Chemical distinctions between Stradivari's maple and modern tonewood

Hwan-Ching Tai[a,1,2], Guo-Chian Li[a,1], Shing-Jong Huang[b], Chang-Ruei Jhu[a], Jen-Hsuan Chung[a], Bo Y. Wang[a], Chia-Shuo Hsu[a], Brigitte Brandmair[c], Dai-Ting Chung[d], Hao Ming Chen[a], and Jerry Chun Chung Chan[a]

[a]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan; [b]Instrumentation Center, National Taiwan University, Taipei 10617, Taiwan; [c]Private address, 86567 Hilgertshausen-Tandern, Germany; and [d]Chimei Museum, Tainan 71755, Taiwan

Violins made by Antonio Stradivari are renowned for having been the preferred instruments of many leading violinists for over two centuries. There have been long-standing questions about whether wood used by Stradivari possessed unique properties compared with modern tonewood for violin making. Analyses of maple samples removed from four Stradivari and a Guarneri instrument revealed highly distinct organic and inorganic compositions compared with modern maples. By solid-state ^{13}C NMR spectroscopy, we observed that about one-third of hemicellulose had decomposed after three centuries, accompanied by signs of lignin oxidation. No apparent changes in cellulose were detected by NMR and synchrotron X-ray diffraction. By thermogravimetric analysis, historical maples exhibited reduced equilibrium moisture content. In differential scanning calorimetry measurements, only maples from Stradivari violins, but not his cellos, exhibited unusual thermooxidation patterns distinct from natural wood. Elemental analyses by inductively coupled plasma mass spectrometry suggested that Stradivari's maples were treated with complex mineral preservatives containing Al, Ca, Cu, Na, K, and Zn. This type of chemical seasoning was an unusual practice, unknown to later generations of violin makers. In their current state, maples in Stradivari violins have very different chemical properties compared with their modern counterparts, likely due to the combined effects of aging, chemical treatments, and vibrations. These findings may inspire further chemical experimentation with tonewood processing for instrument making in the 21st century.

Cremona | stringed instrument | wood treatment | wood aging | Italian violin

The invention of the modern violin has generally been attributed to Andrea Amati, who initiated the golden age of violin making in Cremona, Italy (1550–1750). The most famous Cremonese violin maker was Antonio Stradivari (AS, or Antonius Stradivarius, 1644−1737), whose instruments are renowned for their tonal qualities. Stradivari's success in violin building was only matched by his neighbor, Giuseppe Guarneri "del Gesù" (DG, or Joseph Guarnerius, 1698−1744), and leading violinists today still mostly prefer to play AS and DG instruments. It remains a great mystery why functionally equivalent instruments have not been successfully constructed to replace these heavily repaired Cremonese antiques, despite rapid technological advances over the last 200 y. For both historical and practical purposes, it is important to understand what types of materials were used to construct these famous violins.

Violin acoustics is mainly determined by vibrations of the front and back plates, made of spruce and maple, respectively. It has long been speculated that Stradivari's wood possessed unusual properties not found in tonewood used by modern makers. Based on visual and microscopic inspections, experts suggested that wood varieties chosen by Stradivari have always been commercially available (1–3). Wood densities in Cremonese violins and modern tonewood also appeared to be similar, judging by computed tomography measurements (4). There is little evidence to suggest that the Cremonese tradition was lost due to diminished wood supply or deforestation, or that Stradivari preferred denser woods that grew slowly during the Maunder Minimum (5).

Elemental analyses of AS and DG maple specimens conducted by Nagyvary et al. (6) detected unusual minerals, which implicated chemical treatments. They also reported severe degradation of the lignocellulose−hemicellulose matrix in violins through hydrolysis and oxidation, which was attributed to chemical manipulation (7). However, the conventional belief held by some violin restorers was that Cremonese maple plates appeared stiffer or more elastic than modern counterparts, generally assessed by tapping and listening (8). This apparent paradox motivated us to analyze the maples of five Cremonese instruments from three independent sources and compare their organic fiber composition, cellulose crystallinity, moisture content, thermooxidative properties, and inorganic elemental composition.

The maple samples analyzed in this study are listed in Table 1 (see *SI Appendix*, Table S1 for details). Four of our historical specimens were removed from Cremonese instruments during interior repairs of back plates. Three of them have been previously analyzed by Nagyvary et al. (1717 AS violin; 1731 AS cello; 1741 DG violin) (6, 7), with the remaining materials transferred to us by courtesy of J. Nagyvary. The other back plate sample (1707 AS cello) was repaired at a different workshop (courtesy of Guy Rabut). We also received the original neck of a 1725 AS violin (courtesy of Chimei Museum). The neck was originally affixed to the body with nails, which eventually rusted. It had to be modified

Significance

There have been numerous attempts to elucidate the "secrets" of Stradivari violins, to explain why functional replacements have not been reproduced over the past two centuries. Whether there are systematic differences between Stradivari violins and later imitations has been heatedly debated. Our analysis of Stradivari's maples from three independent sources showed reproducible differences in chemical compositions compared with modern maples. Stradivari's use of mineral-treated maples belonged to a forgotten tradition unknown to later violin makers. His maple also appeared to be transformed by aging and vibration, resulting in a unique composite material unavailable to modern makers. Modern chemical analyses may, therefore, improve our understanding of Stradivari's unique craft and inspire the development of novel material approaches in instrument making.

CHEMISTRY

Table 1. Maple samples analyzed in this study

Sample	Description	Origin
M1	Modern #1	European, flamed
M2	Modern #2	European, flamed
M3	Modern #3	European, flamed
M4	Modern #4	European, plain
M5	Modern #5	European, plain
H1	1707 AS cello	Back plate
H2	1717 AS violin	Back plate, near the lower edge
H3	1725 AS violin neck	Neck heel, original wood
H4	1731 AS cello	Back plate
H5	1741 DG violin	Back plate, center region
H6	Neck extension *ca.* 1800	Heel extension on the 1725 neck

by inserting new wood and reattached by gluing, which probably occurred around 1800 (2, 9). We cut into both the original and extension parts to retrieve previously untouched wood from deep locations (*SI Appendix*, Fig. S1). The extension piece (*ca.* 1800) provided a side-by-side aged control for Stradivari's neck material. The five modern controls were maple tonewoods recently purchased in northern Italy. Our measurements revealed that Cremonese maple clearly differed from modern tonewood with regard to both organic and inorganic compositions, and the reasons for such distinctions were further investigated and discussed.

Results and Discussion

Hemicellulose Decomposed in Historical Maples. The organic fiber compositions of historical and modern maples were analyzed by ^{13}C{^{1}H} cross-polarization magic angle spinning (CPMAS) NMR spectroscopy. Historical maples exhibited reduced ^{13}C intensities at hemicellulose-related peaks (22, 62, 72, 75, and 84 ppm) and lignin-related peaks (56 and 153 ppm) compared with modern maples. These changes were evident across the spectra acquired at different CP contact times (0.2 ms to 10 ms, *SI Appendix*, Figs. S2–S11), and the optimal contact time for

quantitative comparison was determined to be 1 ms, which was also the conventional standard for studies on modern and archaeological woods (10, 11). Typical ^{13}C{^{1}H} CPMAS spectra with contact time of 1 ms are shown in Fig. 1. The peak intensities of these NMR spectra (*SI Appendix*, Figs. S12–S14 and Table S2) were subjected to principal component analysis (PCA), as shown in Fig. 2. We observed that historical maples were clearly separated from the modern controls along the first principal component, which was primarily associated with the following peaks: 22, 56, 63, 72, 75, and 153 ppm. Differences along the first principal component (65% of the variance) were therefore strongly correlated with hemicellulose changes, followed by lignin alterations. The second principal component further differentiated the historical neck samples from the historical back plate samples.

The rate of hemicellulose decomposition was estimated by the hydrolysis of acetyl esters (22 ppm, acetyl CH$_3$) and the chemical transformation of furanoses and pyranoses (C-2, C-3, and C-5 at 75 ppm and C-6 at 63 ppm). After the subtraction of cellulose background signals, the rates of decomposition were found to be similar at these three peaks (*SI Appendix*, Table S3). The average signal reduction of hemicellulose was $36.9 \pm 3.9\%$ (mean $\pm$ SE) in five Cremonese specimens compared with five modern controls ($P < 0.0001$, Welch's t test with unequal variance). Modern and historical samples could be clearly differentiated by the extent of hemicellulose decomposition (Fig. 3A), providing experimental verification for the aged nature of our Cremonese samples. Assuming first-order kinetics, the half-life of hemicellulose decomposition was estimated around 409 ± 56 y (mean $\pm$ SD) by regression analysis (*SI Appendix*, Fig. S15). This was in reasonable agreement with previously published measurements for dry-aged maple (358 y) (12), spruce (833 and 335 y) (12, 13), and fir (739 y, *SI Appendix*, Table S4) (14).

Lignin Became Oxidized in Historical Maples. In historical maples, signal reductions at the methoxy (56 ppm) and aromatic carbons (153 ppm) were indicative of lignin oxidation (*SI Appendix*, Fig. S14). There was only a weak correlation between lignin signal changes at methoxy and aromatic carbons, suggesting that
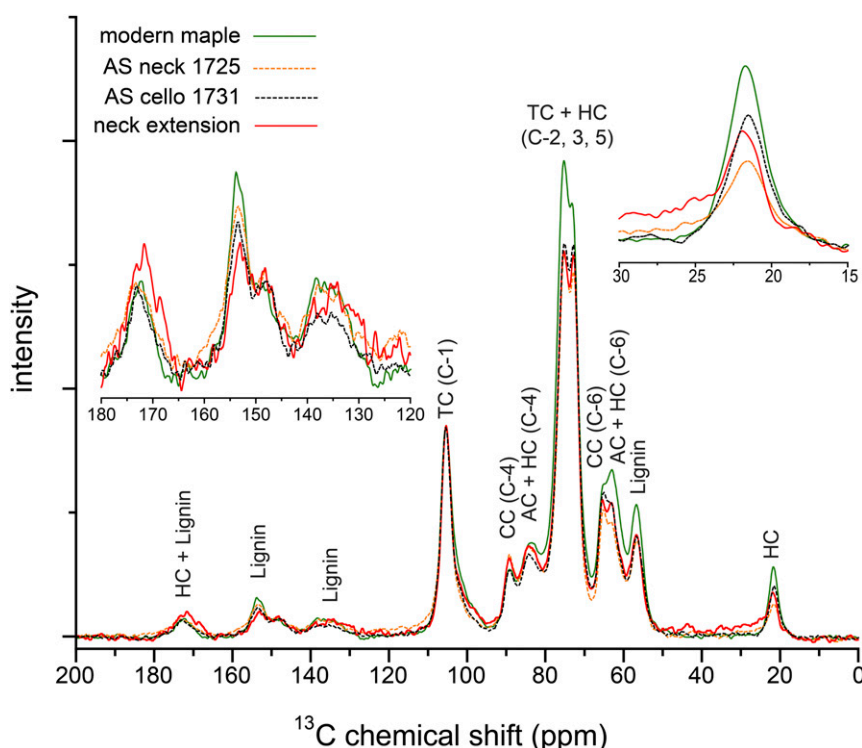
Fig. 1. The ^{13}C{^{1}H} CPMAS spectra of maples derived from modern control (M3) and three historical specimens. The CP contact time was set to 1 ms. The peaks were assigned to lignin, total cellulose (TC), crystalline cellulose (CC), amorphous cellulose (AC), hemicellulose (HC), and lignin.
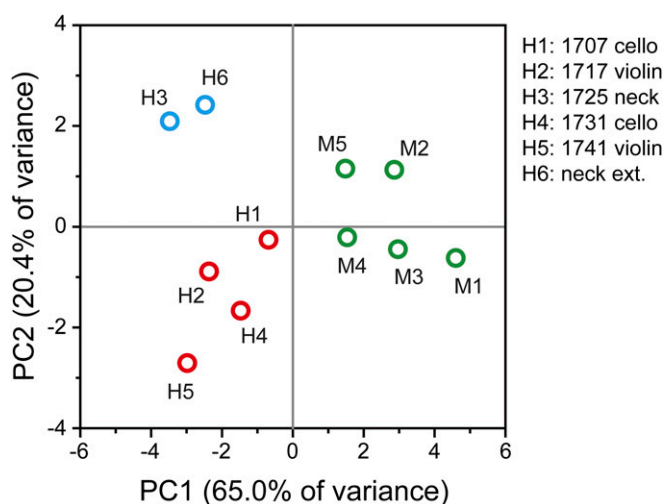
Fig. 2. PCA score plot for the peak intensities of the CPMAS spectra measured in maple samples. The first principal component (PC1) can clearly distinguish the modern and historical maples. Different colors represent different sample origins (green for modern, red for historical back plates, and blue for historical necks).

multiple oxidation mechanisms may have been involved. There were two plausible oxidation mechanisms in Cremonese specimens: oxidation by atmospheric oxygen and photooxidation. Stradivari's own letter indicated the exposure of instruments to sunlight (1), and further light exposures were inevitable over the course of three centuries. Oxidation may cause lignin demethoxylation (15) and the formation of quinone groups (7, 16), resulting in peak broadening due to increased structural heterogeneity, as well as decreased CP signals due to hydrogen loss nearby. In modern wood, the carbonyl peak at 173 ppm is mainly associated with the acetyl groups in hemicellulose. However, the carbonyl signal at 173 ppm in historical maples did not show a corresponding decrease to the acetyl-CH_3 signal at 22 ppm (*SI Appendix*, Fig. S14). This was probably due to the formation of carbonyls and carboxylic acids from lignin oxidation (17), and plausibly from the oxidation of carbohydrates as well.

Cellulose Remained Stable in Historical Maples. Cellulose microfibrils in the wood contain individual rod-shaped crystalline domains surrounded by amorphous regions. Because amorphous cellulose is less stable than crystalline cellulose, the former may preferentially degrade over time, leading to higher crystalline/amorphous cellulose ratios (18). However, this was not observed in Cremonese maples, as we estimated the relative degree of cellulose crystallinity by the intensity ratio of the NMR peaks at 89 and 105 ppm (crystalline cellulose/total cellulose) (11, 19), which appeared to be unaltered in Cremonese samples (Fig. 3*A*). We also measured the lengths and widths of cellulose crystalline domains by wide-angle X-ray scattering using synchrotron radiation, based on the (004) and (200) reflections, respectively (*SI Appendix*, Figs. S16–S18). Crystallite lengths and widths, as well as d spacing, have also remained largely invariant in historical maples (Fig. 3*B* and *SI Appendix*, Table S5). We observed neither the evidence for the degradation of amorphous cellulose, nor the interconversion between crystalline and amorphous cellulose, nor the changes in crystallite size and density. Our findings with respect to cellulose stability, mild lignin oxidation, and significant hemicellulose decomposition in historical maples were in reasonable agreement with the reported effects of dry aging on wood (8).

Quantitation of Cell Wall Composition by Different NMR Techniques. Previous, Nagyvary et al. (7) have shown by $^{13}C\{^1H\}$ CPMAS that hemicellulose and lignin signals were severely reduced in

1717 AS violin and 1741 DG violin compared with modern maples and 1731 AS cello, which was interpreted as evidence of special chemical treatments applied to violins but not to cellos. However, our $^{13}C\{^1H\}$ CPMAS data did not agree with their previous findings. Our reanalysis of the same violin samples detected only modest changes in hemicellulose and lignin, based on extensive comparisons using different CP contact times (0.2 ms to 10 ms, *SI Appendix*, Fig. S11). We also applied the multiple-cross polarization (multiCP) measurement method (*SI Appendix*, Fig. S19 and Table S6), which has been recently proposed to improve quantitation accuracy in $^{13}C\{^1H\}$ CPMAS NMR (20), to reconfirm our observation. There were only minor spectral differences among the 1717 AS violin, 1725 AS violin neck, and 1731 AS cello in multiCP measurements (*SI Appendix*, Fig. S19).

Two factors may have led to the discrepancy between our NMR data and those of Nagyvary et al. (7). First, the maple shavings of 1717 and 1741 violins previously studied by Nagyvary et al. were removed from interior areas that exhibited surface blackening, possibly caused by surface heating. This discoloration was highly unusual for Cremonese instruments, and we were informed by J. Nagyvary that the darker surface portions have been used up for analyses in the original reports (6, 7), whereas we only received residual samples from deeper regions (>0.3 mm from the surface) showing normal coloration consistent with the yellowing of naturally aged wood (*SI Appendix*, Fig. S20). Second, Nagyvary et al. (7) used a fixed CP contact time of 5 ms for all of the NMR measurements, where it was implicitly assumed that all carbon signals would exhibit the same decay rate during the contact time. By contrast, we carried out the CP experiments with different contact times, and, indeed, we observed that there was a large variation in signal decay rate for the carbon signals across different samples (*SI Appendix*, Fig. S11 and Table S7). Consequently, the spectra acquired with the contact time of 5 ms were not warranted for quantitative analyses.

Thermal Analyses of Historical Maples. Interestingly, a peculiar difference was found between Stradivari's violin and cello samples through differential scanning calorimetry (DSC) analyses (Fig. 4 and *SI Appendix*, Table S8). When gradually heated to 600 °C under air atmosphere, the thermograms of modern maples and two AS cellos exhibited similar exothermic profiles with only two peaks. In contrast, both 1717 AS violin and 1725 AS violin neck exhibited three exothermic peaks. The unique DSC profile associated with Stradivari violins has never been observed in natural wood, but only in fungus-degraded wood (21) and simple mixtures of holocellulose and lignin powders without mutual impregnation (22). It was noted that when holocellulose and lignin were mixed together by coprecipitation to promote molecular adhesion, the thermogram only showed two peaks, just like natural wood (22). Hence, the
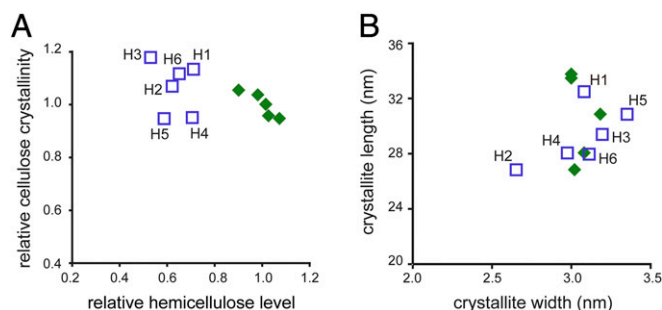
Fig. 3. (*A*) Relative cellulose crystallinity plotted against relative hemicellulose levels measured by $^{13}C\{^1H\}$ CPMAS. (*B*) Crystallite lengths and widths estimated from X-ray diffraction patterns. Filled diamonds, modern maples; open squares, historical specimens.
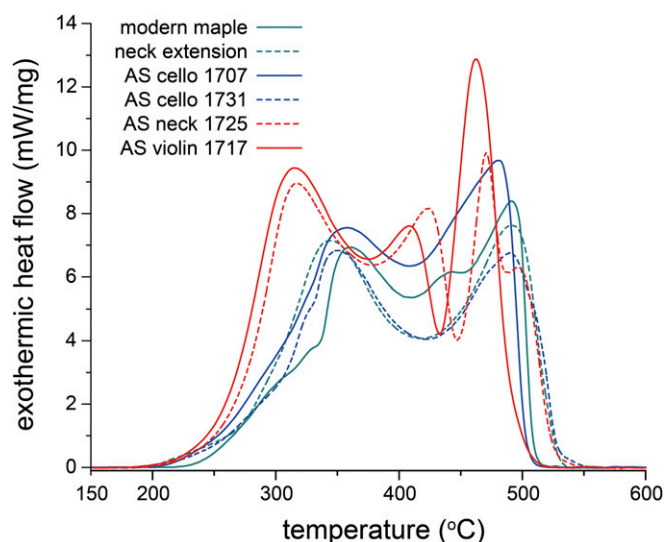
Fig. 4. DSC thermograms of modern maple (M3) and five historical specimens.

molecular adhesion between holocellulose and lignin appeared to have been reduced in Stradivari violins, even compared with his cellos from the same era. This may help explain why Nagyvary et al. (7) observed obvious discrepancies between Stradivari's violins and cellos by $^{13}C\{^{1}H\}$ CPMAS NMR, as changes in wood fiber ultrastructure may affect the spin dynamics of the CP process.

By thermogravimetric analysis (TGA), we also observed a reduction of moisture content in Cremonese maples by about 25% (Fig. 5 and *SI Appendix*, Table S9). Four modern maples exhibited an average equilibrium moisture content (EMC) of $11.55 \pm 0.33\%$ (mean ± SE) at about 25 °C and 58% relative humidity, in good agreement with reported values for maple (23). The four Stradivari maples exhibited $8.67 \pm 0.53\%$ EMC, and the difference was highly significant ($P < 0.01$, Welch's t test with unequal variance). Reduced hygroscopicity in historical maples may be attributed to the decomposition of hemicellulose (24, 25), which is more hygroscopic than cellulose and lignin (26).

Cremonese Maples Received Mineral Treatments. To understand whether chemical treatments had possibly altered wood properties, three historical samples (1731 cello, 1725 neck, and neck extension), with sufficient materials, were quantified for 25 elements using inductively coupled plasma mass spectrometry (ICP-MS), with the results listed in *SI Appendix*, Table S10. These included 20 metals and 5 metalloids/nonmetals (As, B, Ge, Sb, and P), but Cl, S, and Si could not be included due to instrumental limitations. In the PCA analysis of the quantified elements (Fig. 6), the neck extension and modern controls were closely clustered and represented wood receiving little or no mineral treatment, with total metal content around 2,000 ppm. By contrast, the total metal content was elevated to ~9,000 ppm in the 1725 neck and 1731 cello, which clearly stood out as being "unnatural" in the PCA diagram. These two Stradivari instruments showed similar increases in K, Na, Ca, Cu, and Zn. The AS neck contained elevated levels of Al, and the AS cello was higher in B.

Nagyvary et al. (6) have previously shown in a qualitative manner, by electron probe microanalyzer, that maples used by Stradivari and Guarneri had altered mineral composition. Here we provide a quantitative assessment of elemental changes by ICP-MS measurements. The changes detected in our experiments could neither be simply be attributed to surface applications of potassium silicate (3) nor Pozzolana ash (27), which have been previously proposed as wood sealers used by Stradivari but failed

to be detected by recent studies (28, 29). Modest increases (tens of parts per million) in fungicidal elements including Cu, Zn, and B may have been introduced by either surface application or liquid infusion, but much greater increases in Ca, Na, K, and Al could only be explained by the latter. In the 18th century, mineral infusion could have been achieved by extended soaking and/or sap displacement procedures using gravity flow (30). Both soaking and sap displacement could help remove sap nutrients that support microorganism growth and help introduce various preservatives such as alum, sodium chloride, or vitriols (sulfates of copper and zinc).

Because minerals initially introduced into the wood could have been washed out during later treatment steps, the residual elements currently detected in Stradivari's maples are insufficient for ascertaining the original mineral formulations or application procedures. There is also no available method to detect past heat treatments such as boiling, steaming, baking, or fuming. It is therefore plausible that chemical or physical treatments may account for the different DSC profiles between Stradivari's violins and cellos, but different vibration frequencies may also be critical. Even a few hours of vibration has been shown to reduce the internal friction of wood, presumably by rearranging hydrogen bonds and polymer chains (31). Therefore, it is conceivable that high-frequency vibrations could have gradually altered the ultrastructure of wood fibers, acting in concert with hemicellulose decomposition over time. The interactions among mineral preservatives, age-dependent chemical changes, mechanical vibrations, and the composite nature of wood are extremely complex, and the potential outcomes are not well understood. Although chemical changes of wood generally have measurable effects on its vibrational properties (8), the acoustic effects associated with the specific chemical alterations observed in this study remain to be investigated.

Availability of Mineral-Treated Wood. Violin models designed by Stradivari have been widely copied for over two centuries by violin makers hoping to recreate similar playing qualities, but gaining access to wood materials resembling Stradivari's maple may be difficult. First, it is unclear if there are accelerated aging methods that can faithfully mimic the effects of natural aging. There have been numerous anecdotes about artificial treatments in modern instruments that led to wood structural damages and irreparable failures after just 10 y to 20 y of playing. Secondly, wood infusion with mineral solutions was not a widespread practice and it has long been obsolete (32). Because violin plates are only a few millimeters thick, dimensional stability is an extremely important tonewood quality. Immersion of dried tonewood into liquids is likely to cause swelling damage and compromise dimensional stability, and is therefore generally
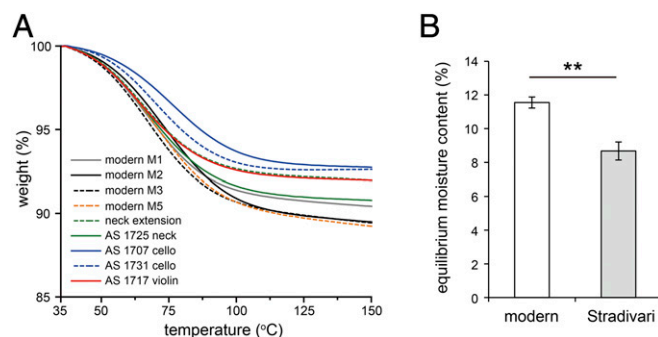
Fig. 5. (*A*) TGA curves of modern and historical maples. (*B*) EMC values derived from TGA data (**$P < 0.01$ by Welch's t test with unequal variance; $n = 4$ for each group).

Tai et al.
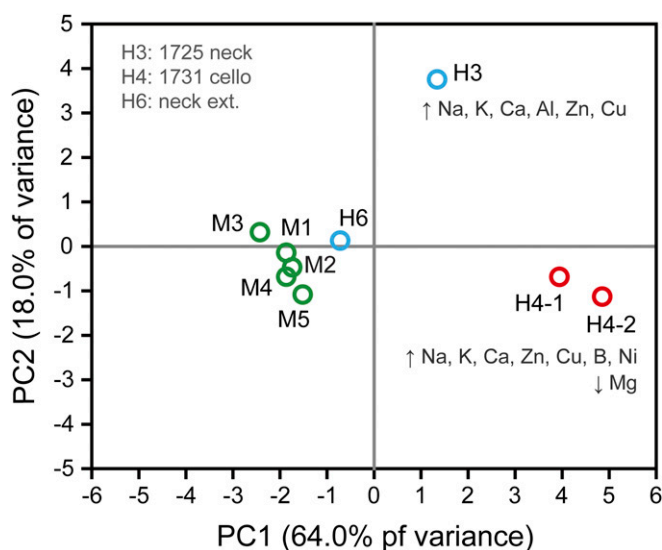
Fig. 6. PCA score plot for elemental compositions measured in maples by ICP-MS. The 1731 cello (H4) was analyzed twice using two separate wood fragments. Different colors represent different sample origins (green for modern, red for historical back plates, and blue for historical necks).

avoided. Before the introduction of pressurization methods in the 1800s, extensive mineral penetration by soaking or sap displacement was probably only achievable with water-saturated wood, before full drying took place—likely applied by wood suppliers rather than violin makers.

To our knowledge, current supplies of commercial tonewood are not mineral-infused, but just air-dried for 3 y to 10 y or even up to a century to achieve ideal dimensional stability (8). Mineral infusion was not detected in our modern controls and the neck extension sample (Italy, *ca.* 1800), nor in the Jay viola (England, 1769) and Gand & Bernardel violin (France, *ca.* 1845) previously analyzed by Nagyvary et al. (6). Moreover, mineral treatment of wood has not been mentioned in published treatises on violin making that contain lutherie knowledge tracing back to the 18th and 19th centuries (1–3, 33, 34). Building stringed instruments using mineral-treated maples probably belonged to a long-forgotten tradition with few practitioners to begin with. To this date, we have not identified the use of mineral-infused wood outside Cremona, which may partly explain why some restorers have noticed that worm damages were relatively rare in Cremonese instruments.

Nevertheless, wood preservation using mineral treatment had a long history in Italy and surrounding countries. Alum treatment of wood was first recorded by ancient Romans for flame retardation (35), and Paracelsus described, in the 16th century, the use of "sal gemma" (alum) to enhance wood durability (36). Writings from the 16th century about the positive effect of mineral treatments on instrument acoustics have been recently rediscovered (37). Chemical seasoning of wood using various minerals was still used in the 20th century timber industry, but infrequently (32). With our limited analytical data, it is difficult to elucidate the effects of mineral treatments in Stradivari instruments. For instance, we do not know if the pH was sufficiently acidic or basic during the treatment to promote hemicellulose hydrolysis. It is also possible that Al and Ca ions added to the wood may act as chemical cross-linkers—being chelated by hydroxyl, phenol, and carboxylate groups on hemicellulose, lignin, and cellulose (38, 39)—to compensate for the natural degradation of hemicellulose over time. Additional antique instruments from Cremona and other Italian cities need to be analyzed to elucidate if there were unique wood properties associated with Cremonese makers or Stradivari himself.

Conclusion

In this study, we provided a quantitative assessment of wood chemical changes in antique musical instruments, using a combination of five analytical methods: NMR, synchrotron X-ray, DSC, TGA, and ICP-MS. In Cremonese maples, we observed normal chemical changes associated with dry aging, including hemicellulose decomposition, lignin oxidation, and reduced EMC. However, we also observed an unnatural elevation of certain inorganic elements, which could be attributed to the use of mineral-treated maples by Cremonese makers.

From a conservation perspective, it appears that maples in Stradivari cellos are reasonably preserved. The crystallinity of cellulose has remained intact, as well as the adhesion between holocellulose and lignin. The mechanical strength of aged wood depends on the stability of crystalline cellulose as well as the integrity of the surrounding lignin−carbohydrate matrix (25, 40, 41). Hence, it is a concern that continued decomposition of hemicellulose may eventually cause structural breakdown.

In Stradivari violins, we already observe evidence of reduced adhesion between holocellulose and lignin. It is plausible that high-frequency vibration accelerated the breakdown of cell wall components, but whether wood treatment may have also played a role is still unclear. It remains possible that some breakdown was initially promoted by heat treatments or acidic/basic pH. However, it is also possible that increased divalent and trivalent metal ions could cross-link carbohydrate and lignin chains to compensate for reduced molecular adhesion. Additional antique samples and analytical methods are required to further elucidate the complex interactions between aging, wood treatments, and long-term vibrations, which appear to have jointly transformed the chemical properties of maples in Stradivari violins. Changes in spruce soundboards also warrant further investigation. Our findings may inspire further chemical experimentation with wood for 21st century instrument making, applicable not just to violins but also to wooden instruments across different cultures. Stradivari's maple may represent a singular case in the history of wooden musical instruments, but its implications and impact may be far-reaching.

Materials and Methods

Wood Samples. Historical maple samples were taken from these instruments: 1707 AS cello (H1), 1717 AS violin (H2), 1725 AS violin neck (H3), 1731 AS cello (H4), and 1741 DG violin (H5), and neck extension *ca.* 1800 (H6). The modern controls included five tonewood-grade maples of European origin (M1–M5). See *SI Appendix*, Table S1 for details.

NMR Spectroscopy. The $^{13}C\{^1H\}$ CPMAS NMR spectra were acquired at ^{13}C and ^1H frequencies of 150.9 MHz and 600.1 MHz, respectively, on a Bruker Avance III NMR spectrometer (14.1 T) equipped with a commercial 4-mm probe. Wood samples (~10 mg) were finely cut using scalpels and spun at 12.5 kHz with recycle delay of 2.0 s. During the CP contact, the ^1H nutation frequency was linearly ramped from 35 kHz to 50 kHz, and that of ^{13}C was optimized for the Hartmann−Hahn matching condition. Proton decoupling of 75 kHz was applied during the t_2 acquisition.

The number of scans was typically 8,192 for measurements with the contact time of 1 ms and 4,096 for experiments with variable contact times (0.2 ms to 10 ms). Because of the limited resolution of the NMR spectra for intact wood, we chose to analyze the peak intensities of the spectra without performing spectral deconvolution. For the variable contact time experiments, the peak intensities were analyzed by the following equation (42):

$$I(t) = A[1-exp(-t/T_{CH})]exp(-t/T_{1\rho}),$$

where $I(t)$ is the signal intensity at the contact time t, A is the intensity factor, T_{CH} characterizes the time constant of the polarization transfer between ^1H and ^{13}C, and $T_{1\rho}$ is the ^1H relaxation time in the spin-locking radio frequency (RF) field. The curve fitting was performed in Origin2015 software (OriginLab).

For the multiCP measurements (20), the spinning frequencies were set at 12 kHz. Typical π/2 pulse lengths of 4 μs and 3.57 μs were applied for the ^{13}C and ^1H channels, respectively. Proton decoupling field strength of 75 kHz was used during the acquisition. A total of nine CP blocks were implemented

with the contact time of 1 ms and the RF amplitude ramping of 90 to 100%. The recycle delay was 2 s, and the duration of the repolarization period t_z was 0.9 s. After the multiCP excitation, a Hahn echo of two rotor periods was applied before the signal detection.

Wide-Angle X-Ray Scattering. The experiments were performed at the BL01C2 beamline of the National Synchrotron Radiation Research Center, in which the ring was operated at 1.5 GeV energy with a typical current around 360 mA. A thin slice of wood sample was fixed with 3M Magic Tape and placed on the sample stage. Two pairs of slits and one collimator were set up to provide a collimated beam with dimensions of 0.1×0.1 mm (H $\times$ V) at the sample. The wavelength of the incident X-rays was 1.033210 Å (12 keV), delivered from the 5-T Superconducting Wavelength Shifter and an Si (111) triangular crystal monochromator. The scattering signal was collected with a Mar345 imaging plate area detector, setting the exposure duration at 30 s. The diffraction angles were calibrated according to Bragg positions of CeO_2 (SRM 674b) standards in desired geometry, and then GSAS II software (Argonne National Laboratory) was used to obtain corresponding one-dimensional powder diffraction profile with cake-type integration. The profile data were exported to Origin2015 software for baseline correction and smoothing. The size of the crystalline domain (L) was estimated using the Scherrer equation

$$L = K \lambda / B \cos\theta,$$

where K is the shape factor equal to 0.94 for wood cellulose (43), λ is the X-ray wavelength, B is the full width at half maximum in 2θ units, and θ is the Bragg angle.

ICP-MS. About 20 mg to 50 mg of finely cut wood sample was weighed and digested with 5 mL of 70% (wt/wt) nitric acid (trace metal grade) in a 50-mL glass centrifuge tube precleaned with 20% (wt/wt) nitric acid. The digestion mixture was heated in a 100 °C water bath for 8 h, followed by dilution with deionized water to 50 mL, and analyzed by Agilent 7500ce ICP-MS. High-purity standards of individual elements (1,000 mg/L) were diluted in 1% nitric acid to prepare standards for calibration curves. ICP-MS was operated at 1.5-kW RF

power and <5-W reflected power, with plasma/auxiliary/nebulizer flow rates at 15/0.8/0.95 L/min.

Thermal Analysis. DSC and TGA experiments were conducted using a Mettler TGA/DSC 1 instrument. Before analysis, finely cut wood samples were equilibrated for 48 h in a sealed chamber with saturated sodium bromide solution, with room temperature around 25 °C and internal relative humidity around 58%. It only took around 5 min to transfer ~5 mg of wood from the chamber to an aluminum crucible with a pierced lid and to have it stabilized inside the instrument at 34 °C. Subsequently, the sample was heated at 10 °C/min under air atmosphere and recorded from 35 °C to 600 °C. EMC was calculated as $(W_{35} - W_{150})/W_{150}$, where W_{35} and W_{150} were weights recorded at 35 °C and 150 °C, respectively.

Color Photography. Small pieces of wood samples were placed on white filter papers inside a desktop photo studio with external lighting using white compact fluorescent lamps. A Takumar SMC 50 mm F1.4 lens (Ricoh) was mounted in reverse using appropriate adapters on a 24.3-megapixel Sony alpha ILCE-7 camera. The reversed connection resulted in a flange focal distance of 45.46 mm and ensured that all in-focus objects had the same magnification ratio. We performed color calibration on wood images by photographing QPcard 203 and using QPcalibration software ver. 1.99b, with final processing in Adobe Lightroom ver. 5.7.1.

Statistical Tests. Welch's t test and linear regression were analyzed using Graphpad Prism software ver. 5.0. PCA was performed with Origin2015 software by choosing the correlation matrix (standardized) option.

1. Hill WH, Hill AF, Hill AE (1902) Antonio Stradivari: His Life and Work (1644–1737) (Dover, New York).
2. Pollens S (2010) Stradivari (Cambridge Univ Press, Cambridge, UK).
3. Sacconi SF (1979) The Secrets of Stradivari, trans Dipper A, Rivaroli C (Libreria del Convegno, Cremona, Italy).
4. Stoel BC, Borman TM, de Jongh R (2012) Wood densitometry in 17th and 18th century Dutch, German, Austrian and French violins, compared to classical Cremonese and modern violins. PLoS One 7(10):e46629.
5. Burcklem L, Grissino-Mayer HD (2003) Stradivari, violins, tree rings, and the Maunder Minimum: a hypothesis. Dendrochronologia 21(1):41–45.
6. Nagyvary J, Guillemette RN, Spiegelman CH (2009) Mineral preservatives in the wood of Stradivari and Guarneri. PLoS One 4(1):e4245.
7. Nagyvary J, DiVerdi JA, Owen NL, Tolley HD (2006) Wood used by Stradivari and Guarneri. Nature 444(7119):565.
8. Bucur V (2006) Acoustics of Wood (Springer, Berlin), 2nd Ed.
9. Hart G (1909) The Violin: Its Famous Makers and Their Imitators (Dulau, London).
10. Bardet M, Foray MF, Maron S, Goncalves P, Tran QK (2004) Characterization of wood components of Portuguese medieval dugout canoes with high-resolution solid-state NMR. Carbohydr Polym 57(4):419–424.
11. Gil AM, Pascoal Neto C (1999) Solid-state NMR studies of wood and other lignocellulosic materials. Annu Rep NMR Spectrosc 37:75–117.
12. Pishik I, Fefilon V, Burkovskaya V (2011) Chemical composition and chemical properties of new and old wood. Lesnoi J 14(6):89–93.
13. Kranitz K (2014) Effect of natural aging on wood. Doctoral thesis (Eidgenössische Technische Hochschule Zürich, Zurich).
14. Kacik F, Smira P, Kacikova D, Reinprecht L, Nasswettrova A (2014) Chemical changes in fir wood from old buildings due to ageing. Cell Chem Technol 48(1-2):79–88.
15. Paulsson M, Parkas J (2012) Review: Light-induced yellowing of lignocellulosic pulps—Mechanisms and preventive methods. BioResources 7(4):5995–6040.
16. Ganne-Chedeville C, Jaaskelainen A-S, Froidevaux J, Hughes M, Navi P (2012) Natural and artificial ageing of spruce wood as observed by FTIR-ATR and UVRR spectroscopy. Holzforschung 66(2):163–170.
17. Evstigneeva EI, et al. (2015) Chemical structure and physicochemical properties of oxidized hydrolysis lignin. Russ J Appl Chem 88(8):1295–1303.
18. Yonenobu H, Tsuchikawa S (2003) Near-infrared spectroscopic comparison of antique and modern wood. Appl Spectrosc 57(11):1451–1453.
19. Wikberg H (2004) Advanced solid state NMR spectroscopic techniques in the study of thermally modified wood. Doctoral thesis (Univ Helsinki, Helsinki).
20. Johnson RL, Schmidt-Rohr K (2014) Quantitative solid-state ^{13}C NMR with signal enhancement by multiple cross polarization. J Magn Reson 239:44–49.
21. Reh U, Kraepelin G, Lamprecht I (1986) Use of differential scanning calorimetry for structural analysis of fungally degraded wood. Appl Environ Microbiol 52(5):1101–1106.
22. Tsujiyama S, Miyamori A (2000) Assignment of DSC thermograms of wood and its components. Thermochim Acta 351(1-2):177–181.
23. Goulet M, Hernandez R (1991) Influence of moisture sorption on the strength of sugar maple wood in tangential tension. Wood Fiber Sci 23(2):197–206.
24. Kohara J, Okamoto H (1955) Studies of Japanese old timbers. Sci Rep Saikyo Univ 7 (1a):9–20.
25. Yokoyama M, et al. (2009) Mechanical characteristics of aged Hinoki wood from Japanese historical buildings. C R Phys 10(7):601–611.
26. Kollmann FFP, Cote WA, Jr (1968) Principles of Wood Science and Technology: I Solid Wood (Springer, Berlin).
27. Barlow CY, Edwards PP, Millward GR, Raphael RA, Rubio DJ (1988) Wood treatment used in Cremonese instruments. Nature 332(6162):313.
28. Echard JP, et al. (2010) The nature of the extraordinary finish of Stradivari's instruments. Angew Chem Int Ed Engl 49(1):197–201.
29. Brandmair B, Greiner PS (2010) Stradivari Varnish (B. Brandmair, Munich).
30. Parnell EA (1844) Applied Chemistry: In Manufactures, Arts, and Domestic Economy (D. Appleton, New York).
31. Sobue N, Okayasu S (1992) Effects of continuous vibration on dynamic viscoelasticity of wood. J Soc Mat Sci Jpn 41(461):164–169.
32. Kollmann FFP, Kuenzi EW, Stamm AJ (1975) Principles of Wood Science and Technology: II Wood Based Materials (Springer, Berlin).
33. Regazzi R (1986) The Manuscript on Violin Making by G. A. Marchi - Bologna 1786, trans Sbarra N (A. Forni, Bologna, Italy).
34. Roy K (2006) The Violin: Its History and Making (Karl Roy, Barrington, NH).
35. Cornell TJ (2013) The Fragments of the Roman Historians (Oxford Univ Press, Oxford).
36. Waite AE (1894) The Hermetic and Alchemical Writings of Paracelsus (J. Elliott, London).
37. Gug R (1991) Salted soundboards and sweet sounds. Strad 102(1214):506–511.
38. Dheu-Andries ML, Perez S (1983) Geometrical features of calcium–carbohydrate interactions. Carbohydr Res 124(2):324–332.
39. Nolte H, John S, Smidsrod O, Stokke BT (1992) Gelation of xanthan with trivalent metal ions. Carbohydr Polym 18(4):243–251.
40. Lionetto F, Del Sole R, Cannoletta D, Maffezzoli A (2012) Monitoring wood degradation during weathering by cellulose crystallinity. Materials (Basel) 5(10):1910–1922.
41. Obataya E (2012) Effects of aging on the vibrational properties of wood. J Cult Herit 13(3 Suppl):S21–S25.
42. Love GD, Snape CE, Jarvis MC (1992) Determination of the aromatic lignin content in oak wood by quantitative solid-state ^{13}C-NMR. Biopolymers 32(9):1187–1192.
43. Fernandes AN, et al. (2011) Nanostructure of cellulose microfibrils in spruce wood. Proc Natl Acad Sci USA 108(47):E1195–E1203.

Tai et al.