String Theories: Chemical Secrets of Italian Violins and Chinese Guqins

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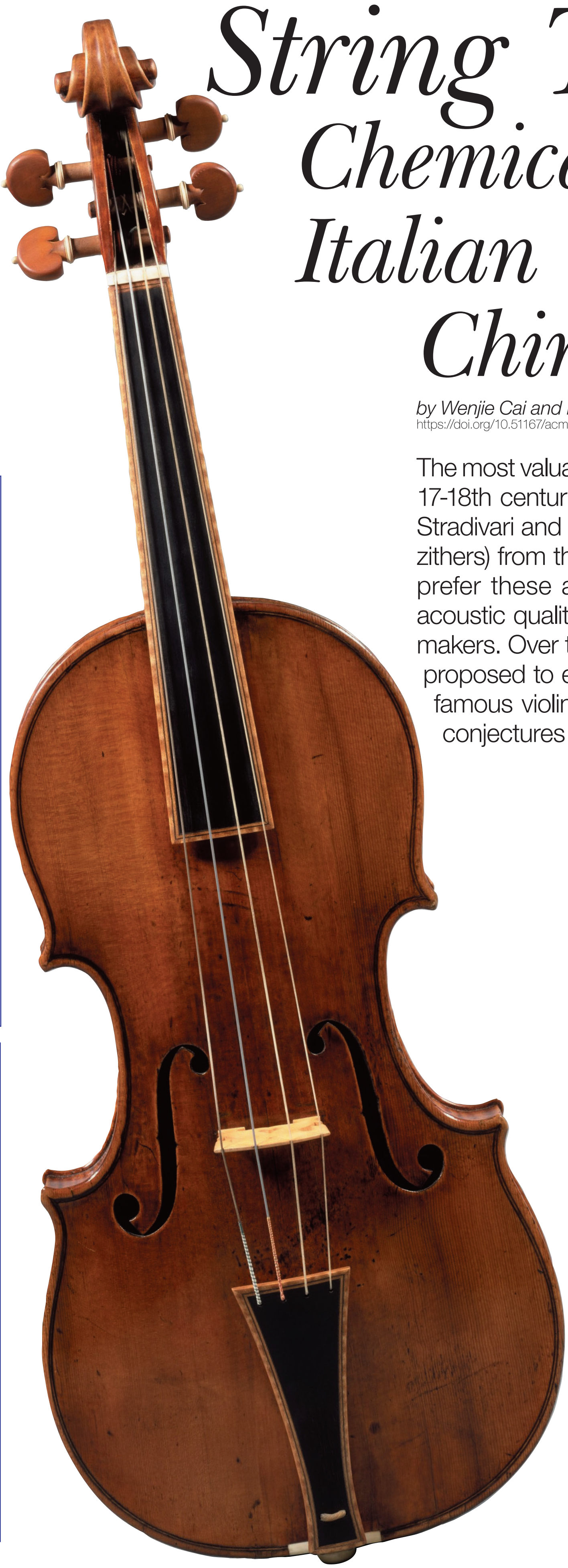

The most valuable musical instruments in the world are 17-18th century violins from Cremona, Italy (made by Stradivari and Guarneri), and Chinese guqins (7-string zithers) from the 8-13th century. Today, musicians still prefer these antique instruments for their superior acoustic qualities that cannot be reproduced by later makers. Over the centuries, many theories have been proposed to explain the unique playing properties of famous violins and guqins, but most are based on conjectures rather than factual evidence.

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(China)

THERE IS LITTLE understanding of their unique acoustics and psychoacoustics qualities. Recent evidence suggests that the sweet and brilliant tone of Stradivari violins may originate from imitating the resonance properties of female singers. Although violins and guqins are relatively simple in their wooden box structures, their complex material properties can significantly affect the acoustics. Modern analytical techniques have been increasingly applied to examine their varnish compositions and wood properties. Many experts used to believe that Stradivari's varnish, in addition to its unparalleled visual qualities, plays a critical role in acoustic tuning. However, recent findings suggest that wood chemical treatments and wood aging may be the key to the Cremonese tone. Ancient guqin makers also believed these to be key acoustic factors. Wood treatment and aging can jointly affect hemicellulose degradation and cellulose rearrangement, which may affect the damping and elasticity of wood. The secrets of superlative musical instruments may be hidden within the chemistry of the wood.

It is a popular concept among chemists to consider chemistry as the "central science." Chemistry plays a bridging role between physics/engineering and biomedical/environmental sciences, both conceptually and empirically. The central science should also connect our past, our present, and our future. Chemistry is undoubtedly coupled to our future because energy, climate, and food issues involve large-scale chemical transformations of matter. However, the role played by chemistry in our past receives relatively little attention in current academia. This may be partly due to the negative connotation of pre-modern chemistry (alchemy) being associated with the unsuccessful transmutation of metals, to the point that even Isaac Newton's role as a leading chemist of his time had long been denied and ignored.

In this article, we will discuss why chemistry can help us solve the mystery of highly prized antique musical instruments, the marvels of ancient technologies. These include the famous Baroque violins made in Cremona, Italy by Stradivari and Guarneri, and millennium-old Chinese guqins. Over the past decade, their prices have soared to new heights and raised many eyebrows. In 2010, a Chinese guqin (7-string zither), made in 1120 for the Song-Dynasty Emperor, auctioned for 20 million USD. This was followed in 2011 by the auction of the 1721 "Lady Blunt" Stradivarius violin for 16 million USD.

In contrast, violins and guqins newly built by leading luthiers can be acquired for less than 0.5% of these record prices. It is the consensus of leading musicians that highly prized antique violins and guqins exhibit superior acoustic qualities that modern makers cannot reproduce. This is a rather mysterious phenomenon if we consider that violins and guqins are hand-made wooden boxes with relatively simple structures Most musical instruments do not inherently increase in value over time. Instruments like Chinese guzheng (21-string zither) will break down after a few decades of playing and are not considered collectibles. Other instruments like guitars and pianos can remain durable for a century or longer, but do not seem to improve over time – only a few may become collectibles due to memorabilia value. In contrast, finely crafted violins and guqins are generally believed to improve in acoustics over extended periods. Many players and collectors actively seek Italian violins more than 200 years old and Chinese guqins more than 400 years old. Is it just the passage of time that improves the sound of these instruments? Or did old masters possess special know-how that is lost to us? This has always been one of the most intriguing questions at the interface of art and science.

Joseph Michelman, a pioneer in the scientific investigation of Stradivari's varnish, had aptly explained in 1946 why Cremonese violins represent a significant conundrum in the face of modern science[1]:

> *For two hundred years, the art of violin making has not experienced any improvements. This is singular in view of the tremendous advances made in the arts and sciences. Again the advice of Ole Bull [a famous violinist] is inspiring: "… it would be absurd to say that persistent inquiry must fail to unravel a skein of so many ends."*

Richard Feynman famously said: "What I cannot create, I do not understand." Indeed, the overall complexities of instrument vibration, psychoacoustic perception, varnish chemistry, wood properties, and long-term material transformations still present great challenges to both theoretical and experimental sciences. People often think of instrument acoustics as a physics and engineering problem, and musical perception as a neuroscience problem. But few realize that what distinguishes famous antique instruments and their modern copies is material properties. Only chemical forensics can reveal the true nature of the materials technologies of old masters. This article will briefly summarize the current understanding of the acoustics, the varnish, the wood of Cremonese violins, and how research on Chinese guqin is beginning to catch up with the violin field and providing valuable cross-references. As we look deeply into the wood chemistry, there are some shared secrets between the superlative instruments of the West and the Orient.

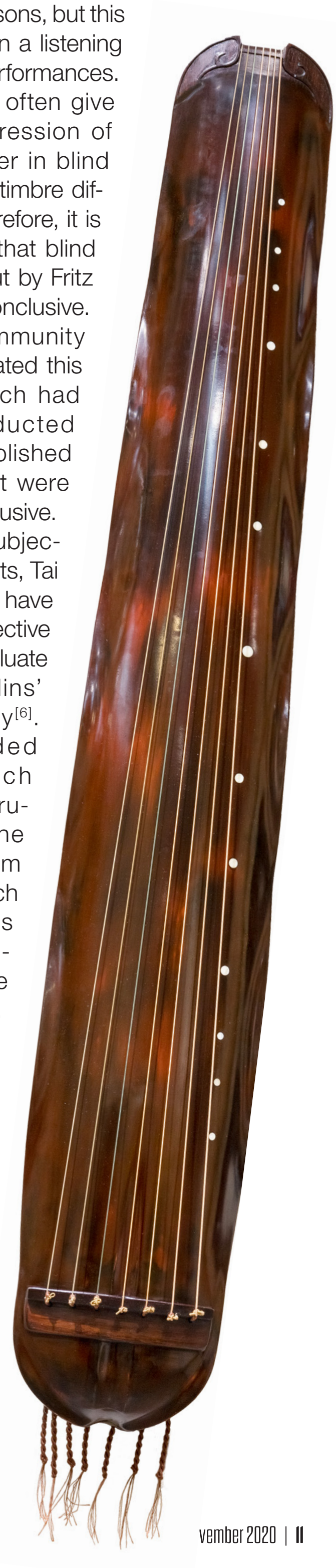
How do they sound?

There has always been a confounding issue in the research of antique string instruments: How do we ascertain that instrument acoustics can change or improve over time? Alternatively, how do we demonstrate that old masters in Cremona make the finest sounding violins? These are indeed very difficult questions to answer. The timespan involved in the first question is too long for ordinary experimental designs. Fortunately, spectroscopic and scattering techniques have now allowed us to detect chemical and structural changes in the wood of antique instruments, as compared to modern wood of the same species. The measurable effects of material aging provide plausible mechanisms for age-related changes in instrument acoustics reported by generations of musicians and collectors. The same musicians and collectors also inform us that two Cremonese masters mostly made the finest sounding violins in the world: Antonio Stradivari (Latinized as Stradivarius, 1644-1737)[2] and Giuseppe Guarneri "del Gesù" (1698-1744)[3]. However, modern acoustics and psychoacoustics research have yet to firmly establish the unique tonal qualities of Stradivari and Guarneri violins.

A musical sound has four basic attributes: pitch, loudness, timbre (tone quality), and spaciousness (spatial projection pattern). Traditionally, it has been said that Stradivari violins carry two acoustic advantages: (1) a sweet and brilliant tone; (2) a favorable spatial projection capability, giving the listener a better sense of proximity and clarity. On the other hand, Guarneri violins are thought to carry a dark and sonorous tone. Recently, Fritz and coworkers have published a series of blind listening tests showing that Stradivari violins are not favorably judged over modern master violins[4]. These results should not be overinterpreted because such blind tests have serious limitations.

First, fewer than 20% of the 500 surviving Stradivari violins remain in top conditions fit for concert violinists, but we do not know the quality of instruments entering these studies. Secondly, short-term memory for timbre quality only lasts for seconds, but it takes minutes for the players to change violins. By the time the next instrument is played, the memory for the previous instrument has severely decayed. Thirdly, the loudness has to be strictly matched to carry out timbre comparisons, but this is not feasible in a listening test with live performances. Louder violins often give the initial impression of sounding better in blind tests, masking timbre differences[5]. Therefore, it is not surprising that blind tests carried out by Fritz et al. were inconclusive. The violin community already anticipated this outcome, which had already conducted multiple unpublished blind tests that were similarly inconclusive.

Instead of subjective listening tests, Tai and coworkers have resorted to objective analyses to evaluate Stradivari violins' timbre quality[6]. They recorded five top-notch Stradivari instruments from the Chimei Museum in Taiwan, which has the world's leading collection of antique Italian violins. Their innovative approach was to apply speech analysis software to violin sounds, using linear-predictive-coding analysis that is not affected by loudness levels. They



discovered that early violins invented in Cremona and Brescia could imitate the vocal tract resonance frequencies of male singers (bass and baritone). Stradivari had further elevated the resonance frequencies to imitate tenors and altos, gaining a more feminine character. This may partly explain why Stradivari violins are considered to carry a sweet and brilliant tone. Nonetheless, perhaps 90% of the qualities that constitute a pleasant musical sound are still beyond our scientific comprehension. Sound waves produced by violins are very complex phenomena, and there is no objective quality standard yet. We have not yet identified the acoustic correlate for the superior projection of Stradivari violins or the dark sonority of Guarneri violins.

How were they made?

To reproduce the playing qualities of Cremonese violins, it is perhaps more important to understand the raw materials and manufacturing process than the underlying acoustic principle. However, two centuries of extensive investigations into European libraries and archives have yielded no insight into how Stradivari made his violins differently. The first of such investigations were launched in the late 1700s by a leading collector (Count Cozio) and a leading luthier (Guadagnini). Still, the descendants of Stradivari and Guarneri already left the trade and offered no useful clues[7]. Therefore, experts and scholars often refer to the lost methods of Cremonese makers as "the secrets of Stradivarius." The only way to recover the lost knowledge is to examine their instruments scientifically and reverse engineer them.

The first scientists to be intrigued by Stradivari violins were 18th-century physicists. Felix Savart was the first to apply Chladni patterns to analyze violin plates, working closely with the greatest violin maker of the 19th century, J. B. Vuillaume. Hermann von Helmholtz was the first to understand the vibration of violin strings and the air resonance inside the body. However, neither Savart nor Helmholtz was able to identify the unique acoustic qualities of Stradivari violins using the primitive tools of the 19th century. Instead, in-depth knowledge of Stradivari violins in the 19th century came from the Hill family, which had handled almost 500 Stradivari instruments as dealers, restorers, and makers. They have firmly established three important facts: (1) Cremonese violins had spruce for soundboards and maple for ribs/backplates. Such high-quality European tonewoods have always been in good supply (to this date); (2) Simply copying the shape and geometry of Cremonese violins is insufficient, even with the use of aged tonewoods; (3) Stradivari's varnish has unique visual qualities that have been impossible to recreate (even to this date), and there must be hidden secrets therein[2].

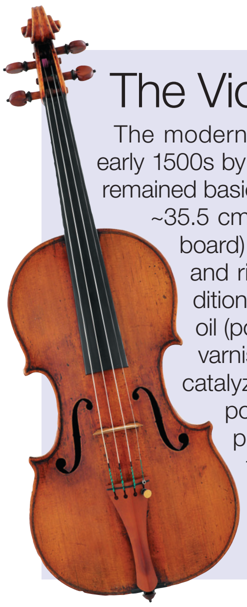
Being the most important biographers of Stradivari and Guarneri families[2,3], the Hill family's opinion that lost varnish recipes hold the key to superior acoustics was mainstream thinking in the violin community throughout the 20th century. From about 1800 to 2000, violin makers and enthusiasts had engaged in an ardent, frantic pursuit for the lost varnish of Stradivari. Their activities often generated wild conjectures and fanciful experiments, resulting in numerous media articles, press stories, lectures, books, and public announcements. This has caused a great deal of confusion about the true nature of Stradivari's varnish. In the following section, we will describe how modern chemical analyses have been increasingly applied to solve the varnish puzzle partially.

Beauty is but varnish deep

While chemists are most interested in the composition and stratigraphy of Stradivari's varnish, violin makers and restorers are more interested in whether these visual observations could be properly explained: (1) How is tinting strength achieved in such a thin and transparent varnish? (2) How does it protect the wood underneath from getting dirty? (3) Why does it give flamed maple a strongly dichroic property (chatoyancy) and a great sense of depth? The inability of the copyists to recreate a varnish matching these visual qualities alerts the chemists about the extraordinary properties of Stradivari's varnish.

The scientific progress on the chemical analyses of Stradivari's varnish from 1945 to 2009 had been previously reviewed in detail[8,9]. Only a brief account will be given here. Joseph Michelman pioneered the field shortly after WWII, a Harvard chemistry Ph.D. who successfully founded a chemical coating company. In the 1970s, Louis Condax, a chemist in the Eastman Kodak Company, worked with the famous violin restorer S. F. Sacconi to analyze many material samples removed from Cremonese instruments during repairs. In the 1980s, Joseph Nagyvary of Texas A&M University, a biochemist trained under Nobel laureates Paul Karrer and Lord Todd, investigated Cremonese varnishes using several microscopy methods. Since 2009, the key publications in this field include the books by Brandmair[10], Pollens[11], and Padding[12], as well as articles by Echard[13,14] and Fiocco[15,16]. Based on decades of research, we finally have a basic understanding of the stratigraphy and composition of Stradivari's varnish. The chemically identified varnish materials are listed in Table 1.

Stradivari usually applied three layers of coating materials, and their basic properties are described in Table 2. The top layer is the color varnish with oil-resin binding medium, made of drying oil (linseed or walnut) mixed with tree resins. The major resins appear to be rosin (from pine or spruce) and Venetian turpentine (from larch). Other additives may include various resins (mastic, sandarac, or copal) or beeswax. However, there is still no good test for the presence or absence of amber. The coloration method appears to be surprisingly diverse and complex. First, the oils and resins could be cooked or processed (adding metal ions) to generate different red, orange, yellow, or brown shades.



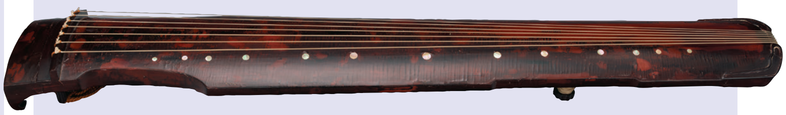
The Violin

The modern violin was invented in Cremona, Italy in the early 1500s by Andrea Amati. Its structure and geometry have remained basically unchanged to this date. The body length is ~35.5 cm, fitted with four strings. The top plate (soundboard) is made of spruce (*Picea abies*). The backplate and ribs are made of maple (*Acer* species). The traditional varnish is oil-resin type, composed of drying oil (polyunsaturated) and tree resins (terpenoids). The varnish dries via oxidation and radical polymerization, catalyzed by UV or metal ions. Spirit varnishes composed of shellac dissolved in alcohol later became popular. Violas and cellos also belong to the violin family of bowed string instruments.

The 1709 Stradivarius violin "Marie-Hall Viotti" (courtesy of Chimei Museum, Taiwan

The Guqin

The guqin was invented in ancient China more than 3000 years ago. The modern form appeared around the 2^{nd} century AD. The body length is around 120 cm. The guqin (7 strings) belongs to the zither family of plucked string instruments, not to be confused with the larger guzheng (21 strings). Common woods used to build guqins include *Firmiana simplex* (*qingtong*), *Paulownia* species *(paotong)*, *Catalpa ovata* (*zi*), and *Cunninghamia lanceolata* (*shan,* Chinese fir). The lacquer (*daqi*) is made of urushiol resin secreted by the lacquer tree (*Toxicodendron vernicifluum*). It dries via oxidation and radical polymerization, catalyzed by the enzyme laccase.



A Chinese guqin, circa 1600-1750

Secondly, red organic colorants like cochineal and madder may be dissolved directly into the medium or precipitated over inorganic substrates (chalk, aluminum hydroxide, or aluminum silicates) to make lake pigments for greater color permanence. Other organic pigments may include indigo (blue), carbon black, and an unidentified green lake. Inorganic pigments are also found, including iron oxide (red), mercury sulfide (red), and umber earth (brown). There is surprising heterogeneity in Stradivari's color varnish composition from different instruments, suggesting that he was constantly tinkering and experimenting.

The complexity of his coloration methods implies that Italian oil painters probably inspired Stradivari. But how did Stradivari achieve strong reddish tints in a thin and transparent varnish? Under the microscope, the density of visible pigment particles is relatively low. He did not incorporate many inorganic pigments with high refractive indices (RI) like iron oxide or mercury sulfide, which would otherwise reduce transparency. The tinting strength probably originates from oil and resin processing, dissolved organic colorants, or semi-invisible lake pigments, but they are difficult to differentiate and quantify.

To prevent the color varnish from going into wood pores, Stradivari applied a pale ground varnish for isolation. The transparent ground varnish contains an oil-resin medium of light yellow color, similar in composition to the binding medium of the color varnish, without the colorants. On some cellos, where thicker varnishes are required, there may be some inorganic particle in the ground layer that can enhance hardness. These particles may include chalk, gypsum, silica, aluminum silicates, or talc, but the combined volume fraction is probably just a few percents. In the coatings industry, such inert particles are called fillers, and those chosen by Stradivari all have similar RI as the oil-resin medium. If ground finely (<5 μm), such fillers can enhance reflective brilliance without adding cloudiness[8]. Another way to apply the mineral fillers is to mix them with a protein medium to fill the wood pores before varnishing. The presence of lead in the color and colorless varnish may act as chemical driers to promote radical polymerization, but still not enough to allow drying in the shade. From Stradivari's handwritten letter, we know that ultraviolet radiation from sunlight was required to dry his varnish[2].

The top layer on Stradivari's violin plates is not bare wood but received some kind of protective coating that impregnated the cell wall to seal the wood. There is no definitive chemical identification for the wood sealer material, but tentative evidence points to the presence of protein, colored stain, and plant gum. The purpose may be to impart some golden color to the wood and to prevent it from getting dirty when the varnish layers wear off. Pietro Mantegazza (1730-1803) told Count Cozio that he used collagen glue to seal the wood and then added a stain extracted from soot[7]. However, Echard et al. have also observed a Stradivari instrument without the sealer coating. It also lacks protein and gum signals under infrared spectroscopy[14]. There is considerable stratigraphic heterogeneity among different varnish cross-section samples from Amati, Stradivari, and Guarneri instruments. It remains possible that old masters chose different varnishing strategies on different wood planks for visual or acoustic adjustments.

Stradivari's varnish produces striking optical effects when applied over highly flamed maple, which has curvy cell growth. That way, wood fibers at the surface reflect light in different directions in alternating stripe regions. Stradivari had found a way to enhance the chatoyancy of flamed maple (changing colors when viewed from different angles) and the illusion of depth when staring into wood fibers. How this was achieved remains a major mystery, but based on existing clues, we may propose a general outline. The initial step was probably smoothing the wood surface, which would require tremendous skills. The tools might involve natural abrasives, metal scrapers, or burnishing stones. Then the top cell layers were stained and impregnated with a protective sealer coating. Ground varnish was then applied to fill the pores. Finally, a thin and transparent varnish with intense colors was applied. Perhaps all of these steps combined are still insufficient to recreate Stradivari's optical illusions. Films of dried oil show gradual increases in RI over time (from 1.50 to 1.58 over 500 years)[17], due to ongoing oxidation and fragmentation of polyunsaturated fatty acids. This gives old master paintings a greater sense of transparency by reducing

substance	refractive index	possible purpose	note
linseed oil	1.48-1.50	drying oil medium	RI of newly dried films
walnut oil	1.48-1.50	drying oil medium	RI of newly dried films
rosin / colophony	~1.54	major resin	probably pine or spruce resin
venetian turpentine	~1.54	major resin/solvent	RI of dried films
mastic	~1.54	minor resin	
sandarac	~1.54	minor resin	
copal	~1.54	minor resin	
beeswax	~1.44	minor binding medium	
protein	~1.54	wood sealer	probably collagen, ovalbumin, or casein
polysaccharide	~1.48	wood sealer	probably plant gum
calcite	1.49, 1.65	inert particle, lake substrate	strongly birefringent
calcium sulfate	~1.52	inert particle	RI for hemihydrate
silicon oxide	1.55	inert particle	RI for quartz
potassium feldspar	~1.52	inert particle, lake substrate	potassium aluminosilicate
aluminum silicate	~1.56	inert particle	RI for kaolinite
aluminum hydroxide	~1.57	lake substrate	
talc	1.54-1.60	inert particle	hydrated magnesium silicate
lead		drier or white pigment	probably lead soap or lead white
iron oxide	~2.8	red pigment and drier	RI for venetian red
umber earth	~2.4	brown pigment	manganese oxide and iron oxide
vermilion/cinnabar	~3.0	red pigment	mercury sulfide
cochineal lake		red pigment	
madder lake		red pigment	
orpiment	~2.7	yellow pigment	arsenic sulfide
carbon black	opaque	minor black pigment	
green lake		minor green pigment	colorant unknown
indigo	~1.50	minor blue pigment	

Table 1. Materials identified in the varnish of antique Cremonese violins

the RI mismatch between pigments and the medium. The refractive index of wood is around 1.55-1.58, slightly higher than freshly prepared oil-resin media (1.50-1.53). We propose that age-related RI increase may also contribute to Stradivari's oil varnish's unusual appearance, which may explain why modern copyists cannot recreate the same effect.

The acoustic varnish?

It is well known that unvarnished violins sound very different from varnished ones. The varnish is necessary for the protection of violins and serves the function of acoustic tuning. The real question is not whether we can alter violin acoustics by applying harder/softer varnishes in thicker/thinner layers, but whether we can recreate Stradivari's tone by reproducing his varnish. The Cremonese varnish ingredients identified via modern science (Table 1) are all traditionally available materials used in paintings and coatings in the 17th century, sold by the alchemist/pharmacist at the local apothecary. Except for inert filler minerals, violin makers have extensively experimented with these varnish ingredients during the 19th and 20th centuries. In the 21st century, we have gained a better understanding of how these ingredients fit into the stratigraphy of Stradivari's varnish. So far, we have not yet identified any magic bullet or unexpected ingredients in Stradivari's varnish via chemical analyses, much to the violin makers' disappointment. To obtain the hardest varnish possible, one could use oil and amber only; to obtain the softest varnish, one would use oil with little resin. Stradivari did not go to either extreme. Although the mechanical properties of the varnish over the violin cannot be directly measured, it would be difficult to imagine if Stradivari's varnish could exhibit drastically different mechanical properties outside the range of what has been created by his imitators.

There was some excitement in the violin community when finely ground mineral particles (0.2-2 μm) were reported in Cremonese varnishes by Nagyvary[18] and Barlow[19]. According to their scanning electron microscope (SEM) images, the volume fraction of the minerals is very high. Some makers subsequently reported positive acoustic effects by incorporating inert filler particles into their varnishes. This is a very interesting development because we now have many types of nanoparticles not accessible to Baroque craftsmen. Nevertheless, the practice of adding filler particles is hardly new. Ancient Chinese luthiers often added mineral powders or deer antler powders into their guqin lacquers for acoustic tuning[20]. Antique lute varnishes are also known to contain powdered glass or minerals. Surprisingly, several follow-up studies failed to find significant amounts of mineral fillers in Cremonese varnishes via SEM/energy dispersive X-ray analysis[10,13]. It raises the possibility that the particulate matters observed in Stradivari's varnish are mostly organic substances, probably resin crystals. It remains to be confirmed if varnish resins could recrystallize after extended periods, which may or may not be affected by the repeated application of French polish (shellac dissolved in alcohol). Whether recrystallization may have an acoustic effect also remains to be determined.

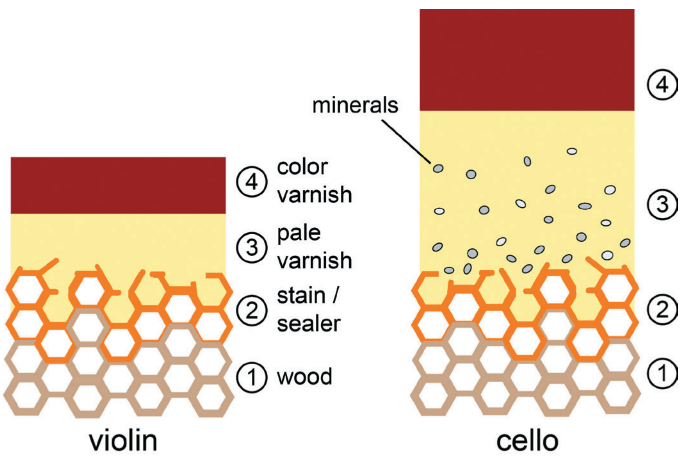
Our understanding of Stradivari's varnish system has advanced dramatically in the past few decades, thanks to the application of modern analytical chemistry. The ingredients identified were common materials well known to artists and craftsmen in the Baroque era. But the way they were put together by Stradivari to constitute a multi-layer varnish system with striking visual effects is more complex than previously thought and much more sophisticated than any varnish recipe found in old manuscripts[9]. As in the case of old master paintings, the key to extraordinary beauty is not determined by the raw materials used, but by well-controlled combinations and executions. After this realization, few and fewer makers now consider the varnish as the key acoustic factor in Cremonese violins.

Secrets in the wood

If not the varnish, where else should we look for the tonal secrets of Stradivari? How about the tonewood—resonance wood specifically grown or selected for musical instruments? Some are worried that tonewood trees are no longer available or no longer growing under the same conditions. But leading experts have assured us that tonewood availability in modern times is just as good as the Baroque period. Spruce *(Picea abies)* is a dominant species in many parts of the Alps and maples *(Acer sp.)* are commonly cultivated for furniture making. The wood densities measured by computed tomography are also similar between Cremonese instruments and modern copies[22]. Although Stradivari's life coincided with the colder climate of the Maunder Minimum, he did not select slower growing trees with higher wood densities.

Some suspect that Cremonese makers had a stash of aged tonewoods at their disposal. However, dendrochronology studies have confirmed that Cremonese makers mostly used recently harvested tonewoods, not old stocks left by their grandfathers[23]. The Hills also reported suboptimal results with aged tonewood[2]. We have examined some 18th-century spruce samples from old European buildings and their X-ray diffraction patterns often show reduced cellulose crystallinity (unpublished data). This is consistent with the warnings of ancient Chinese luthiers about load-induced damage in wood pillars/beams from old buildings[20]. Moreover, tonewood-quality spruce is usually the top 0.1%-1% of lumber selections. The chance that an old beam possesses tonewood qualities was minimal, to begin with.

For violin tonewood, structural durability is of primary concern. The spruce soundboard is only about 3 mm thick but subjected to ~9 kg of downward force at the bridge feet. The wood drying process is crucial for its long-term durability. Tonewood planks are usually air-dried in the shade for at least 3-10 years. Accelerated drying using kilns would compromise its internal structure and make it prone to cracking in the long run. For the past two centuries, the standard practice is to build violins with air-dried spruce and maple without additional treatment. Although there have been

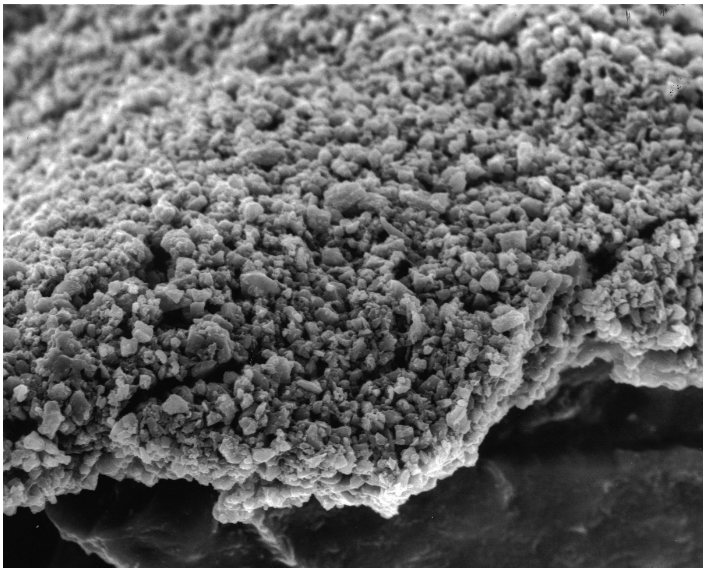


Three coating layers in Stradivari's varnish system

layers	color under white light illumination	color under UV illumination	identified chemical composition
color varnish	yellow-brown with shades of orange-red	salmon-pink	oil-resin & colorants
pale varnish	light yellow	bright whitish-yellow	oil-resin
wood sealer	golden yellow	grey-beige	protein & stain

Table 2. Three visible coating layers observed on Stradivari instruments

Stradivari's varnish applied over flamed maple on the 1709 Marie-Hall Viotti violin (Courtesy of Chimei Museum).



SEM image of the ground varnish from a Stradivari sample, after partial removal of the organic matrix by solvent extraction. The scale bar represents 10 μm. Originally published in Ref.[21]. Courtesy of J. Nagyvary

various attempts to further treat the wood, they usually compromise long-term structural integrity. Common treatments like acidic solutions, alkaline solutions, boiling, and baking can lead to partial hemicellulose hydrolysis and weakening cell wall structures.

The wood cell wall is made of three polymer types – cellulose, hemicellulose, and lignin – and their basic properties are described in Table 3. Hemicellulose is the weakest link and it will show spontaneous decomposition over centuries. However, it came as a great surprise when Nagyvary et al. reported severe hemicellulose degradation in the maple of Stradivari and Guarneri, beyond the expected extent of normal aging. It implies that artificial treatments had been applied[24]. Nagyvary et al. further demonstrated unusual elemental compositions in these Cremonese maples, a strong indication of chemical manipulation[25].

A follow-up study by Tai et al.[26] further confirmed that Stradivari wood specimens from independent sources had been treated with minerals containing these elements: Na, K, Ca, Al, Zn, and Cu. Moreover, the hemicellulose half-life in Cremonese instruments was found to be ~400 years (by 13C solid-state NMR), although artificial treatments could have partly influenced this. The breakdown of hygroscopic hemicellulose polymers also means reduced equilibrium moisture content by ~25% in Stradivari's maples, which means less vibrational damping compared to modern tonewood. In differential scanning calorimetry thermograms, normal maple exhibits two exothermic peaks while undergoing thermal decomposition under air, and so do Stradivari cello maples. However, Stradivari violin maples show three exothermic stages, implying physical separation between hemicellulose and cellulose caused by long-term, high-frequency vibrations. Therefore, there are three basic reasons that Stradivari's wood has distinct chemical properties compared to modern tonewood: (1) initial chemical treatments; (2) age-induced chemical transformations; (3) molecular rearrangements caused by long-term vibrations.

The spruce soundboard is more important than the maple backplate in terms of acoustic radiation and sound quality. Now that we know Stradivari and Guarneri used chemically manipulated maples, there should be similar investigations into their spruce materials. There has already been a strong indication that Cremonese spruces are highly unusual. Soundboards of Stradivari and Guarneri instruments are usually thinner and lighter than their modern copies[27, 28]. Stradivari sometimes carved the spruce plate so thin that it would seem to be doomed for premature cracking, and yet these instruments are still functioning after three centuries. Modern makers use air-dried, unaltered tonewoods to build violins, which has been the gold standard for two centuries. We propose that Stradivari and Guarneri did something very different. We have now gathered a cohort of a dozen Cremonese wood samples, including spruce and maple, and they are undergoing a series of chemical investigations. We will soon understand which chemicals were applied by Cremonese makers and how they affect the spruce and maple.

To age or not to age?

Wood is a relatively stable material under normal indoor conditions, but some chemical changes can occur slowly. The lignin becomes oxidized and turns yellow after some years, but otherwise remains structurally stable if protected from UV. The glycosidic bonds of cellulose break very slowly, but barely noticeable after hundreds of years. Hemicellulose can spontaneously undergo glycosidic bond hydrolysis and monosaccharide decomposition, generating volatile organic compounds like hydroxymethylfurfural and furfural. The half-life of hemicellulose decomposition fall in the range of several hundred years. Many studies have shown that aging alters the mechanical properties of wood. One may reasonably expect violin and guqin acoustics to be affected by wood aging, although there is no direct experimental verification yet. Whether such changes are musically favorable is even more difficult to determine.

The Chinese guqin has a much longer history than the violin (3000 vs. 500 years), and therefore the issue of tonewood aging often appeared in ancient Chinese books. It is said that "after five hundred years, the proper sound will develop" (9th century) and that "wood over one thousand years will lose most of its liquid" (13th century)[20]. This timescale seems to correspond to the degradation of hygroscopic hemicellulose polymers. Today, many guqin players actively seek instruments made in Ming Dynasty (1368-1644) or older, while violin players look for Italian violins made before 1800. It is plausible that wood aging may bring some acoustic benefits or favorable changes in playing responses.

Could the potential benefits of wood aging be reproduced by building instruments with aged wood or artificially aged wood? There may be mixed opinions on this matter, but let us consider its underlying chemistry. In ancient Chinese books, luthiers strongly advocated using aged tonewood and artificial aging methods (weathering under a shade, baking, or lime solution)[20]. As explained earlier, the violin community had generally negative

polymer type	monomers	polymer shape	dry weight	hygroscopicity	crystallinity	stability
cellulose	glucose	linear (24 chains/fibril)	~50%	hygroscopic at fibril surface	40-60%	difficult to hydrolyze
hemicellulose	mixed saccharides	linear/ branched	~20%	highly hygroscopic	amorphous	easy to hydrolyze
lignin	three phenolic alcohols	randomly crosslinked	~25%	hydrophobic	amorphous	very stable

Table 3. Major biopolymers in wood cell wall

experiences using aged tonewood and artificial wood aging. The modern method for artificial wood aging is heating to 140-200°C for hours or days, under dry or humid air, thereby promoting hemicellulose degradation. However, we believe that the underlying chemistry is much more complicated. In our preliminary tests, 13C solid-state NMR, infrared spectroscopy (IR), and small-angle X-ray scattering (SAXS) are used to compare maples removed from 18th-century violins and artificially aged maples (UV, baking, boiling, steaming, lime, and KOH). No single artificial aging method reproduces the same molecular changes observed in antique violin samples (unpublished data). There is only limited understanding about the complex chemical transformations that occur during natural and artificial aging. The role of initial wood treatments in altering the course of subsequent aging is even less understood.

Guqin makers today continue to seek aged tonewood from old buildings or burial structures. In some of the samples shared with us, the radiocarbon dating goes back to AD~1000 and ~200 BC (unpublished data). In most studies of archaeological wood, sample preservation is far from optimal. In contrast, only very well preserved wood of great age can be used as the tonewood, and wood removed from useable musical instruments are generally in excellent condition. Therefore, aged tonewood samples provide us with unique opportunities to study the chemistry of wood aging under optimal storage conditions.

The spontaneous decomposition of hemicellulose is a destructive process that cannot be halted. It means that Cremonese violins will eventually suffer structural failures even under museum storage. It is unclear when deterioration would finally occur, but violins made in 1560 and 1570 still produce acoustic spectra similar to those of modern master violins[29]. Hence, 500 year service life for Stradivari and Guarneri violins is perhaps attainable. Interestingly, Stradivari and Guarneri have applied lime or potash solutions to their wood. We do not know if their pH values were high enough to promote hemicellulose degradation. Modern makers experimenting with alkaline treatments can easily cause excessive damage without careful monitoring using infrared spectroscopy. We have also detected relatively high levels of Al^{3+} in some Stradivari and Guarneri samples, up to several thousand ppm. At these levels, Al^{3+} can increase the elastic modulus of cellulosic materials (unpublished data). We propose that that aluminum crosslinking may enhance cell wall stability and increase the stiffness-to-weight ratio of violin plates. Could this be a compensatory measure for the alkaline-induced or spontaneous decomposition of hemicellulose? Further investigations are warranted, and modern makers may even try other ions such as $Y^{3}+$, La^{3+},Th^{4+}, or Zr^{4+}. Curiously, Guarneri's maple already contained some Zr^{4+}[25], although the element was not discovered until half a century later.

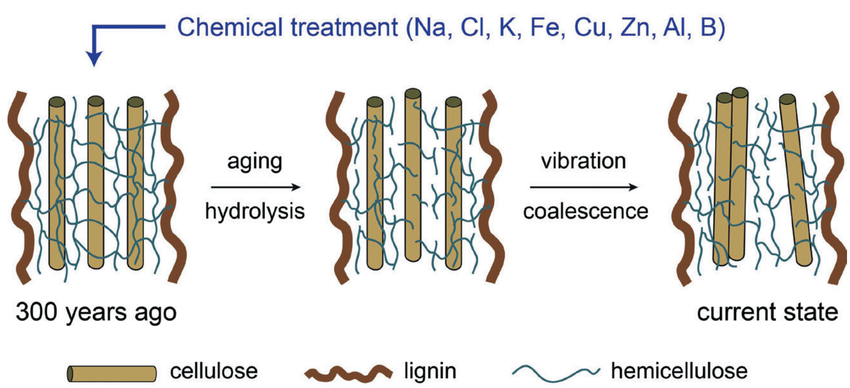
Synchrotron-radiation SAXS allows us to examine the width and the orientation of elementary cellulose fibrils in wood. We observed that common wood treatments (baking, boiling, steaming, lime, and KOH) often have significant effects on both the width and the orientation of cellulose fibrils. We have also observed interesting changes in Stradivari and Guarneri maples and fir wood from antique guqins (1000 and 2000 year old samples by 14C dating) (unpublished data). As shown in the accompanying figure, a 2000 year old fir sample and modern spruce (both are softwoods/conifers) show very marked differences caused by aging. It appears that cellulose fibrils may coalescence into dimer bundles after the surrounding hemicellulose has partially decomposed, but we are still in the process of developing new mathematical models to interpret the SAXS data better. How cellulose rearrangement may affect instrument acoustics is still an unexplored topic. The fact that 2000 year old wood is still making beautiful sounds in a highly prized instrument is a marvel.

Further research into these extremely old samples can tell us if ancient Chinese books were correct about the wood transformations happening over 500 or 1000 years. We propose that hemicellulose breakdown and cellulose rearrangement are key factors that underlie the unique acoustics of famous antique violins and guqins. Aging can promote these processes, and chemical processing can promote or compensate for these changes in complicated ways. This should be the focus of future research.

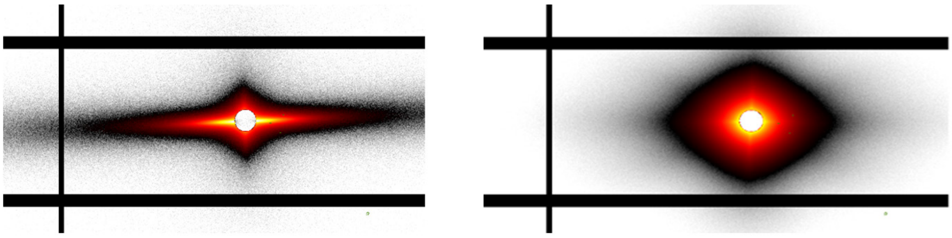
Conclusions and Perspectives

For many cultural heritage objects, scientific studies are often motivated by the need to conserve and restore them. Cremonese violins and ancient Chinese guqin, however, represent a different level of scientific challenge. They remind us to reflect on why space-age technologies are lagging behind pre-industrial handicrafts when it comes to producing certain musical sounds. History has shown that luthiers' empirical methods are insufficient to reproduce the Stradivari violins' visual and acoustic qualities. Proper reverse engineering requires in-depth scientific examinations first. Scientists need to work closely with luthiers to obtain precious material samples collected during restorations and cross-check research conclusions against their empirical knowledge.

For two centuries, violin makers had been fascinated by the extraordinary beauty of Stradivari's varnish and speculated it to be a key factor in acoustic tuning. With the help of modern analytical chemistry, we deciphered its basic stratigraphy and chemical composition, which turned out to be much more complex than previously thought. Nevertheless, Stradivari's varnish ingredients were commonly available, and the resulting mechanical properties are probably nothing extraordinary. Instead of the varnish, we should look into the wood properties for acoustic secrets. It appears that important properties of wood can be altered via artificial treatments and/or subsequent aging. The moisture retention of wood can be reduced by hemicellulose degradation or increased by adding hygroscopic salts. Damping, stiffness, and dimensional



Modification mechanisms of maple wood in Stradivari violins.



2D synchrotron SAXS patterns of modern spruce (left) and 2000-years-old fir taken from a Chinese guqin (right). The differences reflect cellulose fibril rearrangements (unpublished data).

stability are affected by moisture levels in complex ways. The breakdown of hemicellulose gives room for cellulose fibrils to reorient and coalesce under vibrations and weather cycles. How this affects Young's modulus and shear modulus along different directions is still unclear. Wood is a highly anisotropic and non-homogeneous material. When wood is carved into complex shapes, varnished, and glued together into a violin, the vibration patterns cannot be satisfactorily computed using current models. Admittedly, there is little understanding of how molecular compositions translate into mechanical properties, how mechanical properties translate into acoustic patterns, and how acoustic patterns translate into musical perception.

Chinese guqin makers have been fascinated by wood aging and artificial wood treatments for over a millennium and recorded some of their experiments in writing. With guqin tonewood samples over 1000 and 2000 year old being available, we can carry out cross-sectional studies on the chemistry of wood aging, which may shed some light on the future of Cremonese violins and how to preserve them for posterity. Ancient books state that guqins were coated with lacquers (urushi) exuded by *Toxicodendron verniciffluum*, and sometimes deer antler powders or mineral powders were added to improve the sound. However, recent chemical analyses suggest that ancient Chinese lacquers may also contain additives such as starch, proteins, oils, and the lacquer exudate of *Toxicodendron succedaneum*[30]. To understand the acoustic tuning effects of guqin lacquer, detailed investigations of its actual composition is necessary. We know that aging can alter guqin lacquers' visual appearance as seen in the gradual development of different crevice patterns. Could acoustic properties also become affected? So far, there have not been any detailed scientific analyses on the lacquer and wood of antique guqins, but we are beginning to investigate the latter.

It should be noted that, with the help of modern research and information sharing, violin making standards have risen to an all-time high, only next to Cremona in the first half of the 18th century. The last hurdle that separates today's leading makers and Cremonese masters is probably the wood processing know-how. There is a similar renaissance in guqin making as well. The art of guqin making went into decline after the fall of the Ming Dynasty in 1644, and almost fell into oblivion by the middle of the 20th century. It bounced back in a very significant way in the 21st century as guqin regained its cultural prominence as in the time of Confucius. To revive guqin making to the high standards that once existed 400-1200 years ago, guidance from modern research will be required. Cremonese violins as once viewed as a singular case for which ancient methods outperform current technologies. Recently we have found a parallel phenomenon in Chinese guqins. While more published scientific studies support Italian violin research, Chinese guqin research is supported by better historical documentation. These two instruments can serve as valuable cross-references for each other. Some of the underlying scientific principles regarding their woods, coatings, acoustics, and perceptions may have much in common.

The chemistry of wood aging plays an important role in the acoustics of antique violins and guqins. It is uncertain if modern science will ever succeed in simulating that process. If not, we simply have to make the best possible instruments using the best possible materials and methods, and then wait for a few centuries for full maturation. This concept is almost alien under the current fast-food culture centered around "me and now." Ancient guqin makers believed that good sound would be developed after five patient centuries. We can only hope that, by the year 2500, human civilization will continue to persist on this planet to enjoy the fruits of our current labor.

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