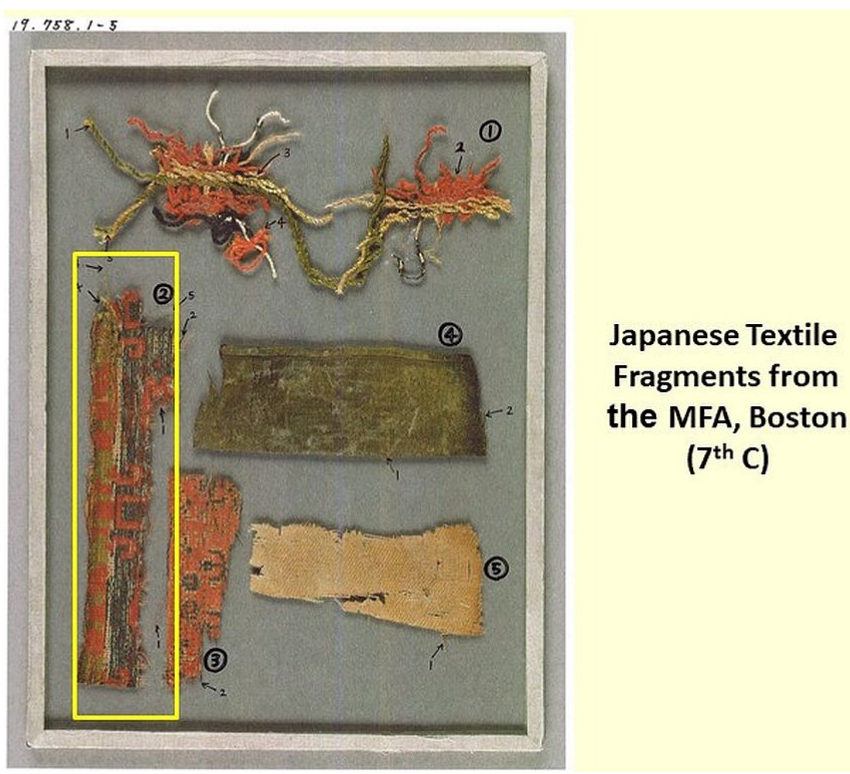

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A number of textiles were stored at Horyu-ji. Apparently, sometime in the late 19th C or early 20th C, monks at Horjyu-ji were hard up for money and sold fragments of some of their textiles to collectors. Some of these fragments eventually made

their way to the Museum of Fine Arts in Boston. This was fortuitous because nowadays all textiles (and other objects) from ancient temples and tombs are considered property of the Imperial Family of Japan and removing samples for analysis is absolutely forbidden. However, the MFA fragments left Japan before this ruling and are not subject to the aforementioned rule. This slide shows several fragments, but the one of interest is that outlined in the yellow oblong box. Unfortunately, the back side of the object is shown and not the front.

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Slide 26

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If that fragment is turned over, it can be seen that the pattern on it matches closely the pattern on a larger Horyu-ji textile that is currently in a museum in Japan and is shown in a book by Yoshioka. The fiber is silk.

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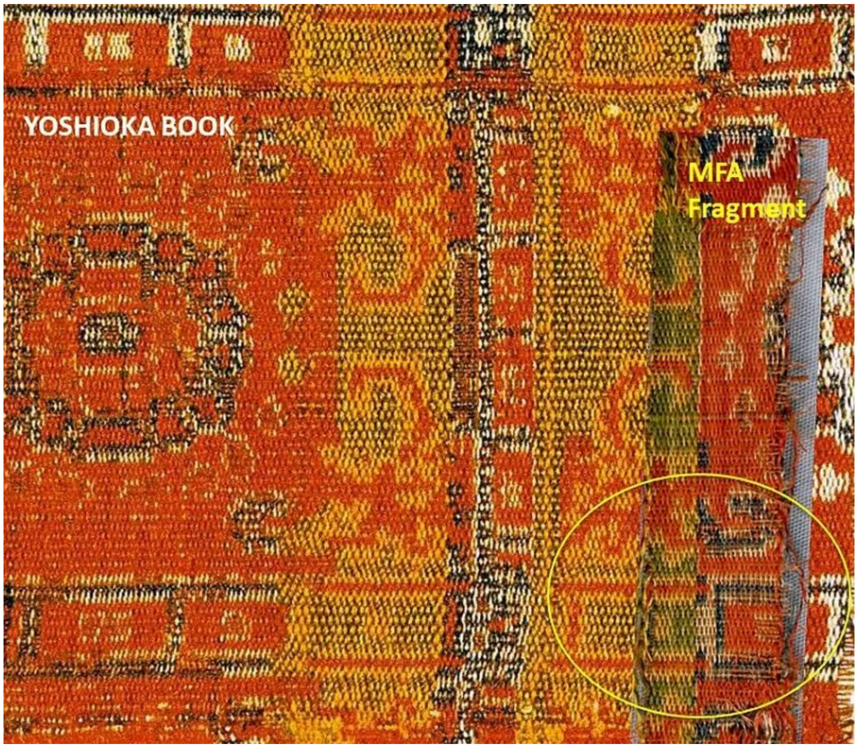

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This is seen better if the fragment is superimposed on the larger textile.

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Slide 28

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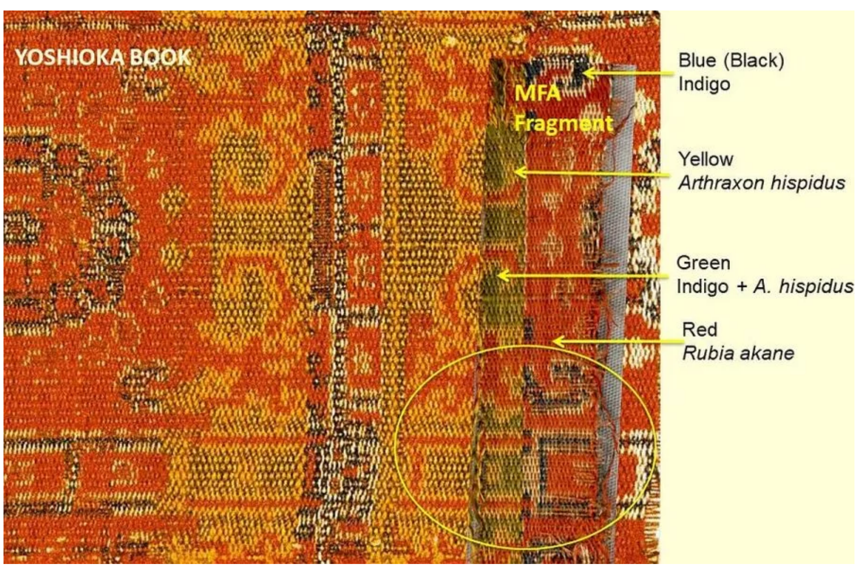

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We then analyzed several colored threads from the MFA fragment and found the following:

Black Indigo (heavy dyeing gives a very dark, almost black color)

Yellow from the grasses, *Arthraxon hispidus* or *Miscanthus sinensis*

Green Indigo (blue) + *A. hispidus* or *M. sinensis* (yellow)

Red   Madder (*Rubia akane*)

Since both *Rubia akane* and *Arthraxon hispidus* are now used only in Japan, we initially deduced that the textile threads (this textile was woven with colored threads) had been made and dyed in Japan.

Interestingly, the black threads in the Yoshioka textile seem to be more worn than in the MFA sample, and the green is more pronounced in the MFA fragment. This is consistent with the presence of indigo, which tends to coat the surface of fibers and sometimes wears off. The same phenomenon is seen with Levi's jeans, in which the blue indigo rubs off at the wear points (e.g., knees).

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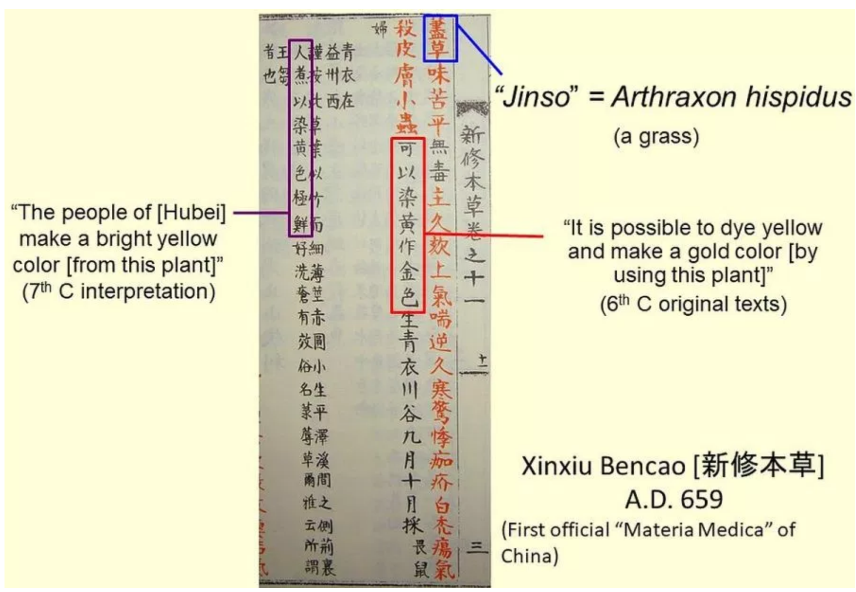

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The foregoing suggested that the textile threads had been dyed in Japan. However, when my colleague, Chika Mouri, who has background in traditional Japanese medicine, consulted the *Xinxiu Bencao*, the first official *Materia Medica* of China, which was originally written in the 6th C, she found that *Arthraxon hispidus* had been used as a yellow dye in China *before* Horyu-ji was even constructed. Furthermore, in our own research we had found species of madder from China that had characteristics of *Rubia akane* which is found primarily in Japan. Therefore, the textile we analyzed could have been made in China. In fact, it probably was, because in those days, China was considered to be sort of the "motherland" for Japan and many items that were considered to

be of high quality were imported from China. Two of the more important of these were silk and the writing system.

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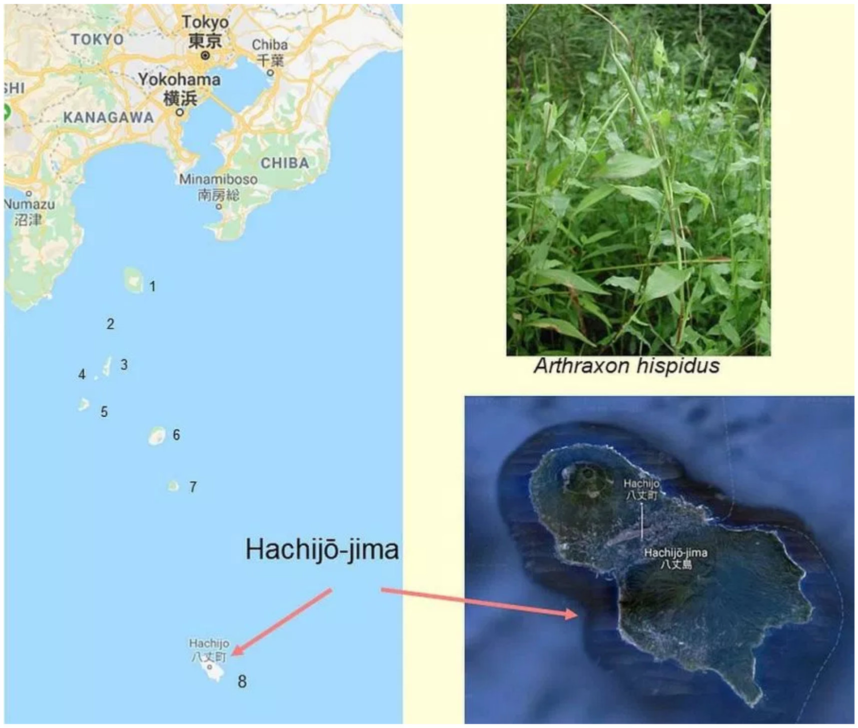

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The association of *Arthraxon hispidus* with Japan comes from the fact that, even today, a yellow dye is produced from this plant only on the island of Hachijo-jima. "Hachi" means 8 in Japanese and it is the 8th in a string of islands south of Tokyo. Hachijo-jima itself is was formed by two now-dormant volcanoes. The dye is called "kihachijo" (literally, "yellow of Hachijo).

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Slide 31

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Kihachijo is used to dye silk a muted yellow color, along with a reddish brown and a black color, which are woven to make (expensive) kimonos and other products (see https://www.youtube.com/watch?v=fqjbat5bILI).

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Slide 32

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This slide shows two of those kimonos. [One of the volcanoes can be seen in the background of the un-cropped photo below.]

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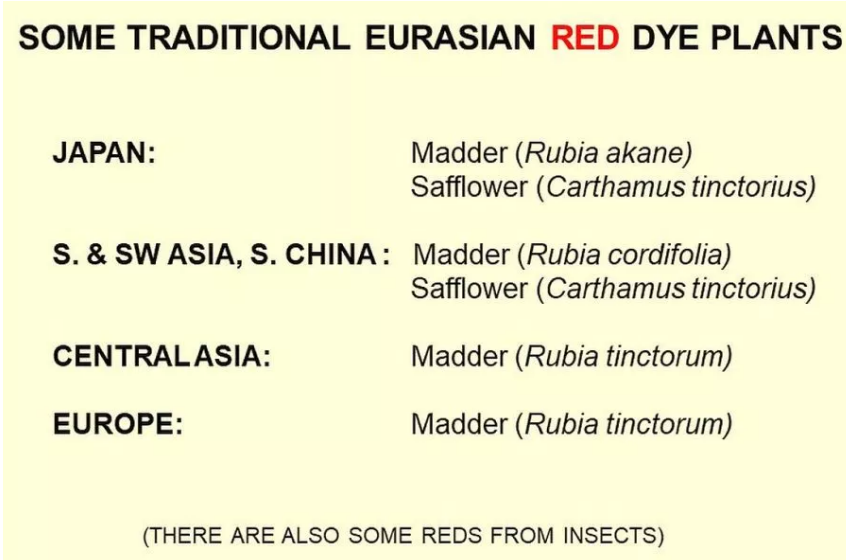

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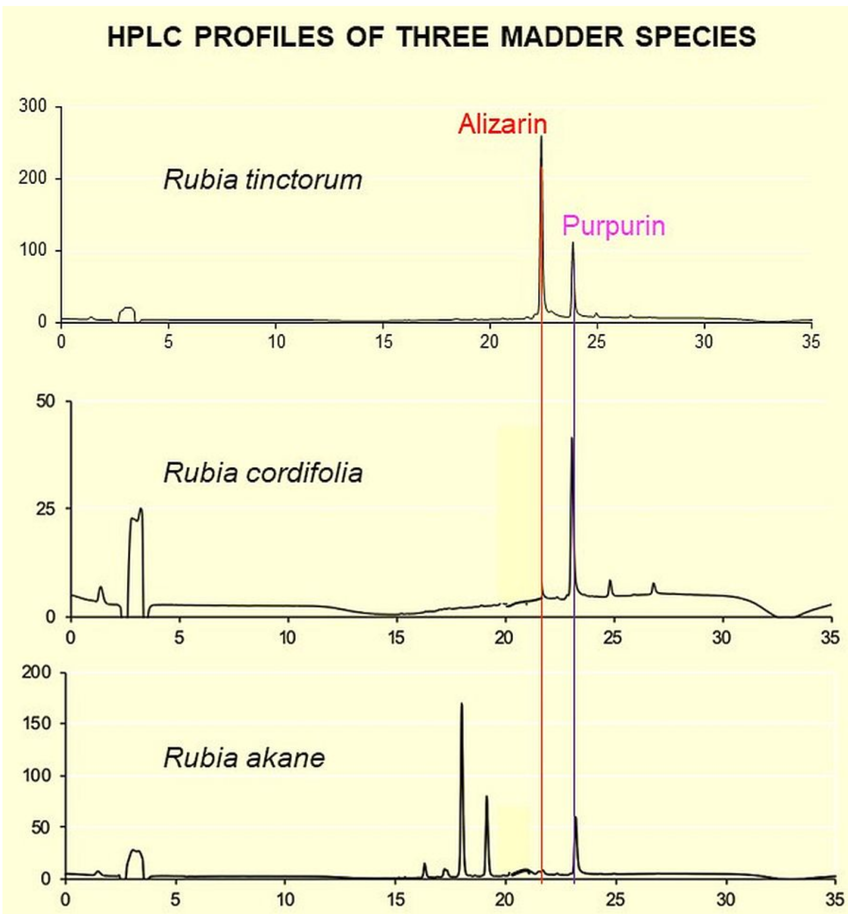

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There are three commonly used species of madder in the world today. These are easily differentiated by HPLC. All contain the red dye, purpurin, but differ in their content of alizarin or other red components.

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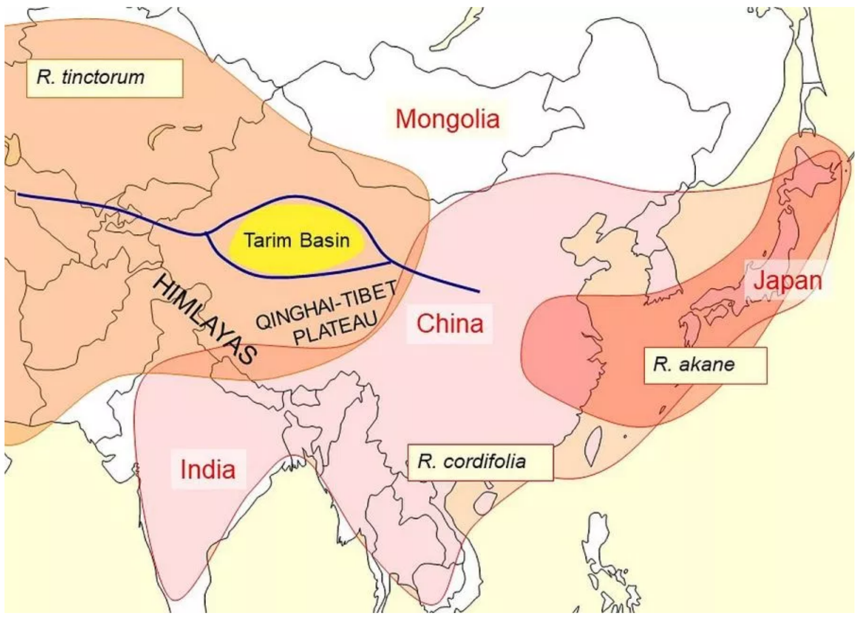

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This slide shows an approximation of the growth ranges of the three species of madder. *Rubia tinctorum* is the species most commonly seen in Europe, the Middle East and Central Asia, including Xinjiang. There is sort of a natural barrier formed by the Qinghai-Tibet Plateau and the Himalayas that seems to separate the growth ranges of *Rubia tinctorum* (to the west) and *Rubia cordifolia* (to the east and south). *Rubia akane* is found in Japan, though it or related species are also found in China.

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Slide 38

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There is only one natural blue dye—indigo. It is produced by many plants, but at present there is no way to determine which plant produced it. It is like table sugar: there is no way to tell whether sucrose was made from sugar cane or sugar beets.

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Slide 40

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This story starts in Xinjiang, China. In 2004, my daughter and I were on a post-conference tour in Xinjiang and stopped at a Kazakh yurt that actually was a sort of luncheonette.

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Slide 42

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During that lunch, we happened to be seated next to a fellow named Guy Petherbridge (on the right; my daughter is on the left), who was head of Heritage Central Asia, a U.N. organization headquartered in Tashkent, Uzbekistan.

This turned out to be fortuitous because we had already explored parts of the Silk Road in China, to the east, and I thought it would be interesting to look at the silk road from the west. So the next year we went to Iran, Turkey and Uzbekistan. Because Guy Petherbridge was my only contact in Uzbekistan, I wrote to him, and he kindly arranged for us to visit, Tashkent, Samarkand, Bukhara and the Ferghana Valley, complete with a car, driver and interpreter.

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Slide 43

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One of the places we visited was the Samarkand Museum of Applied Art, where we found, in the storeroom, a very nice suzani, which, it turned out, had been dyed only with natural dyes.

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Slide 44

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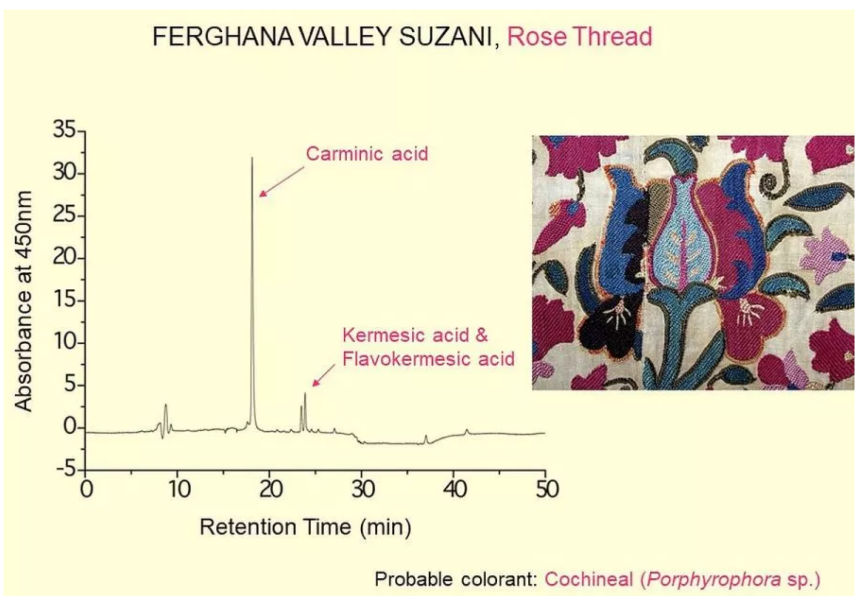

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Later we received, from a collector of suzanis in Germany, a sample of thread which had been dyed with an insect dye (cochineal), which is distinguished by a large carminic acid peak. This was probably an Old World species of cochineal, rather than Mexican cochineal, but it was not possible from these data to be sure.

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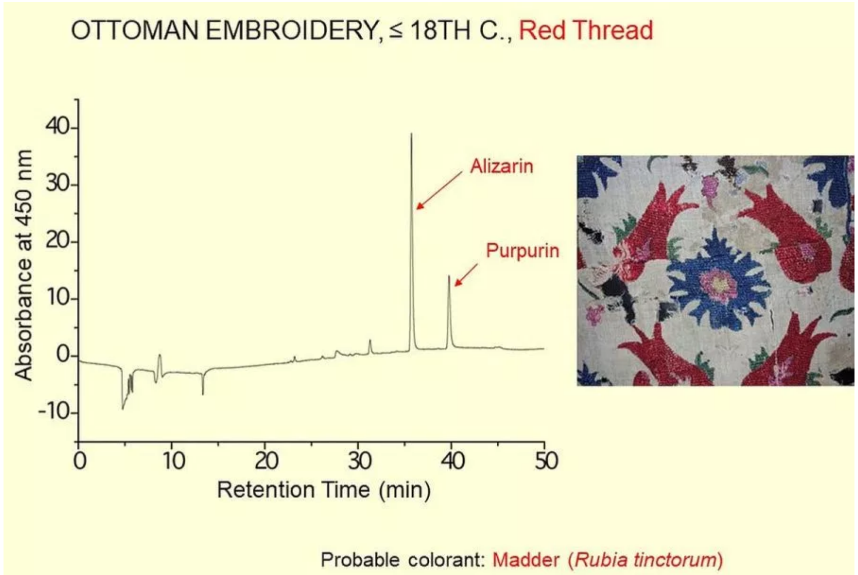

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The same collector also sent a red thread from an Ottoman embroidery that had been dyed with madder (*Rubia tinctorum*), which could be distinguished by the presence of alizarin.

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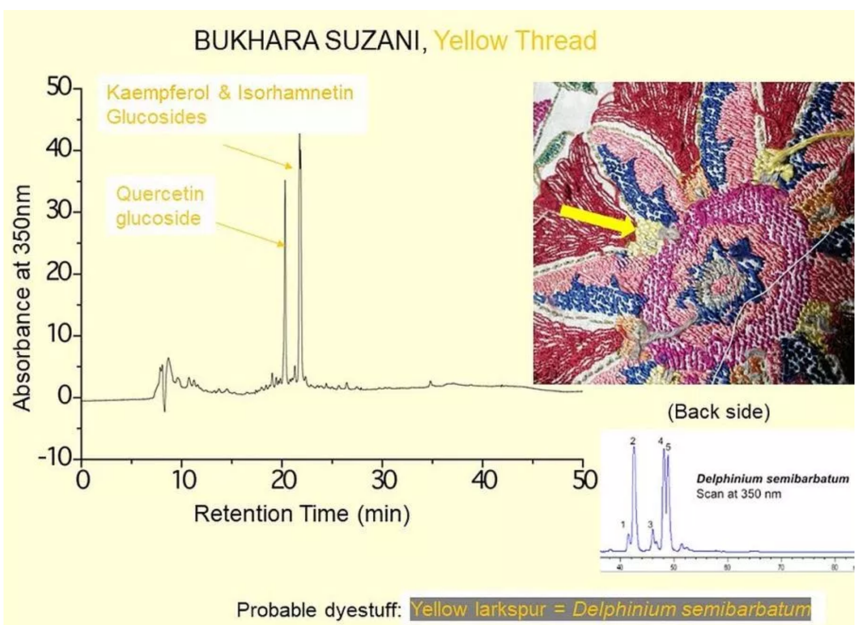

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A yellow thread from a third sample had been dyed with yellow larkspur (*Delphinium semibarbatum*), a very common source of yellow in Central Asia.

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Most species of *Delphinium* are blue, but these are yellow.

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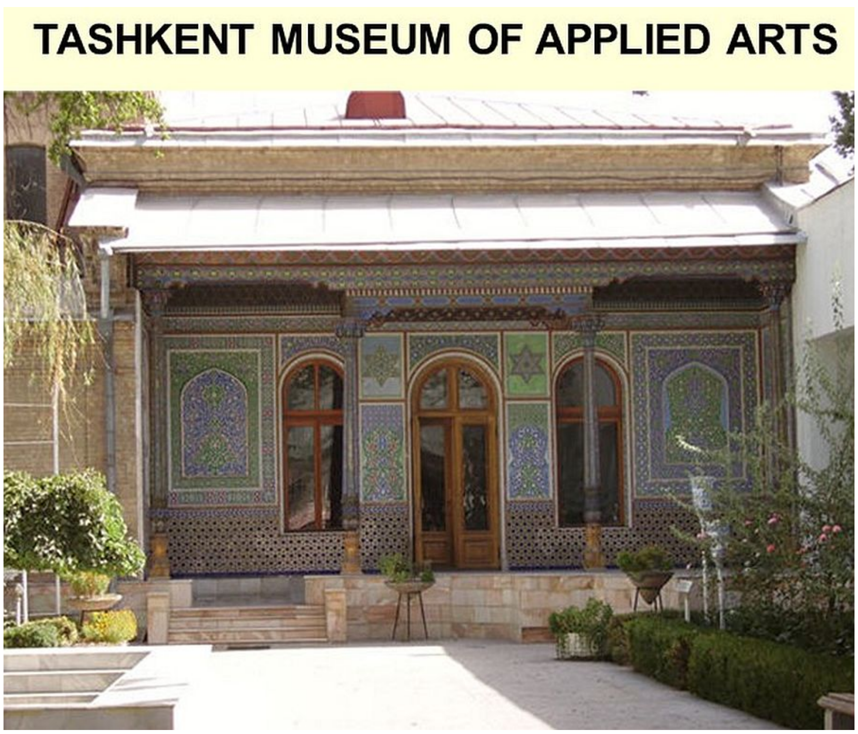

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We also visited the Tashkent Museum of Applied Arts. This had been the home of a government official in the late 1920s and was probably a private residence before that.

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The first gallery in this museum contained a number of suzanis, the very first one being that shown here. Shown here are Svetlana Osipova (facing the suzani) who arranged the visit, her husband (on the left) and a museum attendant on the right. The pair of legs, showing, below the suzani belong to the Museum Director, who was clipping off, using an enormous pair of scissors, loose embroidery threads for us to analyze.

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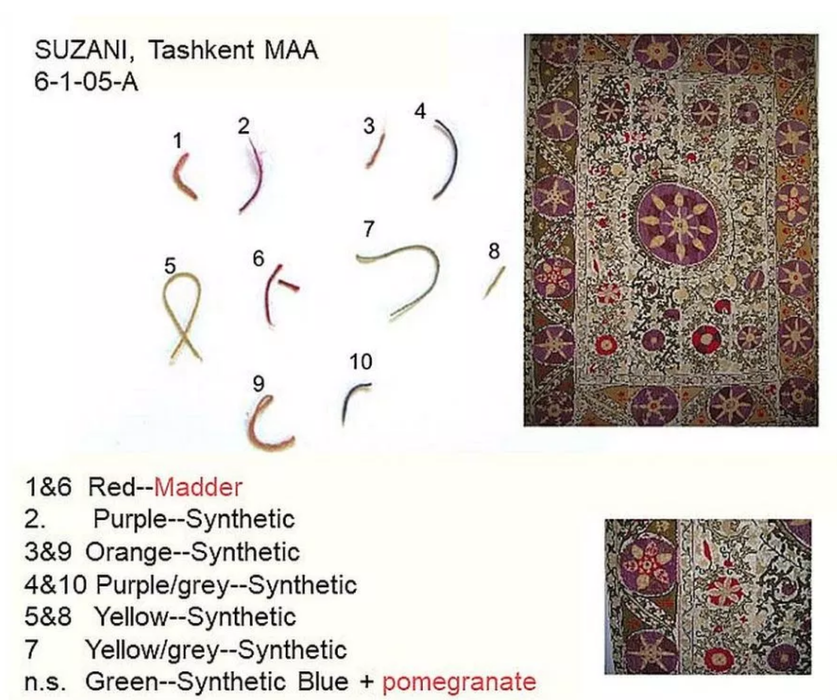

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This slide shows the suzani, some of the threads analyzed and the results of the analysis. Although a few of the threads had been dyed with natural dyes, most of them were dyed with synthetic dyes, which means that this object was embroidered *after* 1865, when the first dye was synthesized by Perkin. This also means that this suzani was not made, as claimed, during the first half of the 19th C. In retrospect, the purple color that is predominant in this suzani should have been a tip-off, because that shade of purple cannot be made using natural dyes.

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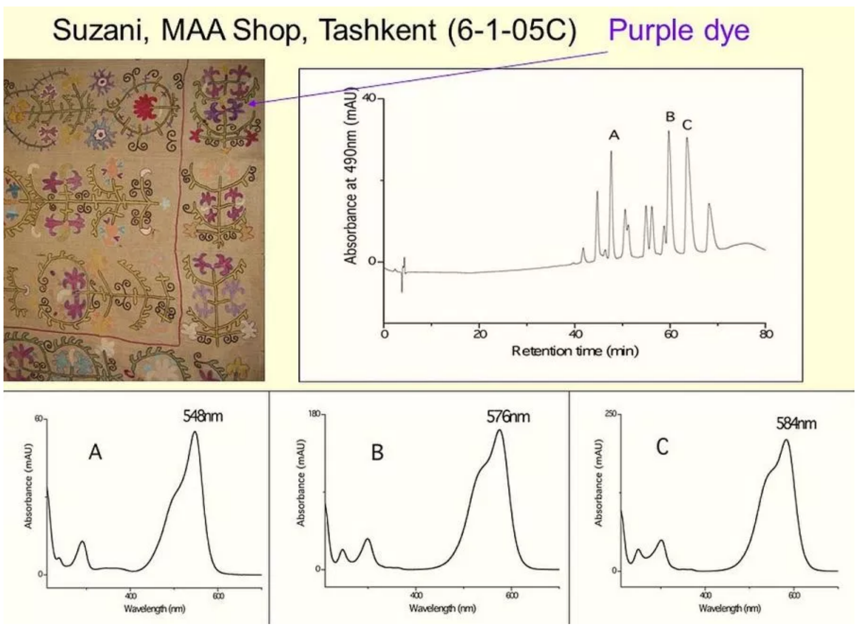

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We also analyzed the purple color from another suzani in the museum shop. This slide shows that the dye was a complex mixture of colorants. Visible spectra of some of them (peaks A, B and C) all have the same shape (a peak with a shoulder on the left) that is characteristic of triphenylmethine dyes, but have different shades of purple.

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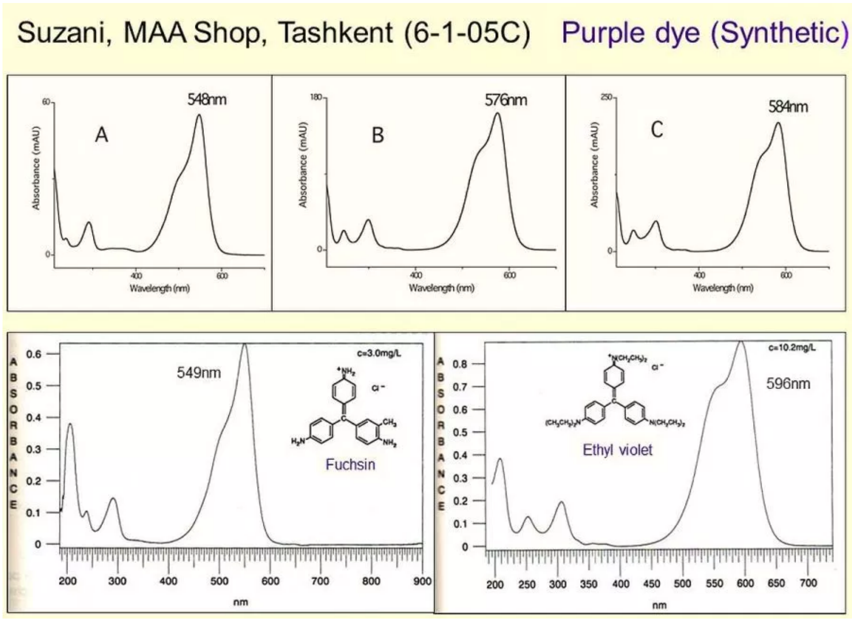

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We do not know precisely what compounds these are, but they are very similar to fuschin and ethyl violet, which were among the earliest commercially available synthetic dyes.

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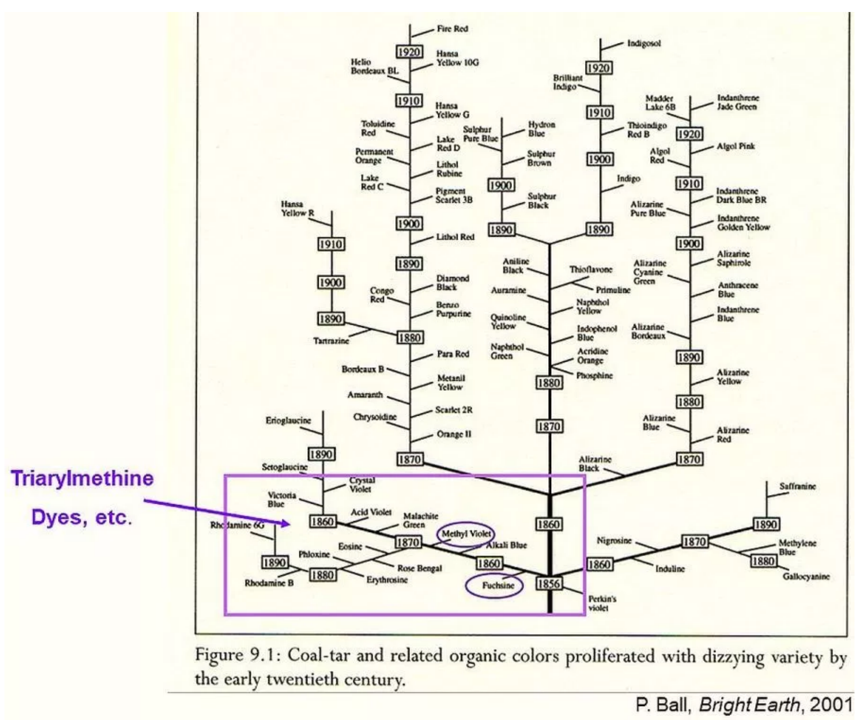

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The synthesis of the purple dye, mauve, by Perkin set off a revolution, resulting in the synthesis of hundreds of dyes by the end of the 19th C. The "tree" shown here indicates some of them. Note that the triarylmethine dyes were among the earliest.

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The synthesis of mauve also set off a revolution in the fashion industry. Everyone (women, at least) wanted mauve-colored garments, such as the gown on the left. This included Queen Victoria, although the color of the gown shown (at the right) in the recent TV series, Victoria, is not quite right (nor is the coffee cup and truck behind).

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Slide 56

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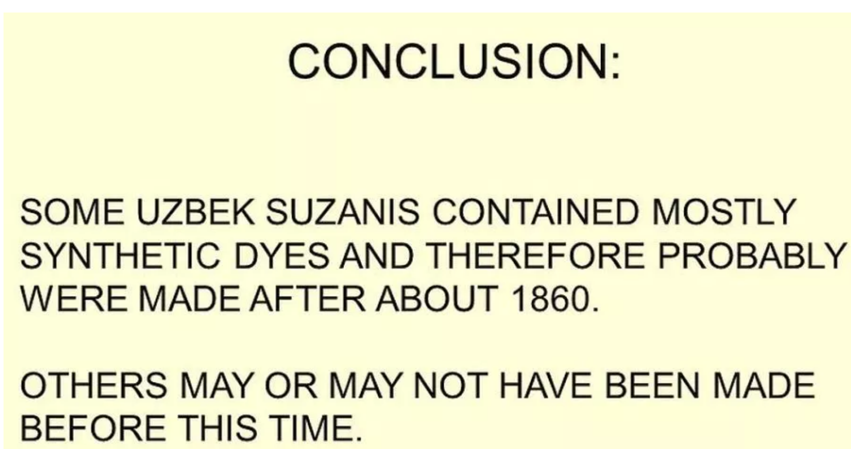

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Slide 57

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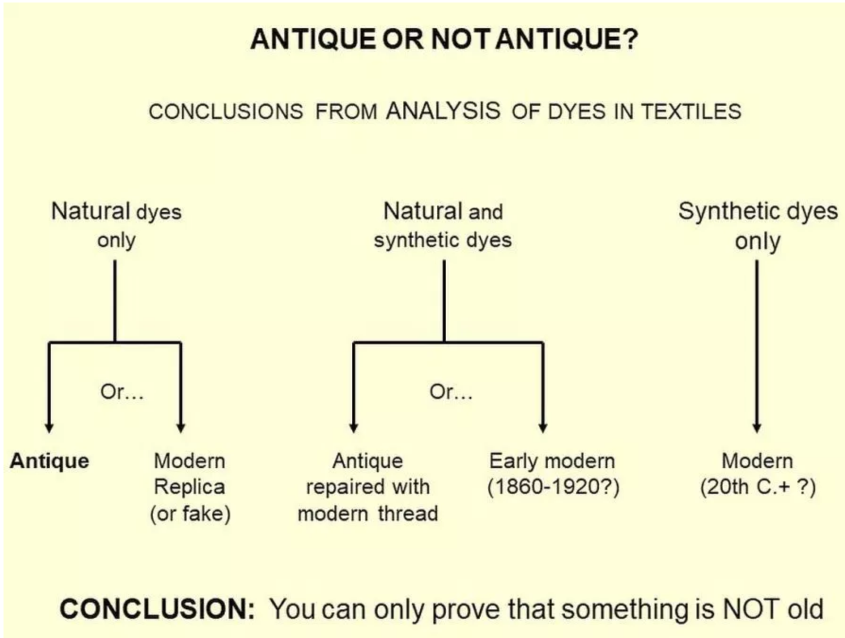

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Slide 58

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I would like to acknowledge the two people who did most of the laboratory work described here. On the right is Xian Zhang, my last PhD student, who initiated the textile dye analysis project and developed the early methods; and Chika Mouri, who came to me from Japan with a Ph.D. in traditional Japanese medicine and from whom I learned a lot about plants during the two years she spent with me in Boston.

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Slide 59

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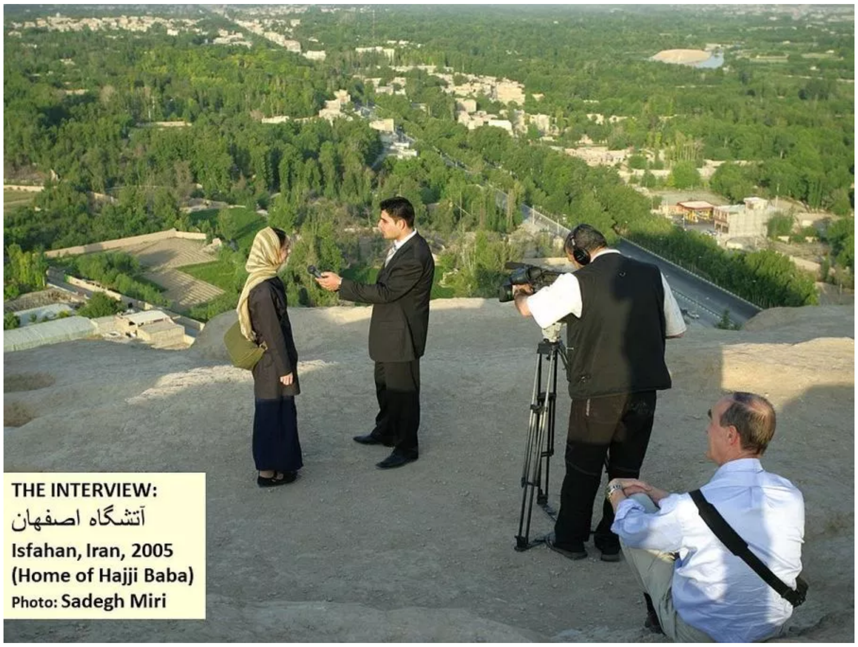

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This picture has nothing to do with the foregoing material, but it is an example of the interesting things that can happen when traveling. Before going to Uzbekistan, my daughter, Sarah, and I spent nearly a week in Iran. Late one afternoon while being driven along a highway in Isfahan (the home of Hajji Baba), our host, Sadegh Miri (https://www.instagram.com/sadegh_miri_photography/?hl=en) pointed out a little hill ahead of us on the otherwise flat landscape. "There's an old Zoroastrian fire tower up there," he said. Sarah, an art historian, said, "Let's take a look at it." So we pulled over and clambered up the hill, with Sarah in the lead, despite her long Iranian-style manteau. When Sadegh and I got to the top, we discovered Sarah being interviewed and filmed by two men. It turned out that they worked for Lebanon TV and were interviewing whoever came up the hill. They were probably as surprised to see Americans there as we were to see them.

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Richard took questions and brought his session to a close.

I want to thank Richard for coming to give this important program, and for working with me after to fashion this virtual version of it.

Michael Kaplan and Jeff Krauss produced this program. Thanks to Tom Goehner for arranging the use of the Textile Museum's Myers Room for this session.

A number of people asked me whether there was to be a virtual version of Richard's program, and here it is.

Enjoy.

'Til next time,

R. John Howe

Here is some additional information on Richard's background, interests and career:

Richard Laursen obtained his BS (1961) and PhD (1964) degrees in chemistry from the University of California at Berkeley, and the University of Illinois at Champaign-Urbana, respectively. After two postdoctoral years at Harvard University, he joined the chemistry faculty at Boston University, where he conducted research in protein chemistry for about 35 years. Following sabbatical leave in the Sherman Fairchild Conservation Center at the Metropolitan Museum of Art, New York, he turned his attention to the analysis of natural dyes in textiles of historical interest—in particular development of new techniques for extraction of dyes from textile specimens and their analysis. For more information, see also: http://www.bu.edu/chemistry/faculty/laursen/ and (for publications) http://www.bu.edu/chemistry/faculty/laursen/publications/

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