

## The materials chemistry of Chinese guqin zithers— Decoding the mysteries of an intangible cultural heritage

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This article is dedicated to Professor Tien-Yau Luh for his contributions to chemical education in Taiwan

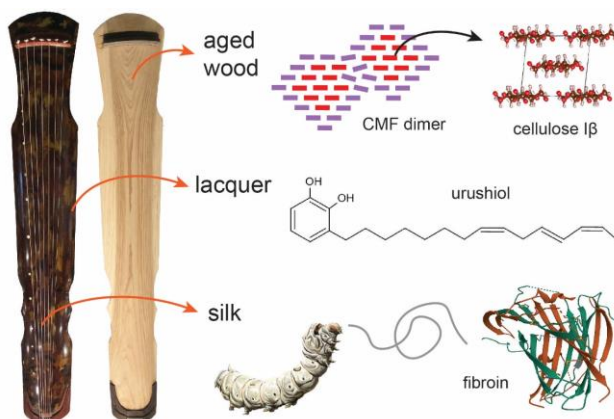
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### Abstract

The guqin, a seven-string Chinese zither invented three thousand years ago, is made of natural organic materials. For optimal acoustics, ancient makers used highly selected materials and experimented with complex manipulations. The sound box was carved from aged wood and artificially aged wood. The urushi lacquer contained organic additives, inorganic additives, and volume-extending particles. The silk string was coated with collagen, starch, and herbal extracts. Here, we review guqin-making materials and methods in ancient records and compare them to current chemical knowledge and analytical evidence. Understanding the technical art history of Chinese guqin is critical for its conservation and revival in the 21st century.



**Keywords:** Musical instrument, Tonewood, Lacquer, Silk string, Wood aging, SAXS

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## 1. Introduction

The *guqin* (古琴), traditionally called *qin*, is a plucked-string zither-type instrument with seven strings, invented in China over three thousand years ago. It is the most revered of traditional musical instruments, generally associated with the literati class. Scholars such as Confucius and Su Shi (蘇軾) were well-known *guqin* players.<sup>1</sup>

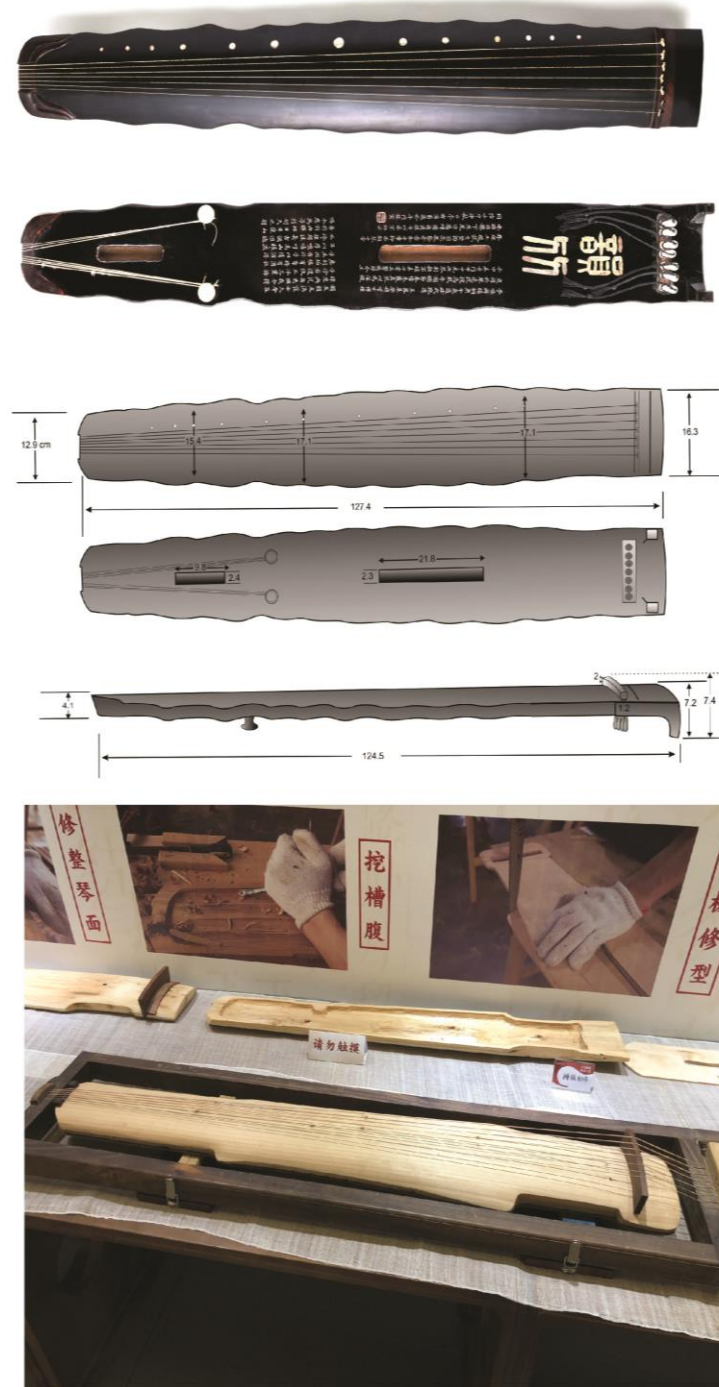
<sup>2</sup> The art of the *guqin* has been declared by UNESCO as an Intangible Cultural Heritage of Humanity.<sup>3</sup>

For ancient Chinese, the musical art of *guqin* was inseparable from beautifully sounding instruments. In *Qinshi* (History of Qin), Zhu Changwen (1039-1098), an acquaintance of Su Shi, wrote that the *qin* possesses four beautiful qualities: the first is fine materials, the second is skillful making, the third is sophisticated playing, the fourth is noble spirits.<sup>4</sup> It was customary for *guqin* players to engage in instrument making or at least basic repairs, so many were intimately familiar with relevant materials. For instance, Li Mian (李勉, 717-788), a royal prime minister, invented new *guqin* construction methods. Su Shi also commented on wood types suitable for making *guqin*.<sup>5</sup> Accruing fine materials for *guqin* making has always been a top priority for many dedicated players, both then and now. The *guqin* sound box is made of a top plate and a back plate assembled by gluing, with two sound holes at the bottom (Figure 1). The top (soundboard) is 15-25 mm thick, and the back is 10-20 mm thick. The protective exterior coating is 1-2 mm thick, mainly composed of Chinese lacquer (*qi* 漆 in Chinese or *urushi* in Japanese). *Guqin* plates and coatings are much thicker compared to those of other string instruments such as the cello or *guzheng* (Chinese 21-string zither), which results in a very quiet sound. The *guqin* was not designed for public performance but for private sessions with just a few listeners.

A key factor affecting *guqin* loudness is the string type. Traditional strings made of silk are the quietest. Today, steel strings and composite strings (steel core wrapped in nylon) are more popular due to louder volume and better stability. Nevertheless, silk strings are still appreciated by some musicians due to their distinct timber. In acoustic science, the sound is described by four primary qualities: loudness, pitch, timber, and spatial projectivity (directionality). The timber, or tone quality, is a vaguely defined term that involves steady-state spectral patterns as well as dynamic properties such as attack and decay. In *guqin* acoustics, the timber is mainly thought to be associated with the harmonics pattern (overtones) of a note.<sup>6,7</sup>

The tone quality of the *guqin* is of great concern to musicians and collectors. Its acoustic output is determined by the complex interplay between the performer, the string, and the resonator. Because strings are

replaceable consumables, musicians and collectors are mostly concerned about the resonance of the instrument body, which is determined by both geometric and material factors. Geometric factors such as instrument shape, plate thickness, and lacquer stratigraphy are relatively easy to adjust during guqin making. Ancient artisans placed great emphasis on material properties as critical determinants of acoustic quality, especially wood.



**Figure 1.** The basic structure of guqin. The top instrument is an 18<sup>th</sup>-century guqin, “Xiangpu’s Treasure” (Metropolitan Museum, accession # 2016.179.1, public domain images). The bottom panel shows unlacquered guqin plates (photograph by Wenjie Cai).

“By selecting fine wood and investing serious attention, the proper sound will develop after five hundred years,” said the famous makers of the Lei family, active in Sichuan Province during the Tang dynasty.<sup>8</sup> Today, thousand-years-old instruments from the Tang (618-906) and Song Dynasties (960-1279) are coveted for their superlative tones. Most collectors also prefer Ming Dynasty instruments (1368-1644) over Qing Dynasty instruments (1644-1912). One might wonder what chemical and physical changes may occur during wood aging to improve tone qualities.

Instead of waiting for centuries for acoustic improvements, ancient artisans conducted many experiments by material manipulations. They often utilized wood planks aged for centuries or accelerated wood aging by artificial treatments. They applied complex composite lacquer coatings with multiple layers, with different additives mixed into each layer. They sought special silk sources for the strings and also applied various additives. Because the guqin was favored by scholars, there were many written records of these tinkering experiments. However, we should not accept ancient writings at face value without verification, as some of them appeared to be more fanciful than practical. First, we need to gather forensic evidence on what materials were used. Second, we need to apply modern knowledge to understand their functional purposes, verified through modern experiments. Here, we will review historical records on guqin making and compare them to recent scientific and technical investigations. This article is divided into three parts: the wood, the lacquer, and the strings.

## 2. Resonant Tonewood

Only very a small number of tree species possess the suitable mechanical properties to serve as the tonewood (resonance wood) for a particular string instrument.<sup>9,10</sup> Within a given species, only a small fraction (below 1%) of trees grown under optimal conditions will produce quality tonewood. Before delving into the chemistry of wood aging and artificial aging, we need to understand the wood species involved. There are two major evolutionary classes of trees: gymnosperms (conifer trees) and angiosperms (dicot trees or broad-leaf trees). By convention, conifer wood is called softwood while dicot wood is called hardwood, although the actual harness may vary by species. Wood cell walls are mainly composed of three biopolymers: cellulose, hemicellulose, and lignin. Differences in the mechanical properties of wood, such as the density and Young’s moduli along different directions, are mainly determined by the morphology of cells and cell wall thickness.<sup>11,12</sup> Moreover, the building blocks of hemicellulose and lignin are fundamentally different between gymnosperms and angiosperms<sup>13</sup>, which means that different chemical reactions may take place during aging and artificial aging.

### 2.1. Wood species identification

Historical knowledge of selecting guqin tonewood has been extensively reviewed by Cai and Tai.<sup>14</sup> Thus, only the key points are briefly summarized here. In ancient texts, the wood species commonly mentioned for plates include *tong*, *zi*, *qiu*, *shan*, *qi*, and *emei song*. Their common and scientific names are listed in Table 1. The use of *tong* and *zi* for guqin was first recorded around the 7th century BC.<sup>15</sup> *Tong* was the most important guqin tonewood but also the most controversial. There has been a historical debate on whether *tong* referred to *paotong* or *wutong* (*qingtong*). Some thought that *wutong* is difficult to carve because it is very hard and cracks easily, while *paotong* is a general-purpose tonewood used for many types of instruments, so the useful *tong* wood for guqin should be *paotong*. Others thought that *wutong*, a tree associated with the mythological creature phoenix, is a perfect match for the aristocratic guqin, while *paotong* is a lightweight and fast-growing wood for mundane instruments, so the best guqin deserves *wutong* wood.

**Table 1.** Tonewood species frequently mentioned in historical records

| Chinese name             | Common name          | Scientific name                                 | Classification |
|--------------------------|----------------------|---|----------------|
| paotong 泡桐               | paulownia            | <i>Paulownia spp.</i>                           | dicot          |
| qingtong 青桐<br>wutong 梧桐 | Chinese parasol      | <i>Firmiana simplex</i>                         | dicot          |
| zi 梓                     | catalpa              | <i>Catalpa ovata</i>                            | dicot          |
| qiu 楸                    | catalpa              | <i>Catalpa bungei</i>                           | dicot          |
| qi 漆                     | lacquer tree         | <i>Toxicodendron spp.</i>                       | dicot          |
| shan 杉, 福州杉              | Chinese fir          | <i>Cunninghamia lanceolata</i>                  | conifer        |
| emei song 峨眉松            | pine from Mount Emei | high-altitude conifer, likely <i>Picea spp.</i> | conifer        |

To identify the wood species in a guqin is nontrivial—relying on the human senses and a magnifying glass is usually unreliable. For scientific classification, a small piece of wood needs to be removed for staining and microscopic examination by trained experts. The results are usually accurate down to the genus or species level, depending on the wood type. Unfortunately, this is a destructive analysis and rarely conducted on museum collections. Another difficulty in guqin research is that ancient makers did not leave personal marks for identification purposes. Even the date of origin is difficult to ascertain, because ancient makers usually aimed to copy the works from previous centuries. For guqin instruments in museum collections, sometimes the wood type and date of origin are specified, but it is difficult to know if the information is reliable. Wood identification combined with radiocarbon/archaeological dating has only been conducted for a small number of antique instruments, and some of the results are shown in Table 2.

The oldest specimen in Table 2 is an archeological 13-string zither (probably a prototype of *guzheng*) uncovered from cliff tombs in Guixi, Jianxi Province, dating back to Eastern Zhou Dynasty (BC 770-256). Its top plate has decayed and the back plate is *wutong* (*Firmiana simplex*).<sup>16</sup> The *qiulai* guqin from the French museum has no back plate and appears to be a decorative piece. Its top was made from *Taxus spp.* (紅豆杉),<sup>17</sup> which was not mentioned in ancient guqin books. Instruments T1-T7 are privately owned instruments with fine sound, from which we identified paulownia, Chinese parasol, catalpa, Chinese fir, and spruce (*Picea spp.*),<sup>18</sup> all but the last have been mentioned in ancient books. Judging from the geographical distribution of spruce<sup>19</sup> and its widespread use in European musical instruments, it may correspond to the high-altitude conifer called *emei song* used by the Lei family. Legend has it that Lei Wei (雷威) entered *song* (pine) forests on Mount Emei during snowstorms to listen to tree-shaking sounds to determine resonance qualities.<sup>20</sup> This reminds of European wood cutters entering spruce forests to tap the tree to determine resonance qualities.

**Table 2.** Wood species identified in antique Chinese guqin

| Instrument           | Structural component                      | Dating result<br>(Chinese<br>dynasty) | Identified tree species        |
|----------------------|---|---------------------------------------|--------------------------------|
| Zither from<br>Guixi | one-piece back (top plate<br>decayed)     | Eastern Zhou                          | <i>Firmiana simplex</i>        |
| <i>Qiulai</i>        | One-piece top (no back plate)             | Ming                                  | <i>Taxus</i> spp.              |
| T1                   | one-piece top (with extra inner<br>shell) | Tang                                  | <i>Cunninghamia lanceolata</i> |
| T1                   | one-piece back                            | Tang                                  | <i>Cunninghamia lanceolata</i> |
| T1                   | exposed layer of extra shell              | Ming                                  | <i>Paulownia</i> spp.          |
| T1                   | base layer of extra shell                 | Ming                                  | <i>Catalpa ovata</i>           |
| T2                   | one-piece top                             | Qing                                  | <i>Paulownia</i> spp.          |
| T2                   | one-piece back                            | Qing                                  | <i>Firmiana simplex</i>        |
| T3                   | one-piece top (with extra inner<br>shell) | Ming                                  | <i>Picea</i> spp.              |
| T3                   | one-piece back                            | Eastern Zhou                          | <i>Cunninghamia lanceolata</i> |
| T4                   | three-piece top                           | Qing                                  | <i>Catalpa ovata</i>           |
| T4                   | two-piece back                            | Qing                                  | <i>Catalpa ovata</i>           |
| T5                   | one-piece top                             | Qing                                  | <i>Catalpa ovata</i>           |
| T5                   | one-piece back                            | Qing                                  | <i>Catalpa ovata</i>           |
| T6                   | one-piece top (with extra inner<br>shell) | Qing                                  | <i>Paulownia</i> spp.          |
| T6                   | one-piece back                            | Qing                                  | <i>Cunninghamia lanceolata</i> |
| T7                   | one-piece top                             | Qing                                  | <i>Cunninghamia lanceolata</i> |
| T7                   | one-piece back                            | Qing                                  | <i>Paulownia</i> spp.          |

A Ming Dynasty scholar said that the best tonewood combination (top/back) is *tong/zi*, followed by *tong/tong* and *tong/shan*.<sup>21</sup> The first two combinations were not found in Table 2, and the third corresponded to specimen T6. Although only a small cohort of antique guqin has been surveyed, it appears that ancient makers often experimented with different wood combinations without adhering to specified rules. Specimen T3 is an example of using highly aged wood to build instruments. It was probably constructed in the Ming Dynasty using new spruce and archaeological Chinese fir (BC 2-4 c.). A plausible source of archaeological conifer wood is the sealing chamber enclosing ancient tombs associated with the Chu Culture (BC 3-5 c.),<sup>22</sup> and the authors have seen such wood being used by modern makers. Concerning the *paotong* versus *wutong* debate, both types have been identified in Table 2. Hence, *tong* wood in ancient books could have meant either. Paulownia is a low-density wood that is less durable, so it is less likely to remain intact in thousand-year-old instruments.

## 2.2. The chemistry of wood aging

The chemistry of wood aging over many centuries is very difficult to investigate under laboratory settings and, therefore, poorly understood. One approach is to examine collections of aged wood specimens, but their preservation condition may vary greatly, with some being more degraded than others. Even if they appear to be well preserved, damages could have been caused by microorganisms, weather cycles, mechanical loading, etc.

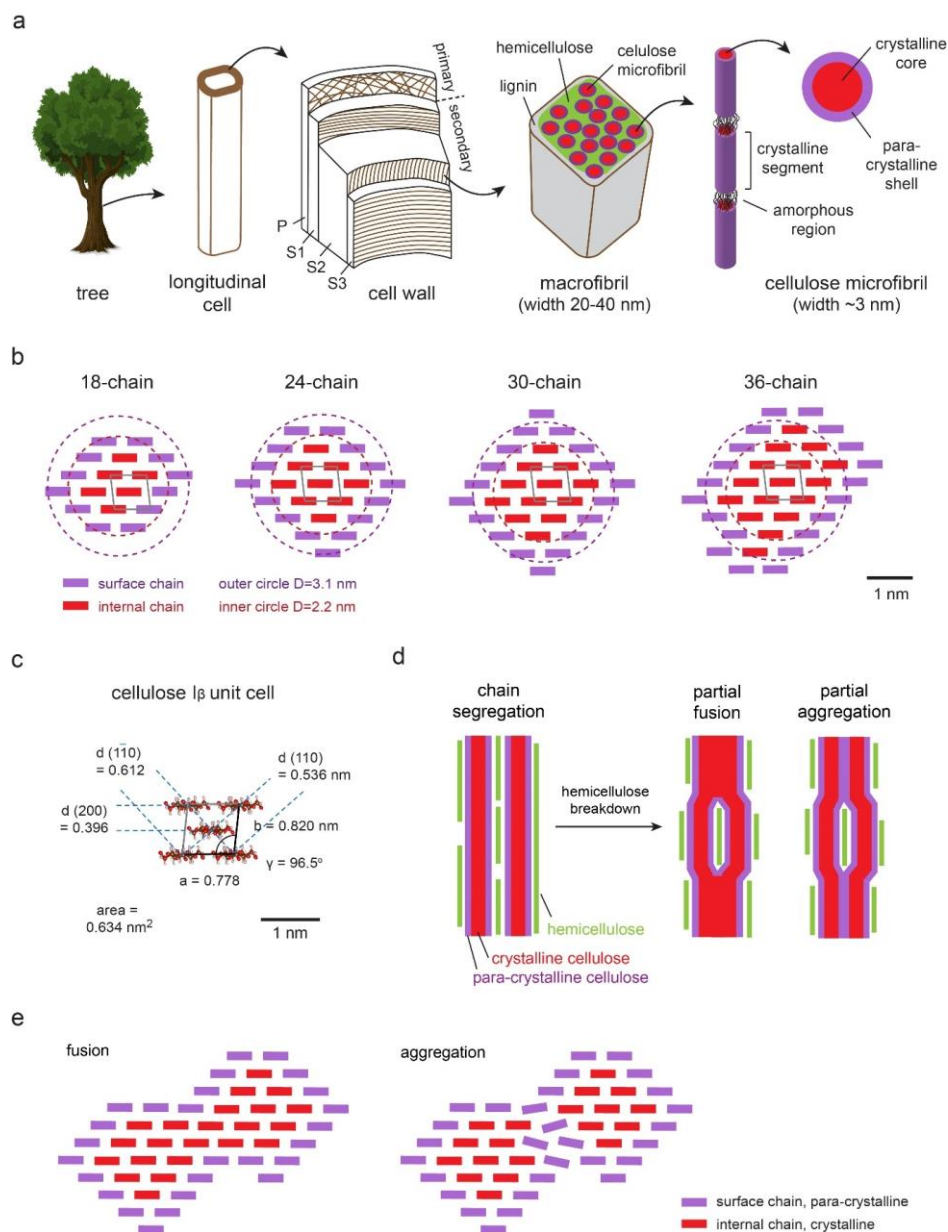
Another approach is to conduct artificial aging using heat, ultraviolet radiation (UV), hydrothermal treatment, or other semi-destructive means. How closely can artificial aging recapitulate the natural aging process remains unclear, because the latter is also highly dependent on environmental variables (physical, chemical, and biological). Based on our experiences in comparing naturally and artificially aged wood, the resemblance is often superficial. An artificially aged sample may resemble naturally aged wood in a couple of tests but show significant differences in yet another test.

From decades of research into natural wood aging (under ambient conditions without biological attack), a few general conclusions may be drawn.<sup>23-25</sup> The lignin, made of crosslinked phenolic alcohols, breaks down easily under UV or direct sunlight, but otherwise, it is much more stable than hemicellulose and cellulose. Spontaneous oxidation of lignin under atmospheric oxygen leads to yellowing and darkening but not degradation. The hemicellulose, a branched polysaccharide, undergoes spontaneous hydrolysis. Deacetylation happens first, followed by glycosidic bond cleavage, and then the conversion of saccharide units into volatile organic compounds and eventual carbon loss.<sup>26</sup> Cellulose, a straight-chain polymer of glucose, also undergoes the latter two processes but at a much slower rate than hemicellulose. Wood samples aged for several centuries generally show significant deacetylation and hemicellulose hydrolysis while cellulose remains mostly intact. Archaeological wood aged for thousands of years is generally lignin-rich because much most of the hemicellulose and some of the cellulose are lost.

The acetyl content of hemicellulose is higher in dicot woods than in conifer woods. When deacetylation occurs, the acetic acid being released may catalyze hemicellulose hydrolysis. This may be one of the reasons that dicot wood appears to be more degraded than conifer wood in antique violins.<sup>27-29</sup> Between 200-1000 years of instrument aging, hemicellulose hydrolysis appears to be the most important chemical alteration.<sup>18,30</sup> For both antique guqin and old Italian violins, there is a common belief that their acoustic qualities improve with aging. Interestingly, these two are the only categories of musical instruments sold for millions of US dollars in public auctions. How to scientifically characterize acoustic improvement over long-term aging remains a great challenge,<sup>31,32</sup> but it would be interesting to first investigate whether hemicellulose breakdown could lead to interesting structural changes in aged wood.

As shown in Figure 2, inside each wood macrofibril (20-40 nm diameter), the center is occupied by individual cellulose microfibrils (CMF) (~3 nm diameter) embedded in a hemicellulose matrix, while lignin distribution is more peripheral, forming a hydrophobic sheath.<sup>33,34</sup> The hemicellulose is the most hygroscopic component, followed by cellulose and lignin. Hemicellulose breakdown reduces the moisture content of wood and therefore reduces internal damping, making acoustic emission more efficient.<sup>32,35</sup> However, hemicellulose hydrolysis could also weaken cell wall structures. One of the critical properties of tonewoods is having high sound velocity relative to their density, especially along the longitudinal direction, being stiff and lightweight.<sup>9</sup> This is due to the orderly alignment of elongated cells and their CMFs along the longitudinal direction. In this regard, hemicellulose breakdown may seem detrimental for guqin or violin resonance because CMFs may loosen and rearrange.

Although wood cell walls have been studied for over a century, the nanostructure of wood CMFs is still highly debated. Many textbooks assign 36 glucan chains to a CMF<sup>36,37</sup>, while recent studies proposed that CMFs are synthesized with 18 chains and undergo crystalline fusion with neighbors<sup>38,39</sup> (Figure 2b-e). Based on our recent data, neither model is correct. By developing a novel scheme to interpret wood SAXS signals, a new solid-state nuclear magnetic resonance technique to differentiate crystalline and semi-disordered cellulose, and a new formula to calculate CMF chain number, we recently showed that each CMF contains 24 chains in conifers and dicots. The internal chains are crystalline, while the peripheral chains are semi-disordered, forming a core-shell structure.<sup>40</sup>

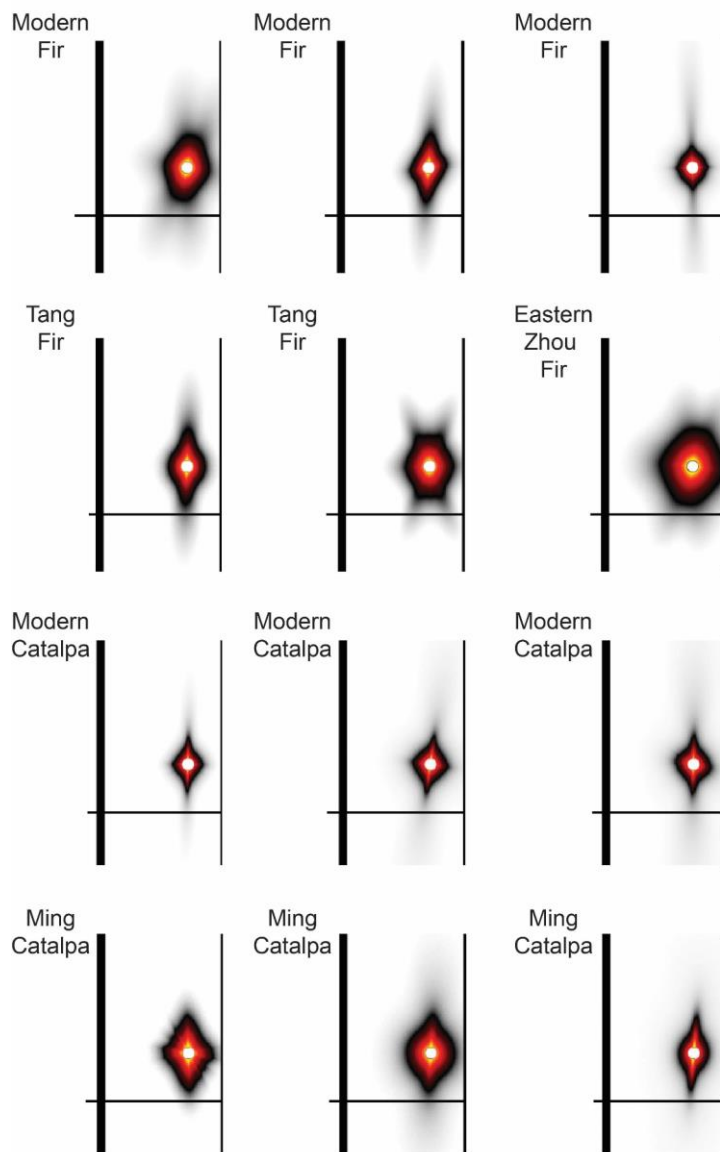


**Figure 2.** Wood cell wall and fiber structures. (a) Wood cellulose microfibrils (CMF) are primarily in the S2 layer of longitudinal cells, with a crystalline core and a para-crystalline shell (semi-disordered). (b) CMF models with 18, 24, 30, and 36 glucan chains, showing just one of many possible configurations. (c) The monoclinic unit cell of cellulose  $I\beta$ . (d) Vertical cross-section of a CMF pair in segregated, partially fused, and partially aggregated states. (e) Horizontal cross-section of a CMF pair in fused and aggregated states.

In the same study, we also examined Chinese fir aged for 1000-2000 years and catalpa aged for ~500 years, taken from fine-sounding antique guqin. Their 2D SAXS patterns are shown in Figure 3. Currently, quantitative analysis is limited to the integrated 1D SAXS profile (intensity versus  $Q$  plot), and the form factor peak in the high- $Q$  region reflects CMF core size. For Chinese fir, there are significant changes in SAXS profiles but not X-ray diffraction (XRD) profiles. This implies CMF aggregation (lateral contact without crystalline continuity) but not fusion (merged crystalline cores) (Figure 2e). Judging from the changes in cross-section aspect ratios and areas, the aggregate species are dimers. The catalpa samples show minor signs of aggregation but not fusion.<sup>40</sup> It appears that the gradual breakdown of hemicellulose creates extra space around CMFs and allows them to



reorient or rearrange. Moreover, guqin plates are put under constant stress and vibrations. Whether these mechanical factors also contribute to the rearrangement of fiber molecules remains unclear. As shown in Figure 3, there are remarkable SAXS pattern changes in antique catalpa samples compared to modern ones, which may suggest the randomization of CMF orientations over time. For modern Chinese fir, one sample (leftmost panel) shows a prominent microfibril angle (>10 degrees) while the others do not, which is likely due to different positions in the tree stem or different growing conditions.<sup>41,42</sup> Unfortunately, there lacks a coherent theoretical framework for interpreting wood 2D SAXS signals. Future progress in this area may help us uncover structural alterations associated with wood aging.



**Figure 3.** Wood SAXS patterns of Chinese fir (*C. lanceolata*) from three modern boards and three antique guqin samples; For catalpa (*C. ovata*), three modern boards and three antique guqin samples. Antique samples are assigned to Chinese dynasties based on radiocarbon dating.

To test the hypothesis that hemicellulose hydrolysis could result in CMF aggregation, we showed that alkaline hydrolysis using calcium hydroxide (lime) or potassium hydroxide (potash) solution at pH 12 were

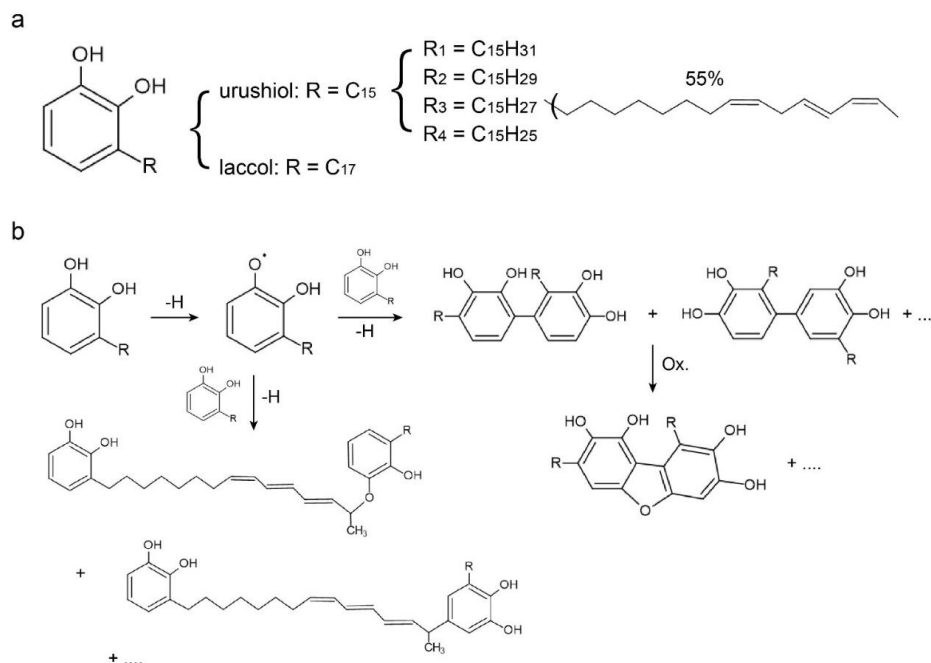
effective in inducing dimeric aggregates. Surprisingly, treatment with hot water, which does not cause significant hemicellulose hydrolysis, induced aggregation in spruce (a conifer) but not maple (a dicot). It is likely CMFs in maple are separated by additional layers or different types of hemicellulose chains compared to spruce.<sup>29, 40</sup> In sum, it appears that cellulose rearrangement may be associated with the acoustic improvement of antique guqin over many centuries.

Among old Italian violins, those made by Antonio Stradivari (1644-1737) and his neighbor Giuseppe Guarneri del Gesù (1698-1744) are most preferred by concert violinists for superlative tone qualities. Interestingly, we have also observed hemicellulose/cellulose rearrangement in the maple of Stradivari violins by differential scanning calorimetry.<sup>30</sup> Compared to the spruce wood used by his master, Andrea Amati, Stradivari's spruce exhibits unusual reductions in second harmonic generation signals, probably due to disrupted cellulose helicity.<sup>29, 43</sup> Cellulose rearrangement in Stradivari's wood does not seem to be caused by natural aging alone, and we detected high potassium in Stradivari's wood and high calcium in Guarneri's wood, implying lime and potash treatments, respectively.<sup>29, 30</sup> Interestingly, ancient guqin makers also gave detailed accounts of baking and lime treatments to artificially age tonewood for acoustic improvement, while admitting that the outcomes are inferior to natural aging.<sup>14, 44</sup> Thus, we propose that cellulose rearrangement may be associated with superlative tone quality in both antique guqin and old Italian violins.

However, caution is required when seeking aged tonewood or artificially aged wood. In *Dongtian Qinglu* (Tranquil Records of Paradise, 1190), it is said that pillars and beams may have their wood grain damaged by heavy loading and, therefore, wood from old buildings should be used cautiously.<sup>45</sup> We have received fine-looking tonewood samples from old European buildings that showed reduced crystallinity by XRD analysis.<sup>46</sup> But such damage was never observed in dozens antique violin and guqin instruments we have examined so far. Moreover, it is relatively easy to over-treat tonewood and cause excessive hemicellulose breakdown during artificial aging. In violins, over-treated wood may lead to premature tone degradation after some years.<sup>47</sup> We recently found that Guarneri violins were treated with aluminum salts, which may crosslink wood fibers to compensate for hemicellulose breakdown.<sup>29</sup> Whether ancient guqin also incorporated chemically modified wood remains uninvestigated. The acoustic effects of wood aging and chemical manipulation are important topics for further research.

### 3. Lacquer Coatings

The Chinese lacquer (*qi*), also called Japanese lacquer (*urushi*), is a natural coating based on the sap of lacquer trees (*Toxicodendron vernicifluum* or *Toxicodendron succedaneum*). The use of oriental lacquer dates back more than nine thousand years. Writings from the 7th century BC named the *T. vernicifluum* (formerly *Rhus verniciflua*) as one of the four trees used for making guqin.<sup>15</sup> The famous philosopher Zhuangzi (莊子, BC 369-286) was once the superintendent of a royal lacquer plantation. The early guqin prototypes excavated from ancient tombs (1-5 c. BC) were already lacquer-coated as expected, and the lacquer appears more durable than the wood.<sup>22</sup>



**Figure 4.** (a) The main component of lacquer tree sap is urushiol (*Toxicodendron vernicifluum*) or laccol (*T. succedaneum*). (b) Enzyme-catalyzed oxidative polymerization of urushiol, forming semiquinone radicals that lead to the formation of biphenyls, dibenzofurans, and crosslinks to unsaturated lipid tails.

The lacquer tree sap is an interesting coating material with unique compositions and chemistries compared to other natural resins and gums. The lacquer can be applied thickly to form a waterproof and heat-resistant (up to 300 °C) coating, which is harder and more durable than other natural coatings. The oldest playable guqin instruments found today originated from the Tang Dynasty, still highly coveted for their tonal excellence. Their remarkable preservation is doubtlessly attributed to the protective properties of thickly applied lacquers.

During the 15<sup>th</sup>-18<sup>th</sup> centuries, European nobles were greatly attracted to oriental lacquerware. European craftsmen tried various means to recreate the mysterious lacquer but failed, because there were no lacquer trees in Europe. Import of raw lacquer sap was also impractical because it became denatured and useless during long voyages. Imported lacquered furniture was disassembled and rebuilt into European-style pieces, and European furniture was even sent to China for lacquering. When missionaries were dispatched to China to investigate the origin of the lacquer, a few fell ill and died after contacting raw lacquers.<sup>48</sup> The mystique and popularity of the Chinese lacquer led to the development of shellac-based alcohol varnishes in Europe, replacing the traditional oil-resin varnish. This may have even led to the disappearance of the traditional Cremonese oil varnish used by Stradivari and Guarneri.<sup>49</sup>

The traditional Chinese guqin is coated with *qi*, also called *daq* (大漆), made from the sap of *T. vernicifluum*. The lacquer tree sap is a water-oil emulsion. It contains ~30% urushiol, a class of alkyl catechols, ~30% water, ~8% plant gum (polysaccharides), and 2% glycoproteins. For *T. succedaneum* sap, the main catechol component is laccol (Figure 4a).<sup>50</sup> The urushiol—also found at much lower concentrations in poison ivy—is a strong allergen that sometimes causes fatal reactions. In China, only people minimally allergic to urushiol would handle the raw sap. The polymerization of the *T. vernicifluum* lacquer is mainly catalyzed by laccase, a copper-containing enzyme, and modulated by stellacyanin, a copper-containing glycoprotein.<sup>51</sup> The reaction scheme is shown in Figure 4b. The hardening of lacquer film requires careful temperature and moisture control to maintain enzyme activity,

and the process is much slower than the non-enzymatic drying of other natural oils and resins.<sup>52</sup> The thoroughly hardened lacquer is no longer allergic and suitable for eating utensils.

### 3.1. Historical lacquer additives

The guqin lacquer usually contains several visually distinct layers, and each layer may be built up by applying multiple coats with similar compositions. The distinct layers contain different additives to modify their physical and chemical properties. A detailed account of ancient lacquering methods could be found in *Taiyin Daquanji* (Complete Anthology of Ancient Sounds), which has been translated into English by John Thompson.<sup>53</sup> The contents of *Taiyin Daquanji* were mainly derived from *Taigu Yinyin* (Sound Bequeathed from Antiquity) of Southern Song Dynasty (1127-1279).<sup>54</sup>

In *Taiyin Daquanji*, the first lacquer layer(s) laid over the wood is called *huitai* (灰胎), meaning ash base. The ash (*hui*) refers to powders added as volume extenders into raw lacquer to increase hardness and abrasion resistance. In *Taiyin Daquanji*, the best powder additive is said to be deer antler powder, followed by cattle bone powder. They may be mixed with powdered copper. The ash base is applied as four successive layers, using progressively finer powers.<sup>53</sup>

In Chinese medicine, deer antlers are first boiled to remove gelatinous substances, and the remaining bony materials are ground into fine powders.<sup>53</sup> In *Wuzhizhai Qinpu* (Qin Scores from Studio of Five Wisdoms), deer antler powder and the “powder of eight gems” (八寶灰 *babaohui*, made of gold, silver, pearl, jade, gemstones, etc.) are said to be highly desirable, but tile powder (瓦灰 *wahui*) is suboptimal.<sup>55</sup> If extra strength and protection are required, a piece of cloth could be pasted using the lacquer as an adhesive. By inspecting historical instruments, both ko-hemp (kudzu) fibers (from Chinese arrowroot vines, *Pueraria montana*) and hemp fibers (from *Cannabis sativa*) were found.<sup>56</sup>

According to *Taiyin Daquanji*, on top of the ash base, a rough lacquer is applied. This rough lacquer is made by stirring the raw lacquer (生漆 *shengqi* in Chinese and *ki-urushi* in Japanese) under the sun.<sup>53</sup> In modern terms, this rough lacquer is called *shouqi* (熟漆) in Chinese, meaning ripe or processed lacquer, and *suki-urushi* in Japanese.<sup>57</sup> The stirring and moderate heating promote pre-polymerization and dehydration, turning the opaque raw lacquer (milky appearance) into the transparent ripe lacquer (reddish to dark brown). The ripe lacquer dries into a dark brown film in the absence of added colorants.

In *Taiyin Daquanji*, the third type of lacquer being applied is called boiled rough lacquer. It is prepared from rough lacquer by boiling and adding potassium nitrate. In another recipe, raw lacquer is first mixed with egg white to increase the luster of the boiled lacquer.<sup>53</sup> Here, potassium nitrate may serve as an oxidizer during heat-induced pre-polymerization. Adding egg white proteins may also thicken the lacquer or make it more durable.<sup>58</sup>

In *Taiyin Daquanji*, the fourth type of lacquer is applied to give a glossy appearance (合光法). There are four ways to make this shiny lacquer. The first method is to slowly boil raw lacquer down to five-eighths of its original weight and then filter it. The second method is to mix raw lacquer and white oil (白油, meaning unclear) in a 1:1 ratio and boil slowly. The additives include massicot (黃丹 *huangdan*, PbO), lead white (定粉 *dingfen*,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ), fruits of *Terminalia chebula* (訶子肉 *hezirou*), and Fraxini Cortex (秦皮, *qinpi*, the bark of *Fraxinus spp.*). The third method includes white lead, calomel (輕粉 *qingfen*,  $\text{Hg}_2\text{Cl}_2$ ), and egg white as additives. The fourth method includes Fraxini Cortex, lampblack, powdered iron, and egg white as additives.

The lead compounds probably act as chemical driers to promote polymerization.<sup>59</sup> The toxic mercury salt may protect against biological attacks. Lampblack is also called soot or carbon black, a black pigment of amorphous carbon.<sup>60</sup> Adding iron powder turns the lacquer black and catalyzes polymerization by forming iron(II)-urushiol complexes,<sup>61</sup> similar to Japanese *kuro-roiro-urushi*.<sup>57</sup> The fruit extract of *T. chebula* is enriched in tannins<sup>62</sup> and Fraxini Cortex is enriched in coumarins.<sup>63</sup> Whether the herbal tannins and coumarins may affect

the lacquer hardening processes or chelate with iron to affect the color will require further investigation.

In *Qinyuan Yaolu* (Important Records of Qin Academy, 12-13 c.), this recipe was mentioned: raw lacquer, sesame oil, lampblack, Chinese honey locust bean (皂角 *zaojiao*, *Gleditsia sinensis*), lead powder, and fruits of *T. chebula*.<sup>64</sup> In *Qinshu Daquan* (Great Anthology of Qin Books, 1590), three additional additives were mentioned: tung oil, huipei (灰坯, unidentified ash, possibly wood ash), and *nifan* (泥礬, unidentified mineral of muddy appearance, possibly impure sulfate salts or iron sulfide).<sup>65</sup> *Yuguzhai Qinpu* (Qin Scores of the Studio of Abiding Antiquity, 1855) said raw lacquer may be mixed with pig bile juice or Borneo camphor (冰片 *bingpian*) and stirred under the sun to make a lustrous lacquer with good flowing quality that can be easily brushed.<sup>44</sup>

The tung oil (a drying oil from the nuts of *Vernicia fordii*) and sesame oil (a semi-drying oil from *Sesamum indicum*) help the lacquer spread more easily. A faintly colored oil may be obtained by pressing unroasted white sesame (白油麻), much paler than tung, linseed, or perilla oils, which may correspond to the “white oil” mentioned above. The Borneo camphor is recrystallized *d*-borneol (boiling point 203 °C) from *Dryobalanops aromatica*, which acts as a thinner for the lacquer. Some modern makers may use oil of turpentine (b.p. ~154 °C) for thinning purposes, but borneol has the advantage of being less volatile. Pig bile is also a lacquer thinner but by a different mechanism, containing mostly water but also bile salt, cholesterol, and lecithin. The Chinese honey locust bean (from *Gleditsia sinensis*) is enriched in tannins, saponins, and galactomannan.<sup>66</sup> The bile and saponin may act as emulsifiers that affect the drying rate and surface appearance of lacquers. The galactomannan might make the lacquer more adhesive.

The lacquer is also used as an adhesive to join the top and the bottom plates. In *Taigu Yiyin*, the lacquer adhesive is supplemented with cow hide glue (*huangming jiaoshui* 黃明膠水, yellow transparent glue) and bone powder.<sup>53</sup> In some modern recipes, the lacquer adhesive is supplemented with deer antler powder, gum Arabic (from *Senegalia senegal*), starch, or glutinous rice.

### 3.2. Analyses of ancient lacquers

Because the lacquer is largely insoluble in most solvents, it has been difficult to analyze its organic compositions by liquid chromatography-MS. With the development of reference libraries for lacquer ingredients by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis, combined with derivatization techniques, researchers can now resolve many organic components in lacquer films.<sup>67</sup> The stratigraphy of guqin lacquer coats may be visualized by two ways: (1) microscopic examination of exposed underlayers at worn out spots or edges; (2) removing a small sample for cross-section examination. As the top lacquer may be damaged by UV and abrasion, the surface of an antique instrument may have been sanded down and re-lacquered. There is no simple method to tell if the top layers are original.

Li et al. recently analyzed the lacquer film of a Yuan Dynasty (1271-1368) guqin. The lacquer is ~1 mm thick with three major layers: the ash base, the mineral-free lacquer layer, and a thin color layer. Energy dispersive X-ray analyses (SEM-EDS) analysis suggests that bone powder was added to the base layer, showing Ca and P elements, also confirmed by Raman spectroscopy. The black color of the top layer may come from carbon black, and its Ca and S signals may represent gypsum extenders. Analyses by Fourier-transform infrared spectroscopy (FTIR) and Py-GC-MS suggest the use of urushiol from *T. vernicifluum* without drying oil, and some type of starch was found.<sup>68</sup> Starch may be used to thicken the lacquer.<sup>58</sup>

Wang recently analyzed lacquer fragments from a Ming Dynasty guqin. Its lacquer is relatively thin, about 0.5-0.7 mm, with three distinct layers. The ash base contains volume-extending particles, the middle layer is transparent lacquer without particulates, and the top color layer also contains particulates. The larger particles analyzed by XRD showed peaks indicative of silica (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), gypsum (CaSO<sub>4</sub>), and sodium feldspar (NaAlSi<sub>3</sub>O<sub>8</sub>). This mixture may have originated from tile or brick powders. XRD also identified particles of HgS, a

red pigment called cinnabar (natural mineral) or vermilion (synthetic). By scanning electron microscope and SEM-EDS, powders of cupronickel alloy (Cu/Ni/Zn) were found.<sup>69</sup>

Modern chemical analyses have not been applied the lacquers of early guqin from ancient tombs (3-5 c. BC). Nonetheless, lacquered objects from such tombs have been analyzed, and they were urushiol based and supplemented with drying oils.<sup>70, 71</sup> Identifying the drying oils based on fatty acid signatures is challenging for highly aged samples, but perilla, tung, and linseed oils were tentatively identified. The pigments found included carbon black and cinnabar/vermillion. Interestingly, ancient lacquer coatings sometimes contained a ground layer with clay powders, similar to the ash base in guqin coating.

In an excavated Song-dynasty carved lacquerware from Zhejiang Province, Hao et al. found an eight-layered lacquer structure. The first layers is the ash base, followed by a fiber layer (cloth pasted using lacquer) and the second ash layer. The fourth layer is mineral-free lacquer, and the fifth to eighth layers are colored red, black, yellow, and black, respectively. By EDS and Py-GC-MS, the identified red, black, and yellow pigments are cinnabar/vermillion, soot, and orpiment ( $As_2S_3$ ), respectively. The lacquer consists of laccol and tung oil. Also found by Py-GC-MS are tannins, which may come from a variety of plant sources.<sup>72</sup> Only the two top black layers contain tannins, which seems consistent with the stated purpose of using tannins (from the fruits of *Terminalia chebula*) for the enhanced luster in *Taiyin Daquanji*, as previously discussed. The laccol lacquer of *T. succedaneum* has also been identified in the export furniture of Qing Dynasty (1644-192), thought to be a cheaper alternative for urushiol lacquer.<sup>73</sup> Although laccol sap is usually associated with Vietnamese lacquerware, its historic use in Chinese guqin cannot be simply ruled out.

Lacquering is a complex craft with many technical variations,<sup>58, 61</sup> so there is no standard or definitive way to lacquer a guqin. It is also a very time-consuming process due to the slowness of enzymatic catalysis. A coat of ash base may take a month to dry, and a week for a coat of ripe lacquer. Multiple polishing and roughening steps may be included, and the entire lacquering process may take 3-12 months. The lacquering methods given in *Taiyin Daquanji* are similar in principle to the analytical results of antique lacquers mentioned above, giving credibility to the ancient records.

### 3.3. Lacquer aesthetics and acoustics

The original purpose of the lacquer is both protective and ornamental. Antique guqin is generally lacquered in plain colors: black, red, dark brown, or a combination of these. Highly decorated instruments with intricate inlaid patterns were last produced in the Tang Dynasty, and a surviving example is found in Shosoin, Nara, Japan.<sup>22</sup> Different techniques can be used to make the lacquer surface glossy or matte. When thinly applied, the lacquer is semi-transparent, so it is also possible to employ the glazing technique—applying thin layers with different colors to create special visual effects.

While lacquer films are very durable, photo-degradation and cracking may be a concern.<sup>50</sup> The lacquer film and the wooden body constantly expand and contract under temperature and moisture fluctuations. Cracks may develop slowly at the lacquer surface as a result of dimensional changes and photo-damage. Some ancient books proposed that cracking patterns may be used to determine the age of the instrument, but many found it unreliable. If one intentionally overlays lacquer coats with different shrinkage properties and applies some heat or UV radiation, a brand new guqin could quickly develop cracking patterns reminiscent of antique instruments. Nonetheless, cracking patterns can create fascinating visual effects which are given fanciful names such as plum flower craquelure, cow hair craquelure, snake belly craquelure, flowing water craquelure, dragon scale craquelure, etc. It has been proposed that microscopic cracks in coatings may act as a low-pass acoustic filter,<sup>74</sup> but this has not been experimentally verified.

From violin acoustics studies, it is apparent that a thin varnish of tens of micrometers in thickness has a

dramatic effect on the vibrational properties of plates.<sup>75, 76</sup> The acoustic effect of a single layer of lacquer is found to be similar to that of polyurethane coating used in modern harp construction.<sup>77</sup> However, a multi-layer lacquer coating system having 1-2 mm thickness is bound to have a much stronger effect on instrument acoustics. The effect may be so great and so variable (differences in stratigraphy, thickness, and compositions) that it is difficult to draw general conclusions. The general shape, the plate thickness, and the wood combination are not standardized in the guqin. These variations will also affect the choice of lacquering methods for optimal acoustics. There is rather limited research on guqin acoustics<sup>6, 7, 78, 79</sup>, and, therefore, it is unclear what acoustic parameters should be pursued. One may wonder if lacquer aging and cracking could also exert acoustic effects.

## 4. Silk Strings

Traditional guqin strings are made of silk, a natural protein fiber produced by certain insect larvae that form cocoons. The agricultural production of silk is called sericulture, which has a history of over 5000 years in China.<sup>80</sup> The earliest string instruments invented in China are believed to be prototypical zithers mounted with silk strings. However, the type of silk used for ancient guqin strings remains a complex and unresolved issue. First, the silkworm may belong to domesticated (cultivated) species or wild species.<sup>81</sup> Second, the larvae may consume different tree leaves. Third, the larvae may be raised under different conditions, which also affects silk quality. Although there are plenty of ancient records discussing sericulture and silk strings, it is often difficult to interpret the biological source of the larva and its food.

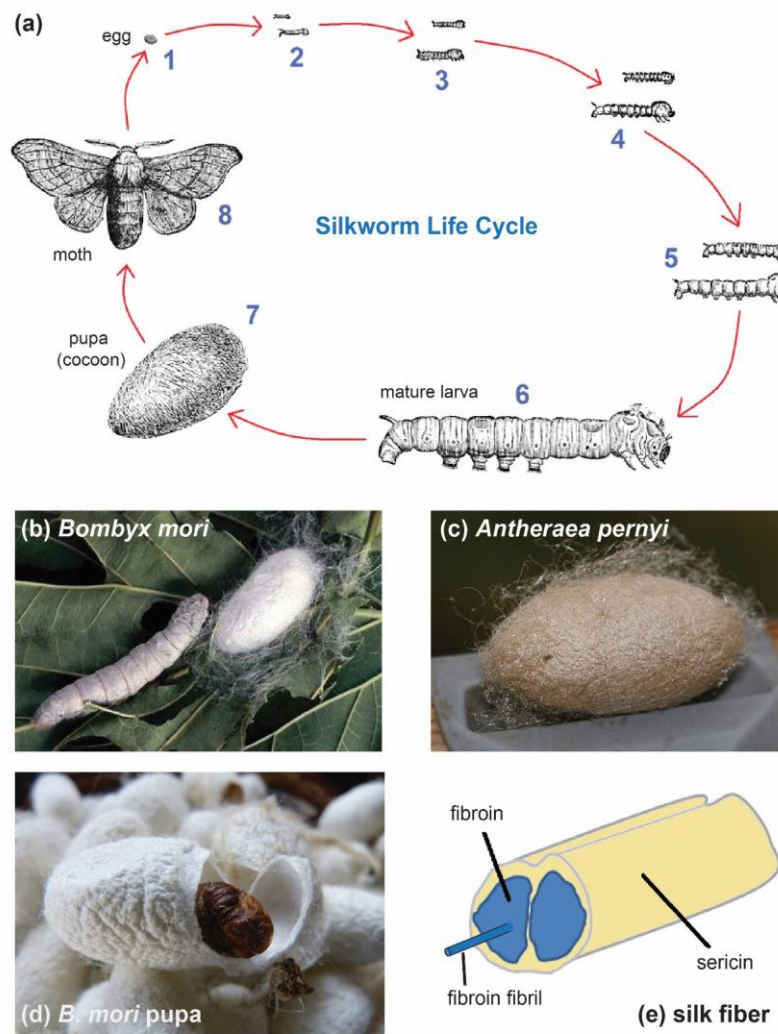
Some guqin players today are dedicated to historical performances using silk strings, similar to the concept of using gut strings for period performances of Baroque music. Unfortunately, the manufacturing of high-quality silk strings based on traditional techniques was completely lost in China during the early or middle part of the 20th century. There has been much effort to revive this lost craft during the past 50 years. But many still believe that modern silk strings are inferior to those made in the pre-industrial age. As we continue to pursue research and development, there may soon be a successful revival and a new golden age of guqin silk strings.

### 4.1. Silkworm varieties

The first domesticated species of silkworms appeared in China several thousand years ago, the mulberry silkworm *Bombyx mori* (桑蠶 *sangcan*). The wild silkworms in China include the *Bombyx mandarina* (wild silk moth, 野家蠶 *yejiacan*, the progenitor of *B. mori*), several *Antheraea* species, *Eriogyna pyretorum* (giant silkworm), *Samia Cynthia*, *Dictyoploca japonica*, etc. The cocoons of wild *Antheraea pernyi* (Chinese oak silkworm, 柞蠶 *zuocan*) have been collected for textiles since the 2<sup>nd</sup> century BC and later became domesticated around the 17<sup>th</sup> century.<sup>82, 83</sup> Today, commercial silk production in China is based on *B. mori* and *A. pernyi*. *B. mori* is fed exclusively with the leaves of the *Morus alba* (桑 *sang*, mulberry tree) to produce white silk (some varieties are bred to produce silk of different colors). *A. pernyi* generally feeds on the leaves of *Quercus* species in the wild, and it is cultivated with the leaves of *Quercus mongolica* (柞 *zuo*) to produce a thicker silk of yellow-brown color (Figure 5). The wild *B. mandarina* generally feeds on the leaves of *Morus* species, producing a yellow-brown silk. The color of the silk depends on the gland secretion of flavonoids and carotenoids from tree leaves, controlled both by genetics and food sources.<sup>84</sup> As discussed below, it appears that *B. mandarina* and *B. mori* are most relevant to guqin string production in ancient China.

According to Kong Anguo (circa BC 156-74), the 12th-generation descendent of Confucius, guqin strings were made by silkworms eating the leaves of mountain mulberry called *yan* (椶, probably *Morus mongolica* or *Morus australis*).<sup>5</sup> According to the poet Cui Yin (died 92 AD), guqin strings were made of silkworms eating the

leaves of *zhe* (柘, *Maclura tricuspidata*) trees in the mountains.<sup>85</sup> In both cases, it is unclear if wild cocoons were collected or tree leaves from the wild were fed to domesticated silkworms.



**Figure 5.** (a) The life cycle of silkworms. (b) Long-term domestication has led *B. mori* to lose its ability of mimicry, so the larva, cocoon, and moth are white. (c) The cocoons of *A. pernyi* and most wild silkworms are yellow-brown. (d) A cocoon cut open to show the pupa. (e) The cross-section structure of a silk fiber. (Image source: Wikimedia Commons, CC license).

In an agricultural manual published in 544 AD, Jia Sixie wrote that the leaves of *M. tricuspidata* were fed to silkworms, and this silk was used in guqin for optimal acoustics, far better than ordinary silk. In the same chapter, he discussed the cultivation of *M. tricuspidata* as well as *M. alba*, which is the most common food for cultivating silkworms.<sup>86</sup> Jia obviously could distinguish these two similar trees in the *Moraceae* family. It appeared that ordinary silk came from *B. mori* eating *M. alba* leaves, while superior silk for strings came from *B. mori* eating *M. tricuspidata* leaves.

During the Tang Dynasty, Qi Song (齊嵩) commented that, around Qinzhou in Shandong Province, *yan* was a variety of mountain mulberry, and the valley people collected its leaves to feed the silkworms, yielding a silk with greater strength and elasticity. This special kind of silk was long lost because, during the disastrous years, the *yan* leaves became unavailable. He also stated that there is still silk production in this region but of a different



kind. Nonetheless, string-making is still possible by choosing the right extraction method. Wild silkworms are used for current production and they produce a softer silk, so it is best to use the “raw extraction” method. Alternatively, steam may be used to produce cooked silk.<sup>87</sup> Here, the wild silkworm may refer to *B. mandarina*.

In another Tang Dynasty account, Chen Zhuo (born c. 880, famous poet, musician, and government official) mentioned that silk from *yan* is different from standard silk from *sang* (*M. alba*).<sup>88</sup> But we do not know if the silkworms were different or just the food. In *Taiyin Daquanji* (Southern Song Dynasty), the best strings were said to be made of white silk associated with *M. tricuspidata* leaves, followed by the autumn silkworm. The third best choice is ordinary silk by “raw extraction,” but salt-preserved silk should be avoided because they are brittle and too hygroscopic.<sup>53</sup> Thus, the best white silk mentioned here may imply *B. mori* consuming *M. tricuspidata* leaves and raised in the spring. In *Yuguzhai Qinpu* (1855), it was said that the best silk for strings came from silkworms fed with *M. tricuspidata* leaves, followed by those fed with *M. alba* leaves, followed by the autumn silkworm.<sup>44</sup> Because this book was published less than 200 years ago, the silkworm involved was probably *B. mori*.

In the passages above, steaming and salting referred to two methods to kill the pupae so that cocoons could be stored for extended periods before thread extraction. In contrast, “raw extraction” meant the timely processing of fully-formed cocoons (before the transformation of pupae into moths) by immersing them in hot water for partial degumming and thread extraction. The cocoons could be raised twice a year, in the spring and autumn, and ancient string makers preferred the spring cocoons.

Judging from the preceding analysis, it is seemingly difficult to ascertain what type of silk was used for guqin strings in historical texts. From antiquity to the present day, the standard, ordinary silk has been the white silk made by *B. mori* fed with *M. alba* leaves, which was obviously familiar to the abovementioned authors. Nevertheless, none of the ancient authors considered this standard silk as the optimal choice for guqin strings, so it probably was not. It is said that *B. mori* cultivated today requires *M. alba* leaves as its main diet. Therefore, some may argue that silkworms fed on *M. tricuspidata* leaves should belong to a wild species. But one may also argue that *M. tricuspidata* leaves are only used as a supplementary diet for *B. mori* in addition to *M. alba* leaves. Based on literature discussions, we speculate that top-quality antique strings were made by *B. mori* (domesticated) or *B. mandarina* (wild) feeding on the leaves of *yan* (*M. mongolica* or *M. australia*) or *zhe* (*M. tricuspidata*).

Recently, well-preserved silk zither strings have been excavated from an ancient tomb of the Chu Culture. Researchers from the China National Silk Museum have examined the antique strings by optical microscopy (for cross-sections), infrared spectroscopy, and amino acid analysis.<sup>89</sup> The antique silk appears similar to modern silk from *B. mori*, but not that of *B. mandarina* or *A. pernyi*, but its diet cannot be determined. It suggests that domesticated silkworms have been used for string production for over two millennia.

## 4.2. Historical silk string additives

The silk contains about 75% fibroin, 23% sericin, 1.5% fat and wax, and 0.5% mineral salt. Fibroin is the filamentous protein and sericin is a globular protein that surrounds the fibroin core (Figure 5e). The sericin, also called silk glue, is removed from fibroin during silk processing to improve the smoothness, luster, lightness, and dyeability of the fibers, which is called the degumming process.<sup>90</sup>

The initial degumming of cocoon fibers may be done by chemical treatments, enzymatic treatments, or boiling in water. In ancient China, boiling in water was the standard practice to produce raw silk. The silk threads were wound into strings of different diameters for different pitches. The wound strings were boiled again for further degumming. Afterward, the strings were stretched out and air-dried. During the boiling and drying steps, various additives could be applied. Some strings were additionally wrapped by a thin layer of silk for surface smoothness, especially on the bass strings. The harvesting and preparation of silk threads and turning them into wound strings

is a lost art. There are many different modern experiments attempting to revive this complex craft, which are beyond the scope of this article. Here, we will focus on the chemistry of the additives.

**Table 3.** Silk string additives listed by Juyue around the 12<sup>th</sup> century

| Chinese term    | English term  | Recipe number | Composition   | Possible function               |
|-----------------|---|---------------|---|---------------------------------|
| 小麥 xiaomai      | wheat   | 1, 2, 3       | starch, gluten protein                                | adhesive coating                |
| 大魚膠 dayujiao    | isinglass, fish glue  | 1, 3          | collagen from swim bladders                           | adhesive coating                |
| 明膠 mingjiao     | animal glue   | 2             | collagen from cow hide                                | adhesive coating                |
| 白芨 baiji        | tubers of hyacinth orchid ( <i>Bletilla striata</i> )                   | 2, 3          | contains glucomannan                                  | adhesive coating                |
| 皂子白 zaozibai    | Chinese honey locust bean ( <i>Gleditsia sinensis</i> )                 | 2             | contains galactomannan (locust bean gum)              | adhesive coating                |
| 香白芷 xiangbaizhi | fragrant roots of <i>Angelica dahurica</i>                              | 2             | contains polysaccharides, volatile oil, and coumarins | fragrance                       |
| 桑白皮 sangbaipi   | root bark of <i>Morus alba</i> (Cortex Mori Radicis)                    | 2             | contains polysaccharides, phenolics and flavonoids    | antimicrobial                   |
| 黃蠟 huangla      | yellow wax (beeswax)  | 3             | wax   | adhesive coating                |
| 巴豆 badou        | toxic seeds of purging croton ( <i>Croton tiglium</i> )                 | 3             | contains alkaloids and triterpenoid saponins          | insect repellent and emulsifier |
| 南星 nanxing      | toxic rhizomes of <i>Arisaema erubescens</i> or <i>A. heterophyllum</i> | 3             | contains alkaloids, glycosides, and flavonoids        | insect repellent                |
| 玄晶石 xuanjingshi | gypsum  | 2             | CaSO <sub>4</sub> ·2H <sub>2</sub> O                  | mineral coating                 |
| 明礬 mingfan      | alum  | 3             | KAl(SO <sub>4</sub> ) <sub>2</sub>                    | coagulant and mordant           |
| 礶砂 naosha       | sal ammoniac  | 3             | a natural mineral containing NH <sub>4</sub> Cl       | mordant                         |

A rather comprehensive collection of historical string-making methods can be found in *Qinshu Daquan* (1590).<sup>65</sup> Among these methods, the earliest Xie Xiyi (謝希逸, 421-466, a famous poet and government official), who stated that guqin strings were boiled with some wheat in the pot until the wheat is fully cooked. Thus, the wheat served as a source of starch (adhesive coating) and a natural cooking timer. In Tang dynasty, Chen Zhuo

mentioned the same boiling method, and the cooked strings were quickly cooled down in cold water and dried under the sun. Another Tang Dynasty author, Qi Song, mentioned adding glutinous rice while boiling the strings. Around the 12<sup>th</sup> century, Juyue (居月), a monk musician, offered several methods for boiling the strings with many different additives (Table 3). The basic method starts with boiling the string with wheat, but the overcooked strings have poor sound emission and the undercooked strings break easily.

It is interesting to note that Juyue's recipes mentioned six types of adhesive coatings: two kinds of collagen (isinglass and hide glue), three kinds of polysaccharides (starch, glucomannan, and galactomannan), and wax. These coatings may help bind silk fibers together, fill microscopic pores, or modify their surface properties. Juyue's recipes included two toxic herbal medicines, probably added to repel insects or offer biological protection. He also mentioned two additional herbs, the roots of *Angelica dahurica* and Cortex Mori Radicis, which contain polysaccharides and many biologically active compounds. The former may provide fragrance and the latter may be antimicrobial.<sup>91</sup> Interestingly, Juyue also mentioned two mordants commonly used in wool dyeing, alum and sal ammoniac. They may promote the fixation of organic molecules (proteins, carbohydrates, or herbal compounds) to silk proteins. In the presence of protein or polysaccharide adhesives, adding gypsum may form a powder coating on the silk surface. Compared to the simpler recipes of only adding starch from the preceding centuries, Juyue's sophisticated recipes are both surprising and eye-opening.

The silk string additives given in Taiyin Daquanji<sup>53</sup> and Yuguzhai Qipou<sup>44</sup> are basically identical—wheat, isinglass, beeswax or insect white wax (明瑩白蠟, from *Coccus sinensis*), tubers of *Bletilla striata*, root barks of *Morus alba*, and tubers of *Asparagus cochinchinensis* (天門冬, *tianmendong*, Chinese asparagus). These ingredients have also been mentioned by Juyue, except for the white wax and Chinese asparagus, which is enriched in polysaccharides and biologically active compounds. In modern silk strings, only a single coating material is applied in most cases, either animal glue (collagen) or rice glue (starch). The recipes given by Juyue are bewilderingly complex by modern standards, and there is little understanding of how to optimize manufacturing procedures involving such complex ingredients.

There are several practical shortcomings with silk strings. The first is that they break easily and are costly to replace. The second is dimensional instability under tension and moisture fluctuations, requiring the strings need to be re-tuned several times during a concert. The third is surface roughness that results in a scratchy sound.<sup>92</sup> Ancient craftsmen, therefore, developed sophisticated recipes and processing methods to address these issues, creating a very smooth type of silk string called the "ice string." The collagen glue may strengthen the string and improve dimensional stability by reducing hygroscopicity. Coating with starch, polysaccharides, and gypsum may improve surface smoothness. The wax may also reduce hygroscopicity. These additives could alter the mechanical properties and playing qualities of the string and lead to improved acoustic performance, but the optimization of manufacturing procedures is very challenging. Advances in guqin string making for the 21<sup>st</sup> century would require further investigations into various additives, and we may look beyond traditional recipes and explore modern chemical additives and manufacturing techniques.

## 5. Conclusions

The guqin was not only a musical art and a spiritual exercise but also the culmination of ancient science and technology. As discussed above, making a beautifully sounding guqin requires the combination of physical, chemical, and biological knowledge. From an ancient perspective, the guqin embodied the principles of the five phases (metal, wood, water, fire, and earth, all of which were used in guqin making) and of *yin vs. yang* (for example, the softness vs. hardness of wood). The ultimate guqin master not only performed the instrument and

knew its cultural history but also possessed the dexterity and technical knowledge to build it. This may be why the qin was ranked first among the four arts of ancient scholars, followed by Go chess, calligraphy, and painting. Written records about guqin-making materials—the tonewood, the lacquer, and the silk—date back over 2,000 years and we now have archaeological findings to corroborate them.

Although wood is a common material, only select trees from select species will yield suitable tonewood for the guqin. The chemical compositions of wood cell wall fibers, their nanostructures, and biosynthetic mechanisms are only partially understood. This remains a forefront challenge in plant sciences. Ancient artisans keenly noticed that wood aging led to acoustic improvements and experimented with artificial aging methods including heat and alkaline treatments. It is well-established that aging and artificial aging leads to hemicellulose fragmentation, but we recently discovered that cellulose microfibrils undergo aggregation as well. We propose that cellulose rearrangement may be an underlying factor for the superlative tone associated with antique guqin and Stradivari violins, and further investigations are warranted.

The lacquer is an ancient coating material but its hardening mechanism is unique, complex, and only recently understood. The natural lacquer remains functionally superior to synthetic resins for guqin coatings. Different layers of guqin lacquer contain different additives for different purposes. The ash base layer contains inorganic particles for increased hardness, sometimes reinforced by cloth fibers. The upper layers may contain black or red colorants, sometimes supplemented with oils, egg albumen, or tannins to adjust the consistency and luster. The lacquer coats have a huge effect on body vibration and its application could be adjusted for acoustic tuning. Unfortunately, the acoustic principles behind desirable guqin tone qualities remain poorly understood, so it is difficult to correlate wood and lacquer properties to acoustic improvements.

Making guqin silk strings is a lost art but there is an intense ongoing effort to revive it. It is difficult to ascertain the silkworm varieties used to produce antique strings, whether it was domesticated or wild *Bombyx* species. Today, we have many domesticated *B. mori* varieties to choose from and they could be genetically engineered or fed modified diets. In addition to having the finest raw silk, it is also important to investigate the benefits of various additives. Modern silk strings are generally coated with starch or collagen, following ancient traditions. But old recipes also called for additional additives such as plant polysaccharides, herbal extracts, and inorganic salts. The chemical and functional effects of these additives remain poorly understood. We should also consider incorporating modern processing methods to overcome the inherent drawbacks of silk strings.

By unraveling how antique guqins were made and what they were made of, we also gain important knowledge on how to protect them for future generations. While it is relatively easy to achieve satisfactory preservation under museum conditions, a guqin inside the glass box no longer functions as a musical instrument. Figuring out how to preserve antique instruments under real-world conditions will be equally important. With further investigations into wood treatment, string manufacturing, and guqin acoustics, we may soon expect a new golden age of Chinese guqin making, producing new instruments that surpass the best antique examples in terms of acoustics.

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Note: Some of the listed references are Chinese publications, including ancient texts and recent scientific literature. Although they may not be readily accessible for non-Chinese speakers, these citations serve as documented proofs to support our comments. Links to online sources are provided whenever possible.

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