Stradivari's Varnish A Review of Scientific Findings—Part I

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Abstract

The violin varnish used by Antonio Stradivari and other Cremonese master luthiers has been a subject of fascination for two centuries. Scientific evidence accumulated over the last few decades has shed some light on its structure and composition. The organic component consisted of drying oils, resins, and proteins. The inorganic constituents included metallic driers, pigments, and inert particles. This article presents an in-depth survey of the scientific literature on Cremonese varnish analyses.

The modern violin is generally believed to have emerged in Italy in the first half of the 16th century [1, 2]. During its golden age (about 1550-1750), the city of Cremona flourished as the violin-making center of Europe. Many believe that the art of violin making reached its peak in the hands of Antonio Stradivari (Cremona, 1644-1737) [3]. The only serious contender to Stradivari's throne happens to be his neighbor, Giuseppe Guarneri *del Gesù* (1698-1744) [4]. After their deaths, the level of violin making rapidly declined in Cremona, and subsequently no violinmaker has been considered their equal in terms of sonic appeal and consistency. Why their success has not been reproduced remains a profound cultural mystery and a subject of fascination.

During the last two centuries, it seems that not a year has gone by without someone claiming to have rediscovered Stradivari's secrets. The reader can be assured that this author makes no claim of this sort. In my opinion, there is little evidence to suggest that Stradivari's materials and methods deviated too far from those of his master or peers. Building upon time-honored Cremonese traditions, his personal success probably could be attributed to a combination of good eyes, good hands, good ears, attention to details, creativity through constant tweaking, and, most of all, artistic inclination. However, the Cremonese tradition of violin making, which enabled Stradivari and Guarneri *del Gesù* to attain such heights, had been largely lost by 1800 [3-5]. After two centuries of experimentation and research, we have regained some, but not all, aspects of their knowledge.

THE QUESTION OF MATERIALS

The sound of a violin is the combined result of its materials and construction. Some believe that Stradivari had unsurpassed intuition that allowed him to perfectly construct each violin, while others believe the key was exquisite materials whose secrets were jealously guarded and lost. Some think both construction and material contribute equally, whereas others even question whether Stradivari was actually any better than leading modern luthiers. While all of these are debatable issues, his violins have become such musical icons that a very basic question deserves to be asked:

What is a Stradivarius violin made of and how do we know it?

Unfortunately, the answer to this seemingly simple question is by no means straightforward. The fundamental difficulty is that, in the heyday of Cremonese violin making (1550-1750), the knowledge of those luthiers was probably transmitted through apprenticeship and not in writing, at least not publicly. The only first-hand account of Cremonese materials is a letter by Stradivari, in which he apologized to a patron for the delay due to drying the varnish under the sun. The facsimile of the original letter was reproduced in the Hills' book [3], and the transcription reads, "compatirà la tardanza del violino perchè è stato la causa per la vernice per le gran crepate che il sole non le faccia aprire." The exact meaning of the sentence has been debated, and the Hills' translation was: "I beg you will forgive the delay with the violin, occasioned by the varnishing of the large cracks, that the sun may not re-open them." An alternative interpretation has been given by Claudio Rampini [6]: "I beg you to forgive the delay in delivering the violin, which is due to the varnish (which needs sunlight to dry). We must take care that the instrument does not split apart due to the sun's heat." Despite the ambiguity, it appeared that the varnish was dried under the sun.

Otherwise, there is second-hand information from Father Fulgentius Micanzio of Venice, writing to Galileo regarding the purchase of a Cremonese violin in 1638 (cited in Ref. [3], p. 242). The letter mentioned an anonymous Cremonese luthier's reply that the varnish "cannot be brought to perfection without the strong heat of the sun." Beyond these two letters there are no reliable written accounts concerning materials actually used in Cremonese violins.

The requirement of drying in the sun indicated that Cremonese varnishes contained drying oil. Drying oils traditionally used in Europe included linseed, walnut, hempseed, and poppy seed oils [7]. Compared to non-drying oils such as olive oil, these oils can solidify satisfactorily due to a high content of polyunsaturated fatty acids (with multiple carbon-carbon double bonds). Drying is mediated by the chemical reaction with oxygen via free radical mechanisms, leading to polymerization and solidification. The drying process could take hours or days, depending on how the oil was processed and what chemical additives were used [8]. It could also be accelerated by the heat and ultraviolet (UV) radiation from the sun. If the Cremonese varnish were entirely based on volatile vehicles such as essential oils or alcohols, then sun drying would be unnecessary. On the other hand, non-drying oils would not dry satisfactorily even under the sun or after prolonged exposure to air.

Given the dearth of trustworthy historical accounts, the dispute over the nature of Stradivari's materials has carried on for two centuries. Many claimed to have found Stradivari's secrets, but in most cases misinformation and folklore overshadowed actual progress. One of the most sensational tales was told by a direct descendant of Stradivari, who claimed to have copied his ancestor's varnish recipe from a then-destroyed family Bible [3]. Others claimed to have acquired the Bible recipe, plus another found in a letter from Stradivari to the Venetian luthier Domenico Montagnana (1686-1750) [9, 10]. However, there is no evidence to this date that such recipes actually existed [11]. I believe there is a need to review this subject based on published scientific findings instead of personal epiphany or hearsay. In this review, I will discuss how advances in analytical methods continuously uncover new details that challenge preexisting views. At the same time, I wish to outline the limitations of each analytical method and the caution that should be paid to interpreting experimental results. Violin material research has two major focuses, the varnish and the wood; it is the former that will be reviewed in this article.

TRADITIONAL MATERIAL PARADIGMS

By the early 1800s, Stradivari and Guarneri *del Gesù* had gained widespread recognition as the greatest violinmakers in history [3, 4]. Throughout the 19th century, many tried to determine the materials used in their violins through simple examination methods—the eye, the nose, and basic instruments such as magnifying glasses and microscopes. These methods and the primitive chemical analyses available at the time were unable to ascertain the actual chemical composition of Cremonese materials. To gain further insights, many resorted to historical and hands-on approaches: either browsing old texts for material knowledge related to violins, or building violins with materials thought to be available in Stradivari's time to see if the final result could match the original. It was through such investigations that the violin community first formed some general opinions about what types of materials could have been used in Stradivari violins.

It is important to recognize that Stradivari's color varnish did not touch the wood. When the color varnish chips off (and it easily does so on some specimens), a transparent, lightly colored substratum can be observed over the wood surface. This important observation has been repeatedly emphasized by credible sources. In the 19th century, Charles Reade [12] came to such conclusions through direct inspection of Stradivari violins in pristine conditions, and his opinion was cited in Heron-Allen's classic treatise on violin making [13]. In the 20th century, Simone Sacconi [14], a leading restorer who repaired more than half of the world's known Stradivari instruments, recapitulated Reade's observations in his monumental study of Stradivari instruments. In addition, this two-strata anatomy has been confirmed in the scientific reports of Baese [11], Condax [15], and Nagyvary [16]. It may therefore be confidently stated that Stradivari's varnish is a composite coating with at least two distinct layers. The outer stratum is strongly colored and henceforth it will be called *color varnish*. The transparent, slightly yellow or golden substratum [12, 14, 17] will be denoted as the *ground*. According to Sacconi [14], the ground layer is a hard, durable, insoluble and impermeable film tightly bound to the wood. It penetrates into the wood and cannot be removed without damaging the wood surface. Sometimes the ground is also called the filler, priming coat, sealer, or size, because it supposedly fills or seals the pores on the wood surface. From this point on, the entire coating system of Cremonese instruments, including the color varnish and the ground, will be collectively called the *wood finish*.

Unfortunately, the term *varnish* in the existing literature has been used rather liberally, resulting in some confusion. Sometimes the term refers to the color varnish and at other times the entire wood finish. The term *ground varnish* could also mean the ground, or a clear coat of varnish (without the colorants) applied above the ground but beneath the color coats (varnish with colorants). Moreover, it should be emphasized that most authorities agree that Stradivari's wood finish is generally similar to those of other Cremonese masters [3, 12, 14, 17, 18]. Thus, the actual subject under review is the Cremonese wood finish, which was applied to the violin as well as other instruments of the violin family.

During the 19th century, through historical and hands-on approaches, certain basic ideas about what materials were used in Cremonese violins were formulated:

1) Color varnish: The term *varnish*, in its generic sense, refers to a "liquid which, when coated over a solid surface, dries to a transparent film" [19], and in the case of the violin it is colored. The violin varnish should at least contain some medium that dries properly and some colorants. Most agree that Stradivari's color varnish had drying oil as the principal medium, and chipped away easily [3, 12, 20]. Beyond these basic observations there was hardly any consensus. The controversy centered on the organic additives to the medium, such as resin, glue, wax, gum, protein, essential oil, and even alcohol. Inorganic substances played a lesser role in the debate, although they could also be added as siccatives or colorants (mineral pigments or binders for lake pigments) [2, 13, 20, 21]. Endless arguments about the composition of the organic media circulated around the violin community, both privately and publicly. (Michelman [17] has reviewed some of the older published accounts.) The nature of the colorants interested many people but was not as hotly contested because Stradivari's violins obviously came in different colors [3]. Fascination about the "lost secret" of Stradivari's varnish, for the most part, revolved around the medium, not the pigment or dyestuff.

2) Ground: This was generally believed to be a coating of organic substances such as oil, resin, glue, wax, gum, or protein. Some thought it was just a clear coat of varnish less the colorants. Heron-Allen [13] thought it contained a yellow resin such as gamboge or aloe dissolved in spirit. Bachmann [21] believed it was a layer of glue, a practice commonly seen in the Mittenwald tradition [2]. Count Cozio di Salabue [5], informed by Italian luthiers of the late 18th century, such as the Mantegazza brothers and Giovanni Battista Guadagnini, also thought it was

glue (water size). Some thought the Cremonese ground was just drying oil and cited the French luthier Nicolas Lupot as a proponent of this view [20]. Sacconi [14] noticed older German and Italian makers trying to imitate Stradivari's ground using animal glue, while English makers used a layer of ordinary varnish colored faintly yellow. Additional claims about Cremonese ground materials, including latex and propolis, have been reviewed by Zemitis [22].

I will refer to these ideas as the "traditional material paradigms" of the Cremonese finish. Though not universally accepted (all kinds of eccentric claims existed), they were certainly the mainstream opinion for almost two centuries, iterated and reiterated in many classic texts. Because Cremonese masterpieces have been long considered the Holy Grail of violins, many later luthiers tried to adopt materials and recipes that they considered genuinely Cremonese; others probably tended to believe their own preferred materials to be authentic. Despite the general acceptance of the basic paradigms, there was never any consensus regarding specific recipes or application methods.

Since the 1950s, modern analytical tools have been increasingly applied to characterize Cremonese finishes. Do emerging scientific data support or refute these century-old paradigms? Before delving into that subject, let us first review the key findings prior to the era of modern chemical analyses, as aptly summarized by the Hills [3]. As a family of successful string instrument makers, restorers, dealers, scholars, and players, the Hills had handled more than 500 of Stradivari's instruments when their seminal book on Stradivari was published in 1902, making their first-hand experience unparalleled. In their book they dedicated one chapter to Stradivari's wood finish and another to the wood itself.

THE HILLS' OPINION

In their biography of Stradivari [3], the Hills used the term *varnish* more loosely, denoting the entire wood finish. They refrained from speculating on the constituents of the wood finish and simply stated "that Stradivari used solely a pure oil varnish, the composition of which consisted of a gum soluble in oil, possessing good drying qualities, with the addition of colouring ingredients, is, we think, beyond controversy." The word *gum* mentioned by the Hills would translate into modern lingo as *resin*. Today gums refer to tree exudates mainly composed of water-soluble carbohydrates, such as gum arabic [23]. Carbohydrate gums are insoluble in oil, and instead the Hills were referring to oil-soluble resins, which were also called gums at that time. A varnish made of resin and drying oil is called a fixed oil varnish, where "fixed" means non-volatile, as opposed to "essential" oils, which are volatile.

The Hills also pointed out that the color varnish was "chippy" and possessed unparalleled transparency and brilliance. With regard to tone, they ranked the following factors in the order of decreasing importance: wood finish, construction, and wood quality. The Hills considered Stradivari's finish to be unsurpassed in terms of visual and sonic appeal. Even if not everyone agrees with the Hills on the tonal effects, the visual beauty alone gives us enough reasons to attempt to recreate Stradivari's finish, but how?

When the Hills wrote their book, chemical analysis was too primitive to ascertain wood finish composition from antique samples. To illustrate this point, consider that the 1902 Nobel Prize for Chemistry was awarded for narrowing the possible molecular structures of glucose down to two. It would take another 50 years to determine which of the two was correct [24]. Under the technological restrictions of the 19th century, the most logical approach to reconstruct Stradivari's wood finish was to start with a shelf of materials thought to be available to Stradivari and a list of ancient and modern recipes (the Cremonese ones were lost), and start experimenting. If someone could create a wood finish that looked like Stradivari's, he would then pray for similar tonal effects. Although the acoustical effect of the finish actually depends on its mechanical rather than optical properties, visual comparison was the best analytical method then available. Therefore the Hills' approach to reproducing Stradivari's wood finish was very reasonable for their time, but they also admitted their shortfalls despite tireless efforts.

Countless others, before and after the Hills, have tried to concoct Stradivari's finish following a similar logic. Almost every old varnish recipe, for musical instruments or otherwise, has been resurrected, and every conceivable wood finish material potentially available at Stradivari's time has been tinkered with. This may qualify as the greatest single chemical experiment ever conducted by humankind, a 200-year saga continuing well into the present millennium. Most of it was conducted privately, but still a dazzling number of studies and recipes have been published. Nevertheless, authorities such as the Hills [3] and Sacconi [14] reminded us that the visual glamour of Stradivari's varnish had not been equaled, an opinion that still resounds in the 21st century [25]. Moreover, the violin community at large does not believe that the wood finish wild-goose-chase has led to the recreation of the Stradivari tone, a notion that keeps driving his violins to record prices. It seems that two centuries of experiments have largely fallen short of their goals.

Taking a step back, we might ask why anyone should care about the Cremonese wood finish. Other than its visual appeal, is the finish really important for the tone? After spending decades comparing the wood, construction, and wood finish of classic Italian instruments against modern copies (such as those made in Jean Baptiste Vuillaume's shop), the Hills felt that it had to be [3]. In turn, J. B. Vuillaume (Paris, 1798-1875), the 19th-century luthier whose copies of Cremonese violins won near-universal praise, always kept his wood finish recipe secret from his staff of workers who actually performed most of the wood carving [26]. Modern luthiers can also attest to the tonal effect of the wood finish; otherwise many of them would not have burned their fingers or smoked their shops striving for the ideal confection. However, the effect of different varnishes on the vibrational properties of tonewoods is easily measurable [27-30], although it is unclear what kind of effects are desirable. Therefore, the pursuit of the Cremonese sound via reconstructing the Cremonese finish seems to be a reasonable route, though not necessarily the only or the most important one. Another point that should not be overlooked is that the wood finish is first and foremost a protective coating [2, 22]. The fact that Cremonese instruments still serve top musicians centuries later speaks for the protective power of the wood finish, which is also of considerable interest to modern luthiers trying to secure a place in history.

The next logical question to ask is whether the "traditional material paradigms," which have guided the vast majority of reconstruction efforts to date, are in fact erroneous. After all, these paradigms were formulated when the science of analytical chemistry was in a relatively primitive state. This question must be addressed through modern scientific studies.

BREAKING THE PARADIGM: MINERAL GROUND

The first person to seriously challenge the "traditional material paradigms" of the Cremonese finish was Simone F. Sacconi, a person deeply versed in the tradition of violin making. Like the Hills, he knew Stradivari violins intimately and tried to decipher what factors affected their sound, and likewise concluded that wood finish was a major determinant [14]. Due to the chippy nature of Stradivari's color varnish, many specimens have lost much of the original varnish and often received revarnishing. Sacconi observed that Stradivari's color varnish did not penetrate the wood, due to the presence of a transparent ground layer. He further noticed that the loss of the original color varnish did not abolish the distinctive Stradivari tone, which greatly puzzled him. He suspected that the ground, instead of the color varnish, was a major factor in sound quality. Working quite a few decades after the Hills, Sacconi's investigation benefited from the advances in analytical chemistry.

Sacconi's greatest contribution was to point out that Stradivari's ground contained large amounts of inorganic substances [14], whereas traditional views were primarily concerned with organic materials. Stradivari's ground had been carefully examined by many before Sacconi, but he took the further step of submitting samples to chemical laboratories for analysis. In his book there is no mention of what analytical tests were performed, only that silicon, potassium, and calcium were found. Consequently, he proposed that the ground could be "a silicate of potassium and calcium," or potash-lime glass applied as a water-glass solution.

Since Sacconi publicized the inorganic nature of the ground, several independent research groups have followed up using more powerful analytical techniques. Barlow et al. [31] and Barlow and Woodhouse [32] examined Stradivari's ground layer using the scanning electron microscope (SEM) and published several images. SEM is an instrument that focuses a beam of electrons at the sample surface to resolve topographical features [33]. Because the wavelength of electrons can be much smaller than that of visible light (400-700 nm), SEM has much better spatial resolution than light microscopy. Figures 1 and 2 are electron micrographs of the wood finishes by Stradivari and an old Dutch master (see Ref. [32], also published in two parts in Refs. [34, 35]).

Figure 1 is an SEM image of Stradivari's wood finish, in which a composite material containing micrometer-sized particles extends into wood cells. Above that is a thin, smooth layer, presumably the color varnish, but little is left of it; or it could represent polish material. Figure 2 is an SEM image of the varnish of a cello by Pieter Rombouts (Holland, 1667-1740), with a diagram explaining the observed features, assigned by the original authors. Note that the Rombouts sample shows an oily layer beneath the particulate layer, while Stradivari's particulate layer penetrates the wood [31]. Other images published by Barlow and coworkers include samples from a violin by Francesco Goffriller (Venice and Udine, 1692-1750) and a violin by Nicolo Amati (Cremona, 1596-1684). The former shows a particulate layer above the wood, but the latter does not. Out of the 15 antique samples they tested (those other than the four mentioned, specified as mostly Italian, 1650-1750), about half exhibited a particulate layer. On the other hand, about half of them appeared to have an oily layer. It should be noted that the absence of the particulate layer could be due to resurfacing by unscrupulous repairers and does not necessarily prove its absence in the

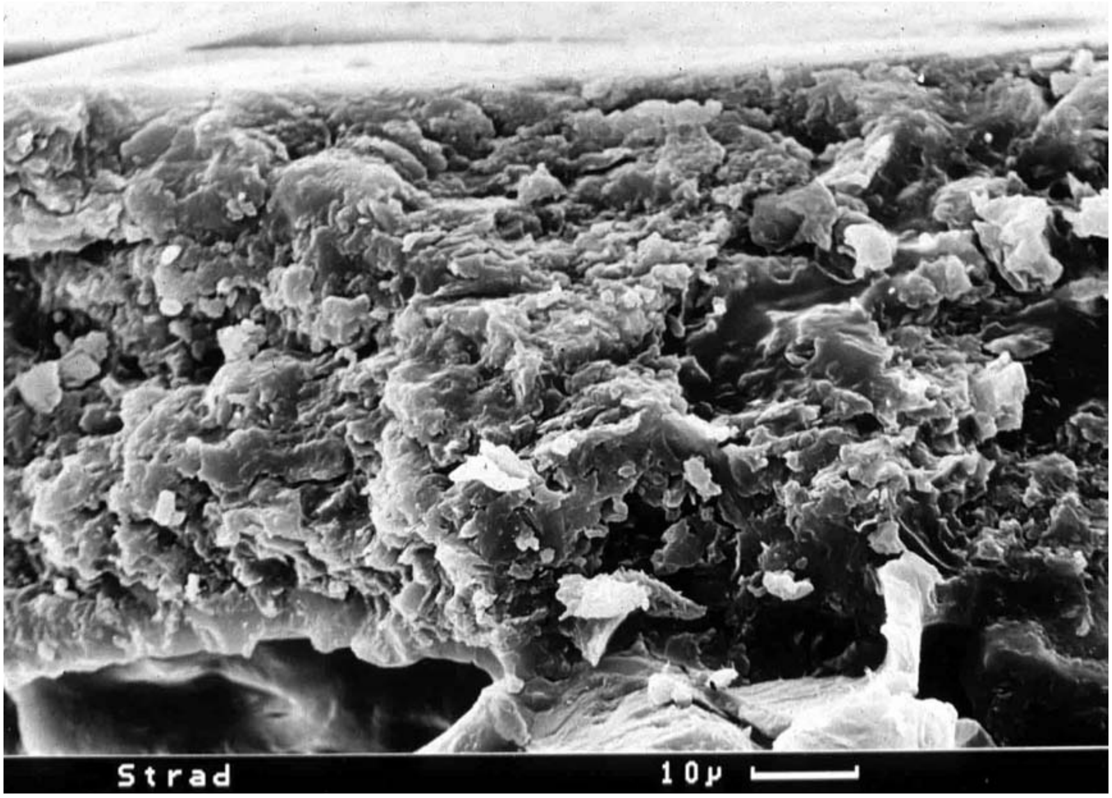


Figure 1. Scanning electron micrograph of a Stradivari wood finish. This micrograph was taken from the updated version of Ref. [32], downloaded from the website of J. Woodhouse (Jan. 2008): <www2.eng.cam.ac.uk/~jw12/JW%20PDFs/CatgutB&W1989.pdf.>. Courtesy of C. Barlow and J. Woodhouse.

original finish. However, does this particulate layer correspond to the silicate filler that Sacconi observed?

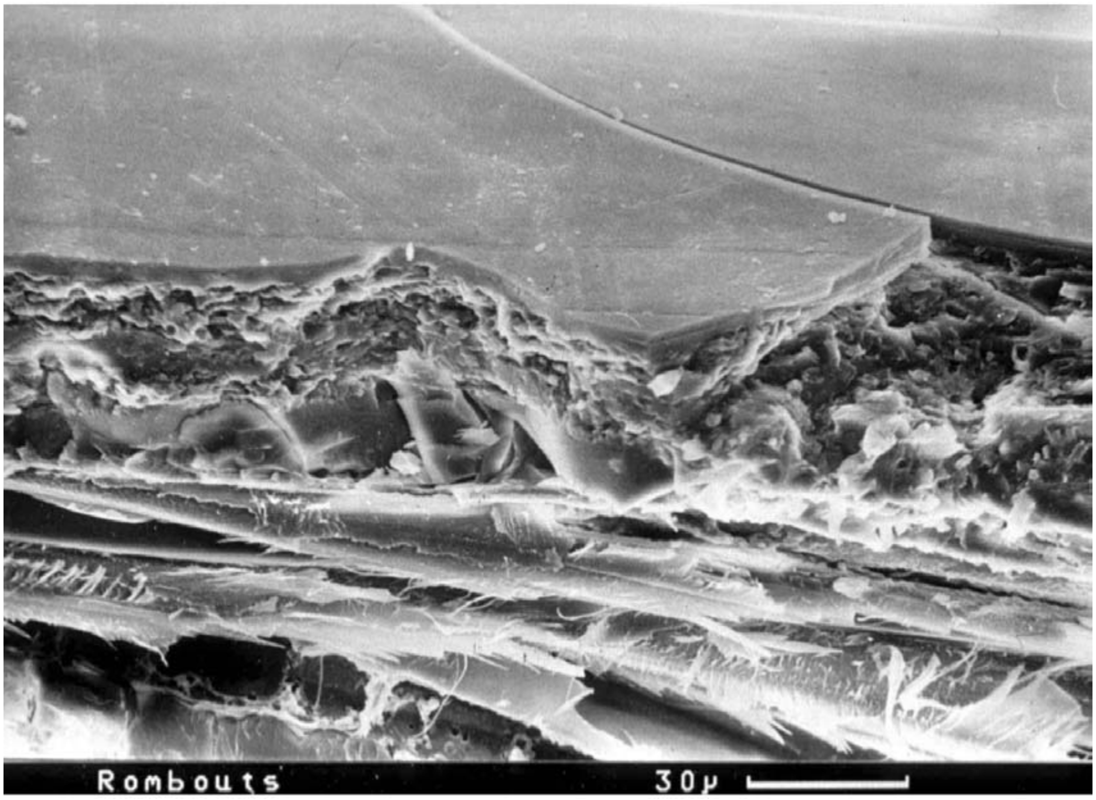
Sacconi [14] proposed that the ground was applied as a water glass solution of potassium and calcium silicates. The electron micrographs did not reveal any glassy substance, but small particles held together by some kind of binder (Fig. 1). As a side note, the basicity of the potassium silicate solution may be a cause for concern. A recent study has demonstrated the degradation of wood fibers, in particular the hemicellulose, in tonewoods treated with potassium silicate solutions [36]. Similar concerns have been expressed for the comparable treatment with sodium silicate solutions [37]. It has also been observed that potassium silicate treatment of the wood surface leads to the detachment and degradation of the color varnish in just a few years [38].

With electron beam instruments such as SEM, elemental analysis can be conducted by the electron bombardment of atoms in the sample, which induces X-ray fluorescence. The energy of the X-ray emitted is characteristic of the atom, providing a fingerprint for each element. When the X-ray emission is detected and resolved according to its energy, the technique is called energy-dispersive X-ray fluorescence (EDXRF). When EDXRF is conducted under the SEM on a small area of the Stradivari violin sample, such as the central region in Fig. 1, semiquantitative elemental composition can be acquired, but the result can be quite variable due to the geometric irregularity and chemical heterogeneity. Probing depth in this case is limited to a few micrometers. In addition, depending on the instrument, EDXRF can only detect elements with atomic numbers in a specified range. In this study, elements whose atomic number is smaller than 11 (H, He, Li, Be, B, C, N, O, F, Ne) or very large, such as lead (atomic number, 82), cannot be detected. Organic materials consist mainly of H, C, O, and N, and therefore EDXRF in general cannot detect organic materials such as wood, oil, or glue.

The EDXRF scans performed by Barlow on two Stradivari samples revealed that the major elements were Si, Ca, S, and Al; the minor ones were K, Fe, Cu, and Cl. Trace amounts of arsenic were also detected. In addition, an earlier SEM/EDXRF study by Nagyvary [39] identified the major elements in the varnish of a cello made by Andrea Guarneri (*ca.* 1626-1698) as Si, K, Ca, Al, Cl, and S. According to Sacconi's proposal [14], the most abundant elements should be Si, K, and Ca, not inconsistent with the EDXRF results. However, bulk sample analysis by EDXRF cannot ascertain the actual composition of individual mineral particles.

Sacconi [14] emphasized that the inorganic ground is tightly bound to the wood and penetrates into the pores. In another electron micrograph of Stradivari's finish published by Barlow et al. [31], the particulate ground was reported to penetrate ~30 μm into the wood, consistent with Sacconi's observation. The SEM image published by Nagyvary [40] from a different Stradivari sample (Fig. 3) also showed a particulate layer contacting wood fibers. However, since the corresponding light micrographs of the samples in Figs. 1 and 2 are not available, it is not entirely clear whether the particulate layers are the ground or the color varnish. In the Stradivari case (Fig. 1), if the particulate layer represents the color varnish, then it would stain the wood directly, contradicting the observations of Reade [12] and Sacconi [14]. It can be reasonably deduced that the particulate layer in Fig. 1 represents the ground. On the other hand, it is less clear if the particulate layer in the Rombouts image (Fig. 2) represents the ground or the color varnish. Varnishes and paints can sometimes include mineral siccatives, lake pigments (dyes affixed to mineral powders), or inert particles [41]. The oily layer of wood under the particulate layer could indicate the use of vegetable oil as the filler [42], which is a common practice in violin making [2, 13]. The smooth layer on the top could also represent polish materials, such as the French polish [2] often applied by restorers. Even though electron microscopy allows us to directly visualize topographic details, data interpretation may not always be straightforward.

It has been noted that not all classic Cremonese instruments have mineral grounds [25]. For example, Dipper has observed that on Andrea Amati (Cremona, *ca.* 1505-1577) instruments dedicated to Charles IX, some possess a ground layer that isolates the pigment from the wood while others don't [43]. In some cases it may be possible to attribute the absence



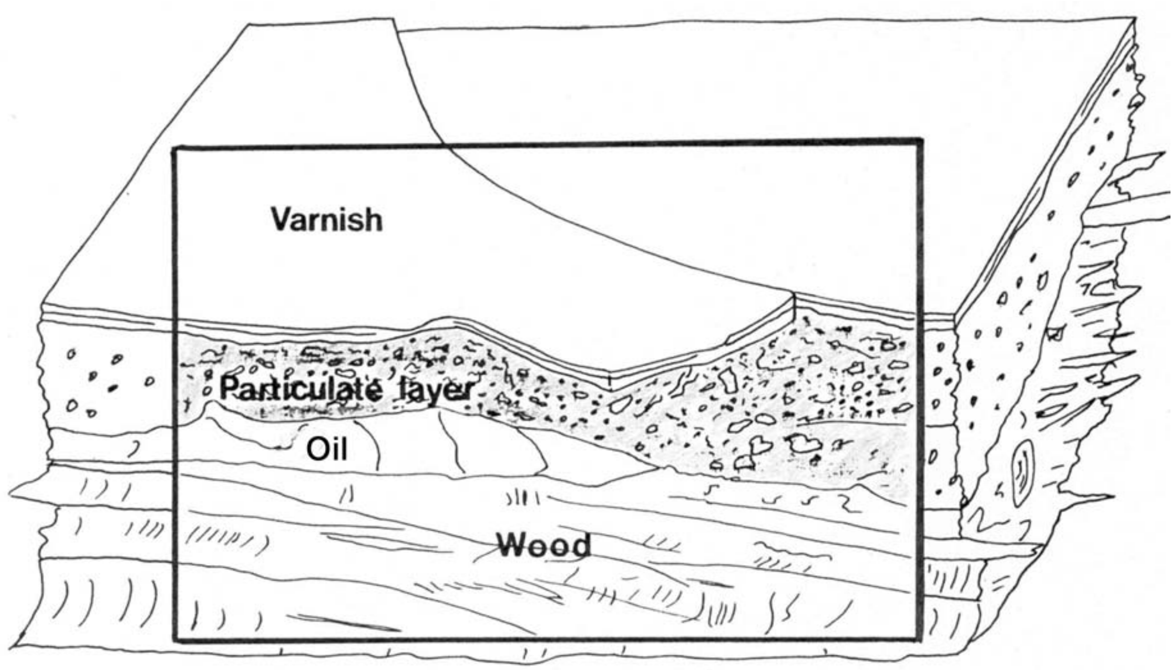


Figure 2. Scanning electron micrograph of a Rombouts wood finish (top) and a schematic explaining the observed features (bottom), as assigned by the original authors of Ref. [32]. Reproduced with permission of the Catgut Acoustical Society.

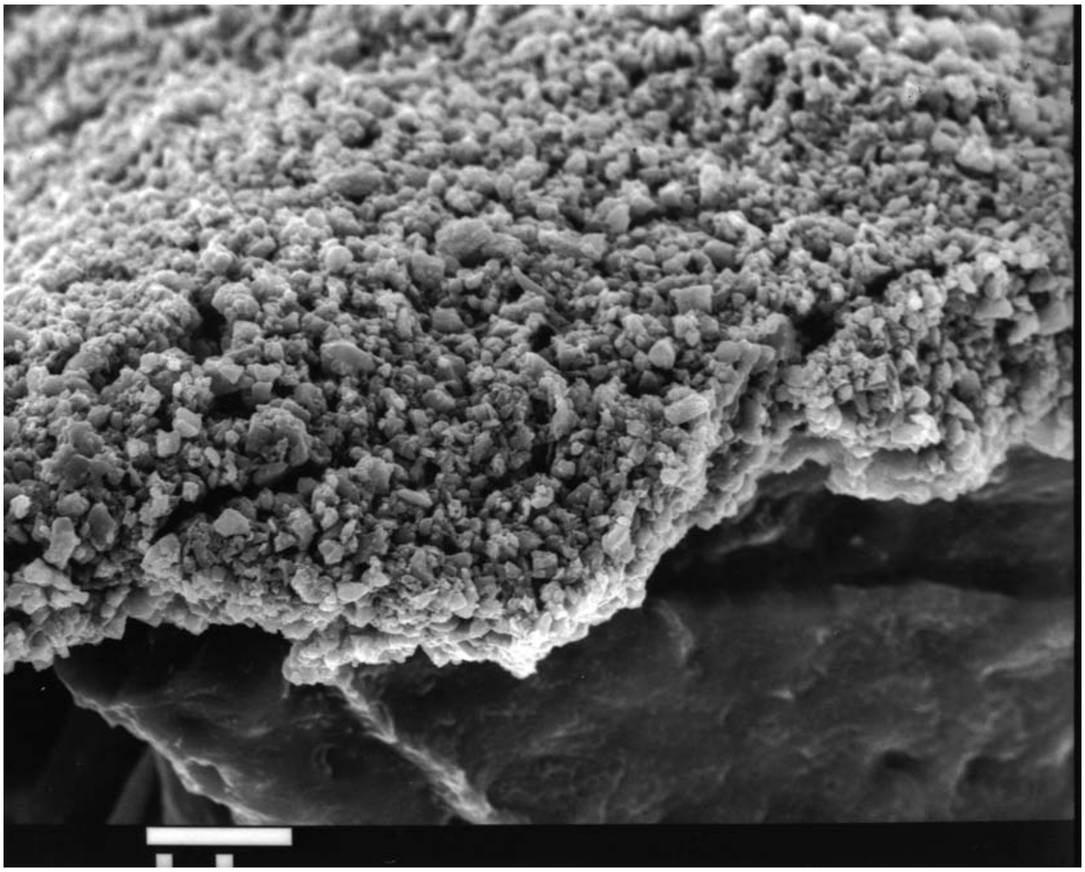


Figure 3. Scanning electron micrograph of the ground layer from a Stradivari sample. The scale bar represents 10 μm. Originally published in Ref. [40]. Courtesy of J. Nagyvary.

to wear and tear or intentional removal. Indeed, more drastic procedures than refinishing often occurred to Cremonese instruments, such as regraduating the plate or resizing to a different instrument [3]. Sacconi, who had worked with a vast number of Stradivari specimens, observed that they were generally covered with the ground, which was supported by the analytical evidence from several research groups [16, 31, 32, 44, 45]. It appears that the presence of the mineral ground on Stradivari instruments is the norm rather than the exception.

WOOD FINISH COMPOSITION: INORGANIC

No topic in violin research has been as zealously debated as the composition of Stradivari's wood finish over the last two centuries. So much has been said, but no consensus is ever reached. The confusion seems inevitable because of sample heterogeneity and the limitation of analytical methods. First, we must note that there is no good reason to believe Stradivari applied the exact same wood finish every time. We can easily see that he tweaked the colors [3] and perhaps other aspects as well. It is also not hard to imagine him occasionally leaving out certain ingredients due to supply shortage (Cremona was caught in war at times [18]). Materials sold to him could have unknowingly changed in composition over the long course of his career, since every chemical ingredient in the age of alchemy was shrouded in some mystery. The theory of the atom was first proposed in the early 1800s [46], and hence in Stradivari's time people had little idea about the chemical composition of anything they used. Inevitably, antique wood finishes have gone through aging and weathering, wear and tear, as well as retouching and marring.

Although the use of UV and infrared lamps can often reveal Stradivari's original finish [11, 44, 47, 48], tiny amounts of contaminants could severely affect certain analyses. Sample authenticity is sometimes a concern as well. If one decides to take a flake of varnish for analysis, it is unclear how much of the ground will lift off with it. It is also hard to know how much of the original varnish has worn away at the surface, because few surviving instruments of Antonio Stradivari have the pristine look of the violin dated 1716 known as *The Messiah* [3, 49]. Moreover, Stradivari's wood finish is without doubt a composite material with distinct layers [12, 14] (see section on *Stradivari's Finish: A New Look*).

To this time, there has been no dearth of confusion about the stratigraphy of Stradivari's wood finish, both in terms of nomenclature and composition. Sometimes when one reads something like "scientific evidence has shown that the ground varnish contains material X," it is not clear what the "ground varnish" refers to or how the author comes to the conclusion about "material X." Without doubt, some of the ambiguities in the original literature will be carried over into this review. Wood finish heterogeneity within a composite finish and between different instruments makes it difficult to draw general conclusions; the scarcity of samples often prevents meaningful statistical analyses.

Despite the difficulties outlined above, a more-or-less consistent picture of the inorganic composition of Cremonese wood finishes has emerged through cross-comparison of multiple studies employing modern analytical methods.

MANY MINERALS

An informative study of the wood finish from a Stradivari cello was published by Fulton and Schmidt [44]. Under UV and infrared illuminations, the whole instrument appeared to be covered with a modern overcoat. The modern overcoat provided enough adhesion to lift the original varnish. Using both polarized light microscopy and SEM/EDXRF, individual particles were successfully identified. Calcite (calcium carbonate) and potassium aluminosilicate were found in the varnish as well as in the wood. This reflects the presence of a mineral ground that penetrates into the wood. Calcite and potassium aluminosilicate contain elements that are abundant in the EDXRF data published by Barlow and Woodhouse [32], as well as Sacconi's original proposal [14]. It appears that different researchers were observing similar substances in their respective Stradivari samples.

Inorganic pigment particles identified were iron-earth (generic term for various iron oxide pigments) and orpiment (arsenic sulfide). Small amounts of other particles were also found, such as tin or cesium oxide (cesium was discovered as an element only much later), which probably represented adulterants. Since it was the age of alchemy, when most minerals used were in fact impure, trace amounts of contaminants were to be expected.

Quite a few studies have examined the elemental composition of Cremonese finishes by a variety of analytical methods, but the results obtained to date are semi-quantitative at best, and in most cases only qualitative. The detection limit for each element depends critically on the analytical method and the particular instrument being used. For example, the various X-ray fluorescence methods often cannot detect elements with atomic numbers lower than 10-15 [50]. Therefore, caution should be taken not to overinterpret the absence of a particular element from a single study. The positive identification of an element is much more meaningful.

EDXRF is a useful technique to conduct multi-element analysis on varnish samples. X-ray fluorescence can be induced by exciting atoms with beams of electrons, protons, or X-rays. Recent advances in EDXRF now permit *in situ* examination of the intact varnish on instruments, as conducted by Echard [47]. Since EDXRF is nondestructive, the most pristine instruments can be examined without fear of causing a scratch. In Echard's measurements, the excitation source was an X-ray beam directed at the instrument. Because X-rays penetrate light elements well, the probing depth probably exceeded the thickness of the varnish; consequently the signal from the wood had to be subtracted to obtain compositional information about the varnish. In addition, UV and infrared illumination were used to ensure that only areas with the original varnish were studied.

Nine of the 11 Cremonese instruments (by

Andrea Amati, Nicolò Amati, Antonio Stradivari, and Giuseppe Guarneri *del Gesù*) examined by Echard contained lead, implying the presence of lead siccatives. The use of lead compounds such as litharge (PbO) or lead white (mixture of lead carbonate and lead hydroxide) was known to the Italians as early as the Roman era [7]. Mercury was detected in three of the seven Stradivari specimens, and red particles 10-40 µm in diameter were found [51] under light microscopy (Fig. 4), implying the use of vermillion (mercury sulfide, also called cinnabar) as a pigment. Arsenic was not found in the Cremonese samples, but it appeared in a viola by Bernardo Calcagni (Genoa, 1710-1750), implying the use of orpiment. Iron and manganese were detected, but it was unclear if they represented pigments, driers, or contaminants. Although calcium, potassium, copper, and zinc were also detected, their significance is unclear due to their presence in human sweat [47]; there are other potential sources of contamination such as, in the case of copper, the use of copper vessels for cooking oil.

Several studies by von Bohlen and coworkers [52-56] have utilized total-reflection X-ray fluorescence (TRXRF) to interrogate historical varnishes. TRXRF is a variant of EDXRF analysis in which the excitation source is an X-ray beam with a very small incident angle [57]. In these studies, elements heavier than and including phosphorous could be detected semi-quantitatively [56]. Among one Stradivari and several Guarneri specimens analyzed, the abundant elements were calcium, potassium, chlorine, and sulfur. Minor elements found were iron and nickel, and lead was only detected at trace levels. When the ground was compared to the color varnish on an Andrea Guarneri cello, the latter had significantly higher iron content, implying the use of iron compounds as driers or pigments, while both contained very small amounts of lead [55]. One Guarneri sample showed very high levels of manganese, in stark contrast to other Cremonese specimens [52]. Manganese compounds could be used as siccatives or pigments, but in this case it might have come from retouching the varnish.

To obtain the depth-profile of elemental compositions of the wood finish, von Bohlen

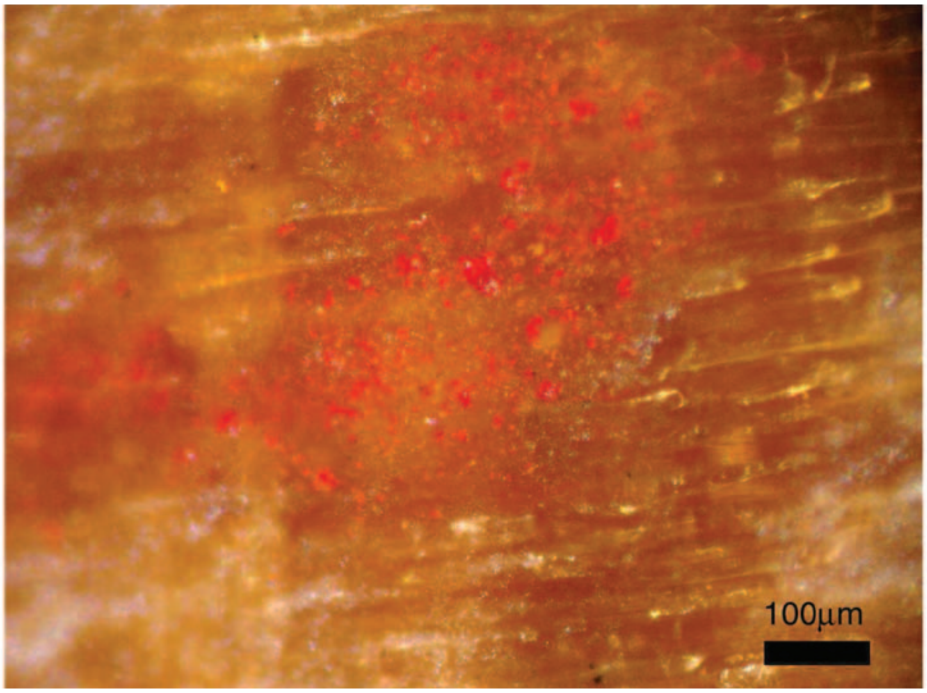


Figure 4. In situ light micrograph of the Sarasate *Stradivari violin of 1724 showing red pigment particles dispersed in the varnish. Reproduced from Ref. [47] with permission of Elsevier.*

and co-workers [58] used a focused beam of protons to excite the atoms to induce X-ray fluorescence. The wood finish was dissected to expose a cross section, subsequently probed by a proton beam ~20 µm in diameter, with a probing depth (in the direction perpendicular to the dissected surface) of ~50 µm. The beam scanned across the cross section of the wood finish, from the top surface into the wood region. If the wood finish contained sublayers with distinguishable mineral contents, it should be revealed in the depth-profile of detected elements. A sample from a cello by Giovanni Grancino (Milan, 1673-*ca.* 1730) probed this way showed, interestingly, several such sublayers (Fig. 5).

Figure 5 clearly shows a wood finish that is not homogeneous. There are two obvious strata with inorganic substances, each ~300 µm thick, separated by an interlayer of low mineral content ~360 µm from the surface, which may resemble the isolating compound observed by Sacconi [14] on Stradivari instruments. Both the upper (top varnish) and the bottom (ground) strata appear to be non-homogeneous. Performing scans at three different locations of this specimen, the original authors concluded that minerals had been applied to either polish the wood surface or fill the pores.

Tove and coworkers [59] also used proton excitation to induce X-ray fluorescence for varnish elemental analysis, with a probing depth of ~100 µm. Elements including K, Ca, Fe, Cu, Zn, and Pb were detected in a violin by Stradivari and in another by Guarneri *del Gesù*. In this study, the same samples were also analyzed by Rutherford backscattering (RBS). RBS, which measures alpha particles bouncing off atomic nuclei in the wood finish [60], was supposedly more quantitative than X-ray fluorescence, and it revealed mostly Si, S, and Ca. The discrepancy simply reflected the technical limitations of both methods. To quantify the elements, both methods had to assume that the wood finish is homogeneous. However, the inorganic components of the wood finish could differ substantially from one sublayer to another, which would lead to miscalculations. Furthermore, the estimates only provided relative, not absolute, quantification. In an earlier study by Tove and Chu using RBS [61], the varnished side of the Stradivari violin exhibited higher amounts of Ca, Fe, and Sn than the unvarnished side.

When Sacconi [14] provided wood finish samples to Condax [15, 62, 63] and Michelman [64-72], the older method of atomic emission spectroscopy (AES, also called spectrographic analysis) was employed for multi-element analysis. AES involves the atomization of the sample followed by measuring the light emitted by excited atoms. The most abundant elements reported by Condax [62] were lead and calcium (3-5%), but in Michelman's results [67] they were aluminum, iron, and silicon (<1%). The discrepancy is most easily explained by the qualitative nature of AES, partly because the atomization process becomes less predictable when the sample is complex [73]. Around the same time, Karl Letter (cited in Ref. [22], p. 98) found iron in a Giuseppe Guarneri *filius* Andrea sample by microchemical analysis (minute-scale chemical reactivity test). Fryxell [74] proposed, based on Michelman's data, that Cremonese finishes did not contain significant amounts of minerals and that the inorganic materials detected represented contaminants. However, it should be obvious that Stradivari's wood finishes shown in Figs. 1 and 3 contain large amounts of inorganic particles, which could not be explained by contaminants such as dust or abrasives [31, 45].

In summary, none of the Cremonese instruments analyzed to date by chemical methods has shown significant amounts of unusual elements. The only surprise came from a violin made in Mantua, where high levels of barium (~65% of the metallic content) were found in Camillo Camilli's (Mantua, *ca.* 1704-1754) violin varnish by AES [72]. It is possible that barium was incorporated into the varnish in the form of barite (barium sulfate), which has also been detected in small amounts in the varnish of an 18th-century Venetian viola [45].

A CLOSER LOOK AT INORGANIC PARTICLES

A study aimed at identifying and quantifying inorganic particles was conducted by Nagyvary [16] and Nagyvary and Ehrman [45] on four wood finish samples of Stradivari, Francesco Ruggieri (or Ruggeri, Cremona, *ca.* 1630-1698), Andrea Guarneri, and an 18th-century Venetian

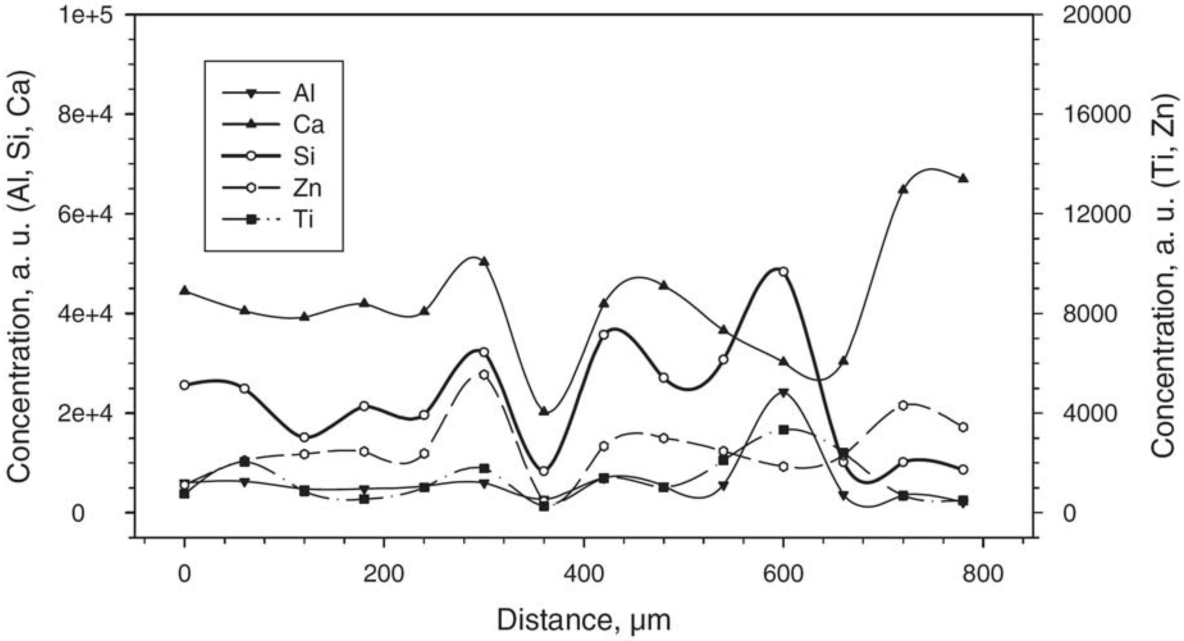


Figure 5. Elemental distribution along the cross section of a Grancino wood finish (~1700). Multiple elements heavier than sodium are detected, but only a few are plotted to illustrate the stratigraphy. Horizontal axis: Scan position from the top varnish (left) to the wood (right). Vertical axis: Elemental abundance in arbitrary units (a. u.). Reproduced from Ref. [58] with permission of Springer Verlag.

viola. Light microscopy under crossed polarizers revealed the presence of many crystals in different colors (these are interference colors; see following section on *Stradivari's Finish: A New Look* for an explanation). The crystals were concentrated in the lower parts of the color varnish and the lightly colored ground layer that penetrated into the wood, in general agreement with the observations of Condax [62]. Under light microscopy, particles 1-2 μm in diameter were observed (smaller particles would be invisible by this technique). But SEM images revealed many more particles in the submicrometer range. The Stradivari wood finish showed few visible crystals under light microscopy, but its particulate nature is clearly revealed in the electron micrograph shown in Fig. 6. What is particularly striking about Fig. 6 is the finely milled nanoparticles with fairly uniform diameters.

In a similar electron micrograph of Stradivari's varnish, the average particle diameter was reported to be 200 nm [16], smaller than the wavelength of visible light (400-700 nm). The uniformity of the particles indicates the use of special techniques to separate them by size. It was indeed a technical tour de force, because such particles could not have been visualized until the invention of electron microscopes in the 1930s. In another electron micrograph, the Ruggieri sample also showed many particles, albeit much larger and less uniform in size [16].

There is little doubt that Stradivari's mineral powders were deliberately prepared for special purposes, though not necessarily for varnishing per se. Even as we enter the 21st century, the age of nanotechnology, milling and separating crystals down to 200 nm remain nontrivial. The discovery of Stradivari's varnish as a nanocomposite reminds us that Cremonese material technology might not have been as primitive as traditionally assumed.

To better understand particle identities and their relative abundances, Nagyvary and coworkers isolated particles from the wood finish and used SEM/EDXRF to identify them individually [16, 45]. The wood finish was extracted with organic solvents, and the remaining fraction contained dispersed inorganic particles with some residual organic materials. From extraction and SEM experiments, inorganic particles were estimated to occupy about 50% of the volume in the Cremonese finish. Ninety particles from the Guarneri cello and 200 from the Venetian viola were successfully identified using EDXRF to detect elements with atomic numbers greater than 10.

In the Venetian sample, a total of 17 particle types were found. The major constituents were calcium carbonate (64 particles), potassium feldspar (potassium aluminosilicate, 25), calcium sulfate (32), and silicon oxide (silica or quartz, 15). Iron oxides (10), aluminum oxide/hydroxide (9), kaolinite (aluminum silicate, 9), barium sulfate (5), zinc oxide/carbonate (5), and zinc chloride (5) were also found. Lead was found as lead chloride (5) and lead oxide/carbonate (4). However, minerals of similar elemental compositions can exist in multiple forms, and the ambiguity is exacerbated by the inability of EDXRF to detect lighter elements. For instance, the particle showing only aluminum could be aluminum oxides (ruby or sapphire) or aluminum hydroxide, an ambivalence that EDXRF cannot resolve. Calcium carbonate could be either calcite or aragonite (different crystal forms), but the former occurs more widely in nature and has been identified by light microscopy in a Stradivari violin sample [44]. EDXRF also cannot differentiate between the hydrated and the anhydrous forms of the same mineral. Aluminosilicates are very abundant in the earth's crust and are found in many types of minerals such as feldspars, mica, and clay—the exact identification is often impossible.

The 90 particles from the Guarneri sample came in 12 types. The predominant ones were calcium carbonate (33 particles), potassium feldspar (14), and silicon oxide (22). Other par-

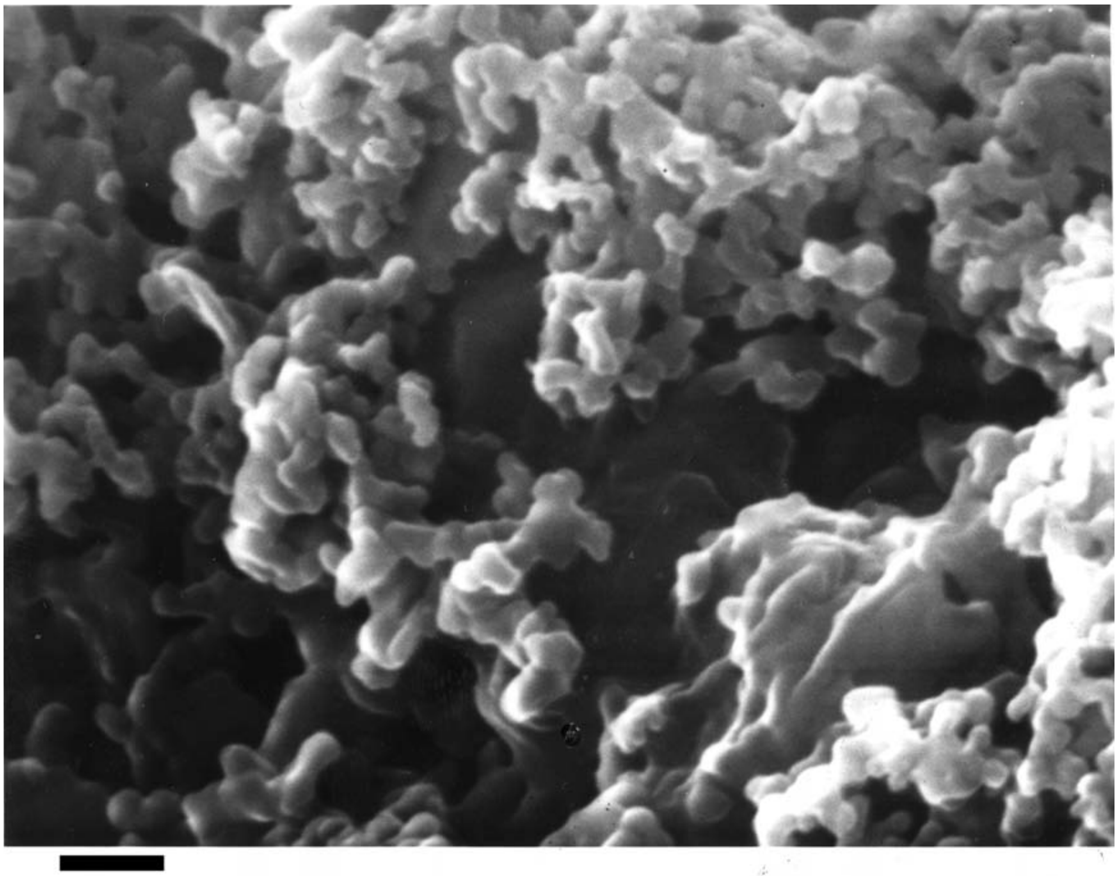


Figure 6. Scanning electron micrograph showing nanoparticles in the color varnish of Stradivari. The scale bar represents 1 μm. Originally published in Ref. [91]. Courtesy of J. Nagyvary.

ticles found included biotite (a type of mica, 5), plagioclase feldspar (4), calcium sulfate (3), and iron oxide (3). No lead-containing particles were detected. A few copper-containing particles showed up in the Guarneri sample as well as the Venetian. The Stradivari and Ruggieri samples were smaller and more resistant to solvent extraction, making particle identification difficult. Feldspars (aluminosilicates with various metal ions) were identified in both, and the latter also contained calcium sulfate flakes and a fibrous form of silica from biological sources.

The silicon oxide particles detected by EDXRF, upon further examination, appear to be quartz crystals [45]. This is consistent with the identification of quartz in the finish of Stradivari [75] (Table 1). The presence of quartz in the Cremonese finish reported in the 1980s came as a sort of surprise. It was known that glass powder was used in Italian paintings dating back to at least the 14th century. Glass can give body to the paint, or act as driers [7, 76] or pigments (tinted glass) [77, 78]. Only a few years ago it was discovered that silica was used by Venetian painters in the 1500s, when the glassmaking industry in Venice led Europe and used high-purity silica as the raw material. The silica source was probably quartz crystals from the pebbles of the Ticino River [77, 78], a tributary of the Po River flowing through Cremona. It is also said that Cremona in the early 16th century had a significant presence of Venetian-school painters [4]. Therefore, the use of quartz powder in instrument finish could have originated from oil painting practices. Powders resembling ground glass have also been observed under light microscopy in the finish of the Venetian master Domenico Montagnana, though the exact chemical composition is unclear [79].

FURTHER CONSIDERATIONS ABOUT THE MINERAL GROUND

An obvious trend is observed when we consider the refractive indices (R.I.) of the most abundant particles found in these wood finishes (for birefringent materials, the average value is given): calcium carbonate (calcite, 1.57), potassium aluminosilicate (potassium feldspar, 1.53), calcium sulfate (gypsum, 1.52), and silica (quartz, 1.55). All values are similar to that of the wood (~1.55) [80, 81]. Many have stated that when colorless crystals and organic binders of similar R.I. to the wood are incorporated into the ground layer, the result would be transparent and the crystals would remain invisible to the eye [16, 49]. From this we might logically deduce that the organic binder in the ground, whatever it is, also has R.I. close to 1.55. Since common minerals come in a wide range of R.I., it appears that Cremonese luthiers had intentionally selected crystals with suitable R.I. These inert particles, largely transparent in the medium, are generally called inert pigments, paint extenders, or fillers in paint formulations. However, some modern makers who adopt the mineral ground found it lacking in transparency compared to Stradivari's [25, 82]. This has cast some doubt on the particulate nature of Stradivari's ground.

To better understand this issue I have consulted recent scientific studies concerning coatings with inorganic particles suspended in organic matrices. The physics of light scattering in such coatings is similar to that of the particulate ground layer. Here we first assume that the organic matrix and the particles are basically colorless and transparent, and hence the transparency of the film is determined by the scattering of light off the particles. In this case, the transparency decreases as the following parameters increase: particle size, R.I. mismatch between the particle and the matrix, particle fraction volume, and coating thickness [83]. To make a highly particulate coating transparent, great attention must be paid to particle size distribution and R.I. matching. When the particle diameters are much larger (>5 μm) than the wavelength of visible light (400-700 nm), the R.I. difference must be smaller than 0.1% to achieve good transparency [84, 85]. In practice, this degree of matching is impossible for a multitude of reasons. For instance, the R.I. of minerals and organic matrices vary differently with respect to the wavelength of light (a phenomenon called dispersion), which means it is often impossible to match them within 0.1% over the entire range of the visible spectrum [80]. Also, the abundant minerals found in Cremonese wood finish do not match within 0.1% among themselves in R.I. It was unlikely that Cremonese luthiers could have controlled the

R.I. of the organic matrix, whatever it was, to 0.1% accuracy. For example, the drying of linseed oil raises its R.I. from ~1.48 to 1.52-1.57 over time [86]. Recent studies have indicated that, as a rule of thumb, a coating transparent to the eye should contain particles smaller than 5 μm even when the R.I. of minerals and media are optimally matched [83]. This may explain why modern recreations of the mineral ground will lack transparency if special attention is not paid to particle size distribution.

Since R.I. mismatch is, for all practical purposes, greater than 0.1%, cloudiness can only be avoided if the particle size of minerals is carefully controlled. As the particle diameter becomes comparable (0.15-2 μm) to the wavelength of visible light, its ability to scatter light is drastically reduced. It is still necessary to match R.I., but the tolerance for mismatch becomes larger. And if particles are much smaller (<50 nm) than the wavelength of visible light, then R.I. matching is almost unnecessary [87]. It should be emphasized that the study of light scattering off small particles is in reality more complex than what is described here, and requires sophisticated theoretical considerations [88, 89] and often actual experimentation. Another factor not to be overlooked is that the light transmittance of a film measured by spectrophotometers does not correlate perfectly to the transparency sensed by the eye, because the two differ in sensitivity to the angle of scattering [83].

Barlow et al. [31] reported that particles in Stradivari's ground have dimensions between 0.5 and 2 μm, which can be seen in Figs. 1 and 3. In Fig. 6 we also observe particles hundreds of nanometers in diameter in the color varnish of Stradivari. Evidently, Stradivari was able to acquire particles with diameters comparable to the wavelength of visible light to prevent excessive scattering. Thus, we have a reasonable explanation of how Stradivari could create a particulate ground of great transparency. He or his material supplier paid special attention to selecting minerals of suitable R. I., ground them finely, and separated them based on size. From the modern perspective, we may say that Stradivari resorted to nanotechnology to enhance the transparency of the particulate coating, but in reality it was probably achieved through trial and error. How powders of such fineness were prepared in 17th-century Italy deserves further investigation, but such procedures were by no means foreign to Italian craftsmen of the time. The separation of pigment particles according to size using levigation was known to medieval craftsmen [90], and hence it represents one possible method.

Following in Sacconi's footsteps, at least three research groups had found, on Cremonese instruments, highly particulate ground layers that contacted the wood, containing at least calcium carbonate, potassium aluminosilicate, and organic binders. Sacconi might not have gotten all the details correct, due to the less advanced analytical methods of his time, but his "mineral ground" theory is now strongly supported by published scientific data [16, 31, 44, 45]. Recent evidence further suggests that mineral grounds were also applied to string instruments outside the violin family by the Old Italian masters (see following section on *Classic Italian Lutes*).

WOOD FINISH STRATIGRAPHY

Many have examined Old Italian instrument finishes by light microscopy. An example of a light micrograph of Stradivari's color varnish is shown in Fig. 7. Similar micrographs have been published by several researchers [14, 16, 40, 62]. The general conclusion drawn from such examinations was that Stradivari's color varnish contained many colored and transparent particles. However, particles smaller than 1 μm in diameter cannot be visualized by light microscopy. Hence, the nanocomposite coating shown in Fig. 6 may appear as a clear varnish even at the highest magnification of light microscopy. Before the application of electron microscopy to varnish investigations, the nanocomposite nature of Stradivari's varnish probably remained unknown for almost two centuries. A simple light micrograph as shown in Fig. 7, though relatively easy to acquire if a varnish flake is available, reveals little about the actual stratigraphy or composition of the wood finish. Fortunately, a set of recently published light micrographs (Fig. 8), showing an exquisite cross section of Stradivari's wood finish, offers us a new look at the old matter.

STRADIVARI'S FINISH: A NEW LOOK

The micrographs in Fig. 8 were taken at McCrone Associates, a world-leading microscopy laboratory for material identification, in collaboration with Nagyvary [40, 75, 91]. The sample came from a Stradivari instrument whose varnish was covered by a modern overcoat. The overcoat allowed the wood finish to be lifted from the wood, with the deepest filler layer still attached. The sample was then cut neatly to expose the cross section as shown. The top picture is a normal micrograph taken under transmitted light. The transparent layer at the bottom was originally lying above the wood. The lower image is the same sample viewed between crossed polarizers. Notice that the bottom image shows additional colors not seen in the top picture, which are interference colors that arise when mineral crystals interact with polarized light. Describing the working principle of polarized light microscopy is beyond the scope of this review, and the interested reader could refer to the classic textbook written by Walter McCrone [92]. To put it simply, the 3-dimensional arrangement of atoms in each crystal will affect its interaction with polarized light. A crystal not symmetric in all axes is classified as anisotropic, and it will show interference colors when viewed between two polaroids perpendicular to each other (crossed polarizers) [93]. Most crystals are anisotropic and their crossed-polarizer colors differ due to the internal structure. In addition to anisotropic crystals, organic polymers with highly ordered structures will also exhibit interference colors, but they are not expected to be found in wood finishes. Some minerals can exist in both crystalline and amorphous forms (many pigment particles are amorphous [80]), and the latter will not show interference colors between crossed polarizers.

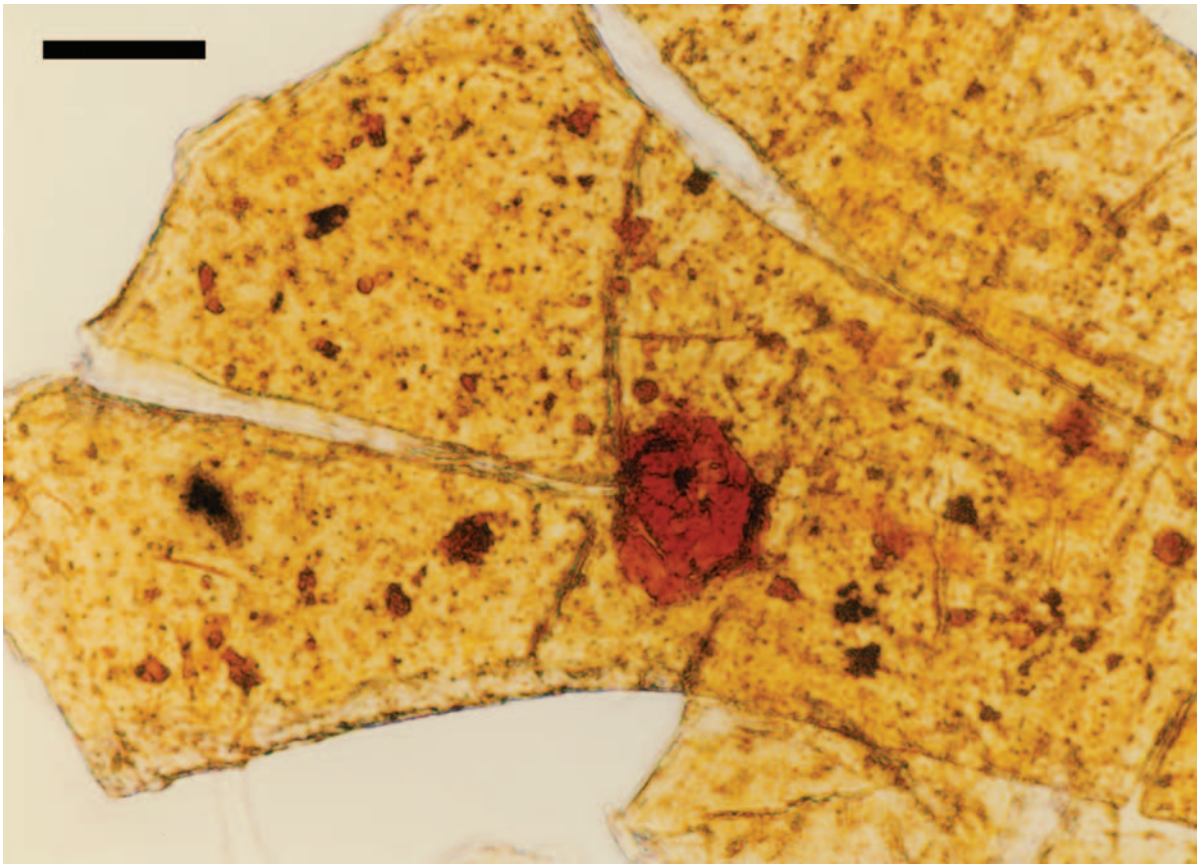


Figure 7. Light micrograph of Stradivari's color varnish. The scale bar represents 50 μm. Courtesy of J. Nagyvary.

Therefore, the additional colors seen in the crossed-polarizer micrograph indicate the presence of anisotropic crystals.

Researchers who examined the cross section shown in Fig. 8 were able to identify at least 12 distinct layers [75]. Furthermore, some of the substances in respective layers have been identified, as summarized in Table 1. Unfortunately, the author who published the finding did not explain the identification criteria, although McCrone Associates is known to be a leading laboratory in material identification [80]. In fact, the standard scientific reference for particulate matter identification, *The Particle Atlas* [80], was published by scientists at McCrone. They also examined a Ruggieri sample and found at least seven layers [75], as summarized in Table 2, but this varnish fragment seemed to have broken off without the ground layer.

Tables 1 and 2 provide a wealth of information about the stratigraphy and chemical composition of Cremonese finishes. However, prudence must be taken when interpreting such data. The Stradivari sample was reported to be covered with a modern overcoat, and hence it is difficult to know which layers in Fig. 8 represent Stradivari's original varnish, and how much of it has worn away before the retouching. Referring to Table 1, it seems likely that layer 1 represents retouching material, while layer 2, the calcium carbonate composite coating, belongs to the original finish. When lifting the finish, it is unlikely to preserve the filler-wood interface, and therefore it is difficult to determine the exact composition of the priming coat. Judging from Fig. 8 and Table 1, it appears that Stradivari's ground/filler is a thick layer of clear coating. However, from the electron micrographs of Figs. 1 and 3, we know the ground layer is highly particulate. Judging from the particle size distribution observed in Figs. 1 and 3 (~0.5-2 μm), the particles would be mostly invisible under light microscopy. If the particles are closely matched to the binding medium in terms of R.I., one could expect a clear, transparent appearance from the highly particulate ground.

As such, some of the clear coating layers listed in Tables 1 and 2 could be particulate composites containing finely milled minerals. On the other hand, a given particulate layer could contain a complex mixture of particles, only some of which are readily identifiable, and to a limited degree of certainty. In layer 3 of Ruggieri's finish, for example, particles of iron oxide and aluminum silicate were identified. Iron oxides could come in various chemical compositions and colors [41]; therefore there remains some ambiguity. The observed aluminum silicate probably represents kaolinite, which is a type of clay (pottery clay). While some clays are near-pure kaolinites, others are mixtures with various other minerals; one should not be surprised to find additional minerals upon further investigation. Moreover, perhaps no Italian was responsible for mixing iron oxide and clay in this case. Certain earth pigments (colored minerals mined from the earth) called ochre and sienna are natural admixtures of iron oxides and clay. For example, the raw sienna from Italy is a yellow earth containing hydrates of iron oxide and clay. When it is heated to remove the water, the ferric oxide turns red or reddish brown—thus called Italian burnt sienna [41]. Therefore, the interpretation of the acquired chemical information is often a daunting task faced with numerous uncertainties.

Tables 1 and 2 suggest a stratigraphy much more complicated than the simple two-strata classification (ground and top color varnish) commonly used to describe Cremonese finishes. In the Stradivari case, perhaps one can claim that layers 2 to 11 represent the color varnish and layer 12 is the ground. When the actual stratigraphy of the wood finish is uncertain, I will adhere to the two-strata classification for lack of better alternatives.

MINERAL GROUND ON CLASSIC ITALIAN LUTES

Baese [94] has noticed that wood finishes of classic Italian lutes made by Maler and Dieffopruchar appear similar to those of early violins from Cremona and Brescia. He proposed that the first Italian violinmakers inherited the wood finish of lute makers who preceded them. Interestingly, recent studies of lute finishes by Echard [51] provided some evidence in support of this theory. Mineral grounds were observed on two classic specimens, an early 16th-century lute by Laux Maler of Bologna and a late 16th-century theorbo (a lute-like instrument) by Magno Dief-

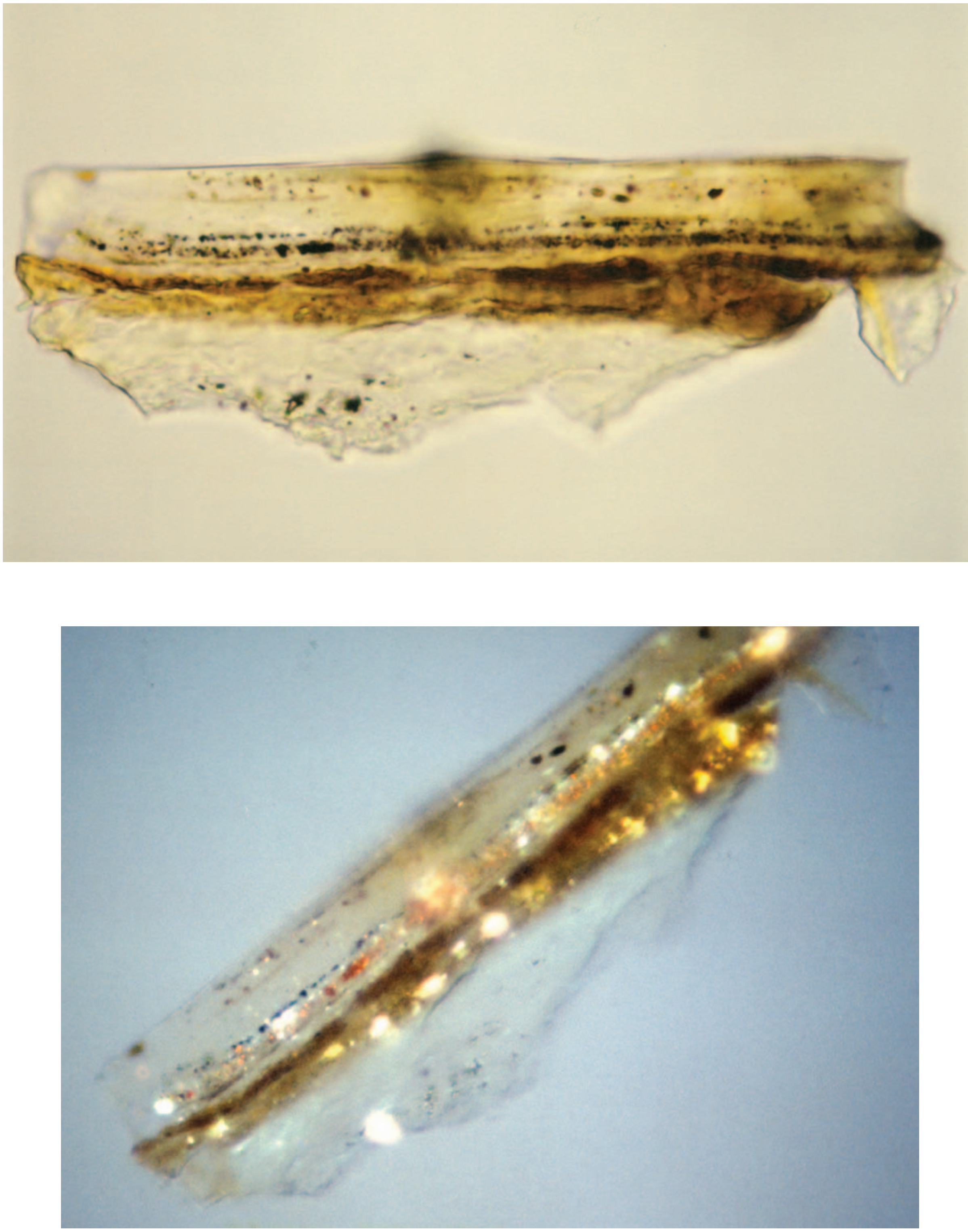


Figure 8. Cross section of a Stradivari wood finish (ca. 1690). The top image is viewed under transmitted light [75]. The bottom image is the same sample viewed between crossed polarizers [91]. Some of the color particles in the bottom image are anisotropic crystals exhibiting interference colors. Courtesy of J. Nagyvary.

Table 1. Wood finish stratigraphy of a Stradivari instrument dated 1690.[a,b]

Layer	Overall appearance	Identified substances
1	Clear coating	
2	Particulate; light brown	Calcium carbonate
3	Clear coating	
4	Light brown coating	Vegetable oil, resin
5	Clear coating	
6	Particulate	Carbon black
7	Clear coating	
8	Particulate	Iron oxide, blue pigment (Prussian blue or indigo)
9	Clear coating	
10	Red to dark brown coating	Red iron silicate and alizarin pigment composite
11	Particulate; light brown	Quartz, calcium carbonate
12	Clear coating	
Wood		

[a] Compiled from the data published by Nagyvary [75].
[b] Thickness: layers 1-11, 30-35 μm; layer 12, 50-55 μm.

Table 2. Wood finish stratigraphy of a Ruggieri instrument.[a,b]

Layer	Overall appearance	Identified substances
1	Particulate	Red particles of iron oxide, aluminum silicate
2	Clear coating	
3	Particulate	Iron oxide, aluminum silicate
4	Clear coating	
5	Particulate	Iron oxide
6	Clear coating	
7	Particulate	Iron oxide
Wood		

[a] Compiled from the data published by Nagyvary [75].
[b] Thickness: layers 1-7, 50-55 μm.

fopruchar (Duiffopruggar), or Magnus Tieffenbrucker, of Venice.

On the Maler lute, the mineral ground contained calcium carbonate and aluminosilicates. Lead was detected in every layer of the finish, but no particles could be found. On the Dieffopruchar theorbo, the mineral ground layer was ~100 μm thick and highly particulate, as is evident in Fig. 9. Particles identified in the ground included calcium carbonate, calcium sulfate, and aluminosilicates, similar to what has been found in Cremonese specimens [44, 45]. Since no intervening substance was observed between the mineral ground and the wood, it appeared that the mineral ground acted as the filler. The coarse, irregular particles in the theorbo ground form a stark contrast to the finer particles of Stradivari's ground in Figs. 1 and 3. Immediately above the ground is a thin, homogeneous, and non-particulate layer showing white fluorescence under UV light. On top of it there are two strongly colored layers of varnish (total thickness ~30 μm), showing particles of silicates and umber earth pigment (oxides of manganese and iron). Above the color varnish is a layer of scattered silicates without any binder, possibly the residue of abrasive materials. The surface layer is ~10 μm thick and non-particulate. The topmost two layers might have originated from some sort of polishing process, perhaps applied by the restorer. In Fig. 9 it is easy to see that the mineral ground isolates the color varnish from the wood, consistent with what Sacconi [14] observed on Stradivari instruments.

The presence of the mineral ground on Laux Maler's lute is particularly interesting when one considers the following passage in the Hills' Stradivari book [3]:

> It appears that the Duke of Ferrara desired to obtain a recipe of the varnish then in use among the Venetian lute-makers, and accordingly wrote to his correspondent in Venice—one Jacopo de li Tibaldi, who, under date January 20th, 1526, replied as follows: "The celebrated lute-maker Sigismond Maler has promised to give me in writing by Monday next the recipe of the varnish he uses, as well as the manner of putting it on the lutes. This master also tells me that he has two kinds of varnish, and that it is his assistants, not he himself, who make it."

From this account the Hills were inclined to deduce that varnish recipes were not considered secrets. The fact that Laux Maler's lute shows a mineral ground layer [51] provides a potential clue as to what the "two varnishes" mentioned by his son Sigismond were. It is possible that one varnish formulation was for the ground layer and the other was for the colored top coats. Needless to say, there are many other ways to interpret the "two varnishes," such as a red versus a brown varnish, or a cheap versus a pricey varnish.

Judging from the classic Italian lutes, it appears that the mineral ground was adopted in Italy before Amati's time and commonly known to luthiers of all sorts, and therefore not a secret of any Cremonese violinmaker. There also appear to be some general similarities between the wood finishes of lutes and violins (Cremona and beyond) from 16th- to 18th-century Italy, insofar as inorganic constituents are concerned. We will encounter more of these general similarities during the discussion of organic constituent analyses. If master lute makers of the time appeared rather forthcoming about wood finish recipes, then is it reasonable to assume that violinmakers jealously guarded theirs? It should be noted that Stradivari also had a minor output of plucked string instruments such as the guitar and mandolin [3].

In Part II of this article, I will survey the scientific evidence with regard to the organic components and the coloration, and a summary table of identified ingredients will be given. Practical and historical implications of the emerging scientific evidence will also be discussed.

ACKNOWLEDGMENTS

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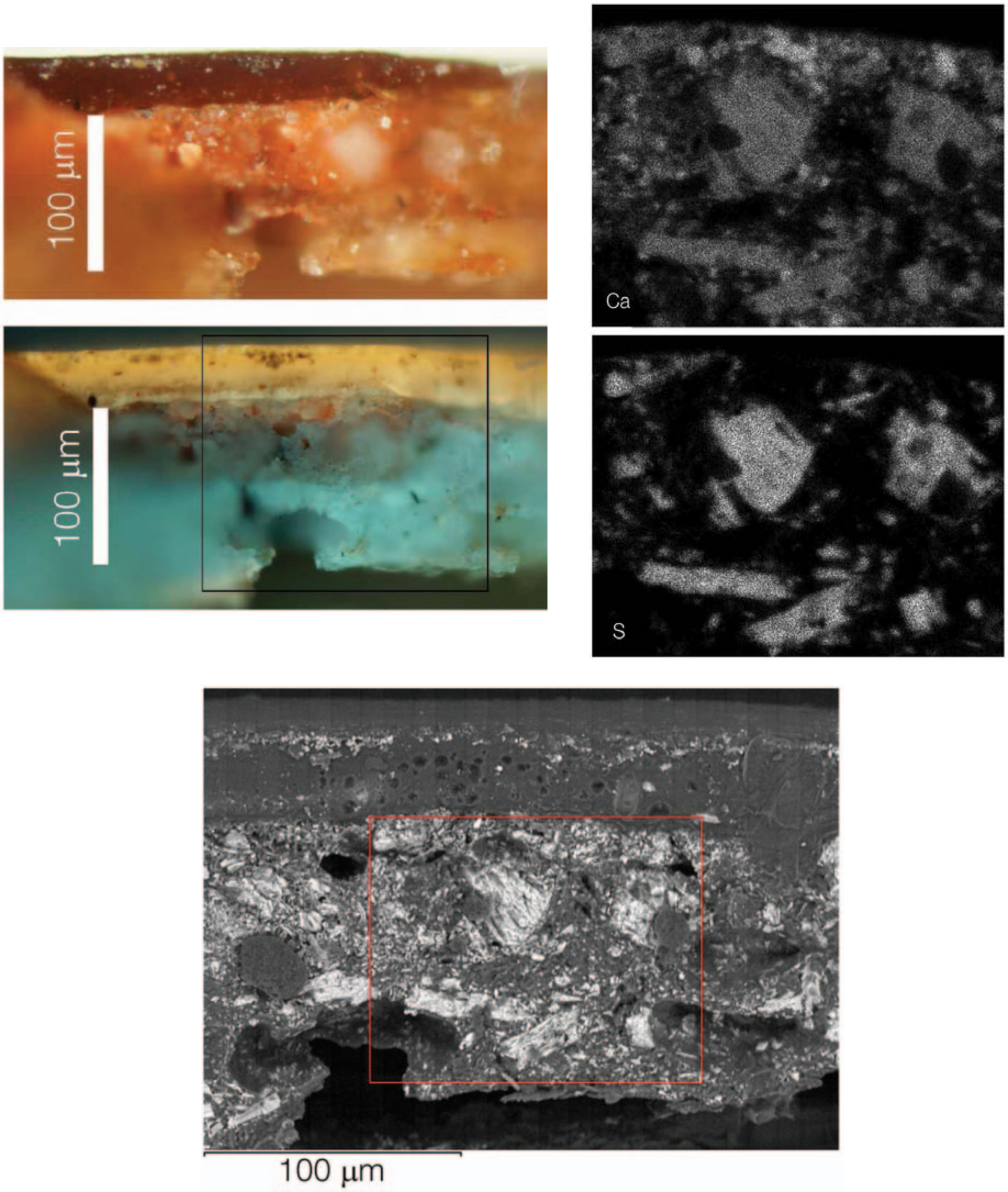

Figure 9. Cross section of the wood finish on a theorbo made by Dieffopruchar, observed by optical microscopy under visible light (upper left) and UV (middle left). The black box region was examined under SEM in back-scattered electron mode (bottom). The red box region was further analyzed by EDXRF to identify individual elements such as calcium (upper right) and sulfur (middle right). Reproduced from Ref.[51] with permission of Cité de la musique.

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